

*Citation:*

Johannes Diderik van der Waals, The volume of molecules and the volume of the component atoms,  
in:

KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 880-890

The following preparations are then analogous to *i*; the quantity of the metasilicate diminishes gradually, compared with the closely intermixed orthosilicate, which presents itself in round or polygonal corns, often twinned in a particular way. The preparations, which are in gross composition very close to  $Li_4SiO_4$ , show the crystals of the orthosilicate often in a highly altered condition; the immersion-liquids also seem to be attacked by the expelled alkali, and measurement is often impeded by it.

The fact, that the crystals of the orthosilicate appear often more or less attacked under the microscope, could make more probable the view, according to which the temperature of  $1256^\circ\text{C}$ . were rather a "transformation"-temperature than an ordinary meltingpoint; the compound would be converted thus into a liquid, with partial dissociation.

In the principal outlines we may say, that the binary diagram of  $SiO_2$ — $Li_2O$  is known now. It will doubtlessly prove for the present impossible, to investigate the behaviour of the components at concentrations between orthosilicate and lithiumoxide in their complete details, because of the enormous volatility of this oxide at these extreme temperatures.

*Laboratory of Inorganic and*  
Groningen, February 1914. *Physical Chemistry of the University.*

**Physics.** — "*The volume of molecules and the volume of the component atoms.*" By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of January 31, 1914).

I think I may assume as known that for normal substances the volume of the molecules expressed in parts of the gas volume at  $0^\circ$  and 1 atmosphere pressure may be calculated in a simple way by means of the critical quantities. When it is not yet taken into account that the quantity  $b$  of the equation of state decreases with  $v$  we find:

$$\frac{RT_k}{p_k} = 8b$$

$$\text{or } \frac{T_k}{p_k} = \frac{8 \times 273}{(1+a)(1-b)} b,$$

in which  $b$  represents 4 times the volume of the molecules. If we do take into account that this factor 4 diminishes when the volume, as is the case for the critical state, has decreased to almost  $2b$ , we find by approximation:

$$\frac{T_k}{p_k} = \frac{7 \times 273}{(1+a)(1-b)} b_g$$

And if this factor 7 was really equally great for all substances,  $\frac{T_k}{p_k}$  would be almost proportional to the size of the molecules. As it is not my purpose in this communication to calculate the exact numerical value of the size of the molecules, and in connection with this the perfectly exact numerical value of the component atom volumes, which perhaps is not yet feasible, among others on account of the imperfect knowledge of the accurate value of  $T_k$  and  $p_k$ , and as this communication more bears the character of a preliminary exploration of the territory, I shall assume the quantity  $\frac{T_k}{p_k}$  as a numerical value, which is really, at least by approximation, proportional to the size of the molecules and by the aid of this value I will investigate what follows for the size of the component atoms from this size of the molecules. The quantities  $T_k$  and  $p_k$  are borrowed from the excellent *Recueil des Constantes physiques* by Messrs. ABRAHAM and SACERDOTE.

As I expected the simplest relations for the saturated hydrocarbons, I began with them, and the values of  $T_k$ ,  $p_k$ , and  $\frac{T_k}{p_k}$  follow here.

	$T_k$	$p_k$	$\frac{T_k}{p_k}$		calculated
Methane	191,2	54,9	3,483	CH <sub>4</sub>	3,483
Ethane	305,16	48,86	6,2456	C <sub>2</sub> H <sub>6</sub>	6,243
Propane	370	45	8,2222	C <sub>3</sub> H <sub>8</sub>	9,003
Butane	not given.				11,763
Pentane	470,2	33,03	14,236	C <sub>5</sub> H <sub>12</sub>	14,523
Isopentane	460,8	32,93	14,	C <sub>5</sub> H <sub>12</sub>	14,523
Hexane	507,8	29,76	17,06	C <sub>6</sub> H <sub>14</sub>	17,283
Heptane	539,9	26,86	20,01	C <sub>7</sub> H <sub>16</sub>	20,043
Octane	569,2	24,64	23,1	C <sub>8</sub> H <sub>18</sub>	22,803
Decane	603,4	21,3	28,35	C <sub>10</sub> H <sub>22</sub>	28,323

For the increase of the molecular volume in consequence of the introduction of 1 atom C and 2 atoms H into the molecule CH<sub>4</sub>, we successively find the values:

2,7626

2,37

2,668

2,7134

2,753

2,802

and with Decane—Ethane 2,781.

The inexplicably small amount for Propane is not able to take away the impression that for these saturate hydrocarbons the volume increases regularly and equally whenever 1 atom of C and 2 atoms of H enter the molecule, and when we consider the almost perfect equality of  $\frac{T_k}{p_k}$  for Pentane and Isopentane, we come to the conclusion that at least in these cases a rearrangement of the atoms is no influence of importance. If for the mean of the above values (with the exclusion of 2,37) 2,76 is chosen, the volumes would be as the calculated values of the preceding table indicate. It is seen that except for Propane, the differences are small, and the question suggests itself whether for this substance there is a cause of error in the determination of the critical quantities, e.g. a certain degree of impurity.

If in what follows the volume of the carbon atom is represented by C, and the volume of the hydrogen atom by H, we have the following two equations for the determination of these two quantities:

$$\begin{aligned} C + 4 H &= 3,483 \\ C + 2 H &= 2,76^1) \end{aligned}$$

$$\text{or } H = \frac{0,723}{2} = 0,3615 \text{ and } C = 2,037.$$

Some other determinations which will be discussed presently, have led me to consider C below 2 as possible. With  $C = 1,9$ , retaining  $CH_4 = 3,483$ , H would be equal to 0,396. Then  $CH_2$  would have fallen to 2,691, so it has changed only little. But whether one assumes  $H = 0,3615$  or  $H = 0,396$ , it appears that there is a great difference with the volume of H or  $H_2$  as it would follow from the critical data of hydrogen. With  $T_k = 32$  and  $p_k = 19,4$  we find  $\frac{T_k}{p_k} = 1,65$ . And if we should assume the formula  $H_2$  for the molecule as I also did at first,  $H = 0,825$  would follow from this, a value which is certainly not in harmony with the above calculated value. And the difference is so great that I was already again on the verge of concluding, as I had often supposed before, that it would be impossible to get in this way to the knowledge of the size of the

---

<sup>1)</sup> From methylethylene(iso) which, the structure being disregarded, has  $C_5H_{10} = 5(CH_2)$  as formula, we find  $\frac{T_k}{p_k} = 13,69$ , which would lead to  $CH_2 = 2,738$ . But from ethylene, which has  $2(CH_2)$  as formula, we should find a somewhat too great value, viz.:  $2(CH_2) = 5,7$  or  $CH_2 = 2,85$ . Is this substance somewhat associating?

atoms. Now however I bethought myself that I had determined the size of the hydrogen molecule already before, and that this size was even the first molecule size that I had at least estimated. From REGNAULT's observations, in which the volume under 1 meter pressure was assumed as unity of volume, I had obtained values lying between 0,0005 and 0,0008, which for our unity of volume corresponds to 0,00038, and 0,00006, from which for  $\frac{T_k}{p_k}$  a value would follow lying between 0,95 and 1,5. And a value lying near 0,95 seems by far more probable to me than the value which would follow from the critical data, and leads me to conclude that at these low temperatures hydrogen associates to double molecules for the greater part.

But nevertheless the value of the volume of the atom H remains decidedly smaller when it is bound to  $\frac{1}{4}$  part of the atom C, than when it is bound to a second atom H. And this is a result which has always appeared correct to me, viz. that the size of the volume of an atom is not only determined by its own nature, but also by the nature of the atom to which it is bound. This is of course in flat contradiction with the assumption that an atom is a perfectly invariable corpuscle, not to be changed by any forces, not by *atomic forces* either. With the molecules as wholes it must, indeed, have the property in common of being invariable to forces of collision of heat and of pressure. But when uniting with other atoms, in which forces of higher order come into play, they behave, I would almost say, as soft bodies, which can vary both with regard to shape and to size. And the conception that an atom is an orbit of electrons round a rigid centre formed by a point in which the atomic weight is concentrated, or when the atom is bi-, tri- or tetravalent, by 2, 3 or 4 orbits round centres in which  $\frac{1}{2}$ ,  $\frac{1}{3}$  or  $\frac{1}{4}$

of the atomic weight is concentrated — a conception called into existence by the study of light phenomena<sup>1)</sup> — can give an explanation of this. We have only to assume the velocity in the orbits large with respect to the velocity of the thermal motion to account for the apparent hardness, and only to assume rotation of the molecules round one or more axes to convert orbits and planes to an apparent volume. When we have two similar atoms which have united, we have two orbits of electrons lying in the same plane, and rotating in opposite direction. Where they are in contact or almost in contact, the directions are in the same sense, hence we have

<sup>1)</sup> Cf. among others Dr. BOHR, Phil. Mag. 1913.

attraction, just as this is the case with electric currents in the same direction. But when one of the atoms is replaced by one of another nature, e.g. of greater atomic weight, the size of the atom that has not been replaced, changes, because a stronger current acts on it, i. e. this atom becomes smaller, whereas the second atom becomes larger than it would be if it had continued to be united with one of its own nature, and the result can be that the new molecule is either greater, or smaller than, or has happened to remain equal to half the volumes of the two molecules, the atoms of which have been exchanged. But we do not yet know the degree of the variability.

But let us after these speculative considerations return to the investigation whether also other observations about the critical circumstances are in agreement with the values of C and H, which we have calculated above for the case of mutual binding.

It had already drawn my attention that  $\frac{T_k}{p_k}$  for isopentane had been found somewhat smaller than for normal pentane, and that, if this should also be the case for other iso-compounds, the earlier calculations, in which these differences were not found, could not be quite accurate. And strictly speaking already in the earlier calculation it can be pointed out that there are differences which have been neglected in this calculation. The volume for all atoms C e.g. was put equal, though there always exist 2, viz. the outmost of the chain, which are bound to 3 atoms H and 1 atom C, whereas there are  $n-2$  atoms C, which are bound to 2 atoms H and 2 atoms C, and which will accordingly be smaller than the 2 outmost. For the iso-compounds the case may even present itself that an atom is bound to 1 atom of H and 3 atoms of C, and perhaps even that one atom of C would be bound to 4 atoms of C. I was therefore glad that for a few iso-compounds the quantities  $T_k$  and  $p_k$  are determined through investigations by SYDNEY YOUNG — viz. for di-isopropyl and di-isobutyl. For the former substance, for which, if the construction is disregarded, the composition is the same as that of Hexane,  $\frac{T_k}{p_k} = 16.3$ , and for the latter, the composition of which would be equal to that of Octane,  $\frac{T_k}{p_k}$  is equal to 22.4. For normal compounds the values are 17.06 and 23.1 in the above list. Also for these compounds the case occurs that the volume is smaller than for normal ones, and even not inconsiderably.

But on account of the uncertainties as to in what way and to

what degree the differences in size of the volume of the different C atoms would have to be taken into account, I shall not attempt as yet to calculate the found differences in size, at least not for the present. For isobutyl, moreover, the difference in size amounts only to 3 percent, and it always remains the question how far the accuracy of the determination of  $T_k$  and  $p_k$  has been carried, and in how far the absolute purity of the substance and the equality of the factor

$\frac{7 \times 273}{(1+a)(1-q)}$  can be relied on. I shall therefore for the present be satisfied with the approximative calculations, which I have used above.

For the methyl-, ethyl-, propyl-compounds etc. there is a whole series of determinations of  $T_k$  and  $p_k$  which can be of use for the calculation of  $\text{CH}_2$ . Then a new kind of atom, or a new group of atoms, which we do not know as yet, is indeed added, but when the new group of atoms is bound in these compounds in the same way, the difference in  $\frac{T_k}{p_k}$ , e.g. for the methyl- and ethyl-series, can then enable us to determine the value of  $\text{CH}_2$ . Thus we find the following values:

	$T_k$	$p_k$	$\frac{T_k}{p_k}$	$\text{CH}_2$
Methyloxyde	127,1 + 273	53	7,55	$\frac{5,57}{2} = 2,78$
Ethyloxyde	193,8 + 273	35,6	13,12	
Methyl and ethyloxyde	167,6 + 273	46,27	9,5	

The value 2.78 coming so near the previous determination, I do not hesitate to call the value  $\frac{T_k}{p_k}$  for the third substance too small. There the value 10.25 is to be expected instead of 9.5. If one should assign the before given value also to the other H and C atoms,  $\text{O} = 1,3$  would follow from this, whereas  $\text{O}_2 = 3$  follows from  $\frac{T_k}{p_k}$ .

Thus we find for:

	$\frac{T_k}{p_k}$	difference
Methylacetate	10,95	
Ethylacetate	13,77	2,82
Propylacetate	16,56	5,61

From this we should therefore derive  $\text{CH}_2 = 2,8$ . So the abnor-

malinity of acetic acid has disappeared in these compounds; of these compounds and others examined by me the group  $\text{CO}_2$  would almost give the value which follows from  $T_k$  and  $p_k$  for  $\text{CO}_2$ , viz. 4,14.

I choose three of the compounds of Cl, and C and H to see in how far the others by means of the values calculated from these, can be derived.

From the values of  $T_k$  and  $p_k$  follows:

$$\text{Chloric ethyl} \quad \text{C}_2\text{H}_5\text{Cl} = 8,435$$

$$\text{and} \quad \text{C}_2\text{H}_4\text{Cl}_2 = 10,61$$

$$\text{and} \quad \text{CHCl}_3 = 10.$$

We find from this  $\text{Cl}-\text{H} = 2,175$ , which means that if in these compounds a hydrogen atom is substituted for the chlorine atom, the volume increases by 2,175, a value which was found equal to from 2,18 to 2,2 another time, a second equation is:

$$\text{Cl}_4-\text{H}_2 = 9.39.$$

From these two equations follows  $\text{Cl} = 2,52$  and  $\text{H} = 0,345$  and we find further  $\text{C} = 2,095$ , a value almost equal to that found before.

For carbon tetrachloride we find 12,175 for  $\frac{T_k}{p_k}$  with these calculated values of Cl, H, and C, whereas the value found directly would be equal to 12.4. But for  $\text{CClH}_3$  there is no sufficient agreement between observation and calculation, and like other substances which have been derived from  $\text{CH}_4$  this substance yields a too large value and is evidently associating. I am even astonished that the derivatives that contain more chlorine behave evidently so normally. When we compare the value found for Cl with that of the molecule, viz. 4,48, it appears that the binding of C with Cl makes the atom Cl larger than is the case with the binding of Cl with Cl. With the values calculated from chlorine compounds we should find:

$$\text{CH}_4 = 3.475$$

$$\text{CH}_2 = 2.785$$

When these are compared with those found before:

$$\text{CH}_2 = 3.483$$

and

$$\text{CH}_4 = 2.76$$

there is reason for us to wonder that the entering of Cl into these compounds hardly changes the values of C and H, if at all.

I shall now proceed to the amine compounds.

We find for the ethyl amine compounds the values of  $\frac{T_k}{p_k}$ :



tri-ethylamine	di-ethylamine and ethylamine
17.7	12.25      6.818

When the volume of C bound to N is represented by  $C_N$  and that of C bound to C by  $C_c$ , we have the three following equations:

$$N + 3(C_N + H_2 + C_c + H_3) = 17.73$$

$$N + H + 2(C_N + H_2 + C_c + H_3) = 12.25$$

$$N + 2H + (C_N + H_2 + C_c + H_3) = 6.818$$

or  $-H + (C_N + H_2 + C_c + H_3) = 5.483$

$$-2H + 2(C_N + H_2 + C_c + H_3) = 10.915$$

and so  $C_N + H_2 + C_c + H_3 = 5.483$  of 5.457.

If we take the mean of these values, and if we take into consideration that for  $C_c + 2H$  has been found before 2.76, we determine:

$$C_N + 2H = 2.71.$$

Hence the volume of C bound to N may be equated to that of C bound to C.

If we do so, and calculate with it the value of the group  $(NH_3)$ , the radical of the amine-compounds, we find:

$$(NH_3) = 1.3 \text{ about.}$$

This value is much smaller than for  $NH_3$ , which we call ammonia. With  $T = 132.3$  and  $p_k = 109.6$  we calculate this value at about 3.7. So there the question rises what difference there will be between these two atom-groups. Perhaps it will have to be looked for in the situation of the orbits of the electrons, which would then have to lie in the equator plane of the trivalent nitrogen atom for ammonia, and for amine in the meridian plane.

For propylamine we should find a slightly too high value; viz.

2.84, for the value of  $CH_3$  from  $\frac{T_k}{p_k}$  with  $(NH_3) = 1.3$ , whereas we

found a somewhat too small value before for propane. I do not, therefore, consider these differences as really existing. For dipropylamine the value  $1.3 + 16.56 = 17.86$  might be calculated with

$1.3 + 6CH_3$ , whereas 17.47 follows from  $\frac{T_k}{p_k}$ . Allowing for the

approximate character of our equations this may be considered as equal.

But the methylamines all yield a too high value, which I consider as a consequence of association, viz. 10.575 instead of 9.58, 7.43 instead of 6.82, and 5.944 instead of 4.06. With monomethylamine there is, therefore, a high degree of association; about half the molecules are double molecules.

I shall now proceed to discuss the substances in which the cyclic bond of benzene occurs.

For benzene itself we find  $\frac{T_k}{p_k} = 11,73$ , and for all the substances in which this cyclic bond occurs,  $C_6H_6$  is smaller than would follow from the saturate hydrocarbons. Of the substances in which the grouping of C and H occurs, as this is the case for hydrocarbons, 6 C alone would already have a value exceeding 12 or close to it. So the question again rises for what special reasons the cyclic bond of the 6 carbon atoms makes them smaller. Perhaps the closed chain, the ends of which coincide, is the cause of this through the mutual attraction of these ends.

That the binding of C to C with 3 valencies could account for this, may be doubted for the present.

But whatever the cause may be — we shall assume  $C_6H_6 = 11,73$  for the cyclic binding, and take the former value for the atoms further entering the molecule, which are grouped as in the saturate hydrocarbons.

For diphenyl we find  $\frac{T_k}{p_k} = 24,17$ ; it is, compared with benzene, a little too great, or perhaps benzene is a little too small. By adding 2,76 to diphenyl we should get 26,93 for diphenyl methane whereas 27,3 would follow from  $\frac{T_k}{p_k}$ . Whether these differences are the consequence of our *approximate* calculation, or whether they have a real signification, I dare not decide. By the addition of  $CH_3$  to benzene  $11,73 + 2,76 = 14,49$  follows for toluene, whereas  $\frac{T_k}{p_k}$  yields 14,27.

We find further:

Xylene (o)	for	$\frac{T_k}{p_k}$	the value	17,1,	calculated from benzene	17,25
„ (m)	„	„	„	17,64,	„ „ „	
„ (p)	„	„	„	17,28,	„ „ „	
Mesitylene	for	$\frac{T_k}{p_k}$	the value	19,3	, calculated from benzene	20,01
Durene	„	„	„	23,62,	„ „ „	22,77
Cumene	„	„	„	19,74,	„ „ „	20,01
Cymene	„	„	„	22,78,	„ „ „	22,77

From Cresol (O) = 15,67 follows for  $-H + (O,H)$  the value 1,17. If the two H cancel each other, we should have O = 1,17, whereas

we calculated  $O = 1.3$  from the ethyl-oxides. If we had a priori assumed  $O = 1.3$ , we should have calculated Cresol = 15.79.

I might add other examples to these, but those given here suffice in my opinion to draw the following conclusions:

1. The volume of the molecules of normal substances may be found from the critical circumstances.

2. The volume of the molecules is equal to the sum of the volumes of the atoms contained in it.

3. The volume of an atom is not constant, but depends also on the atoms to which it is bound, and the way in which it is bound to others.

4. By normal substances we understand such as do not associate or dissociate. For acetic acid 10.415 is found for  $\frac{T_k}{p_k}$  whereas  $C_2H_4O_2$  would lead to 7.823 at the most.

5. The view that the volume of an atom is determined by the size of the orbits of the electrons holds out the prospect to determine the modification of the size in case of mutual binding.

I had just commenced this investigation on the size of  $b$ , when I received the copies of nine treatises by ALBERT P. MATHEWS on the value of  $a$ , in which very remarkable results have been obtained. They appeared in the "Journal of Physical Chemistry" of 1913.

#### A P P E N D I X.

The comparison of Benzene with Naphthaline has given me the conviction that the smallness of  $C_6H_6$ , as was indeed to be expected, must not be ascribed to the H-atoms, but to the C-atoms. For naphthaline  $\frac{T_k}{p_k}$  is equal to 18.91. Now naphthaline is equal to twice  $\frac{2}{3}$  benzene + 2 C or  $\frac{5}{3}$  benzene - 2 H. We have, therefore, the equations:

$$18.91 = \frac{4}{3} \times 11.73 + 2C$$

$$\text{and} \quad 18.91 = \frac{5}{3} \times 11.73 - 2H$$

$$\text{or} \quad 18.91 = 15.64 + 2C$$

$$\text{and} \quad 18.91 = 19.55 - 2H,$$

from which  $C = 1.635$  and  $H = 0.32$  is calculated. The value of  $H$  is of the former order of magnitude. But  $C$  has decreased to 0.8 of its former value. This appears still more clearly when benzene is compared with hexamethylene or cyclohexane. With this latter substance we have also the cyclic binding of 6 carbon atoms; only the coincidence of two valencies for carbon has disappeared. The formula is  $C_6H_{12}$ , and  $\frac{T_k}{p_k} = 13.9$ . Hence the comparison with benzene gives the two following equations:

$$6C + 12H = 13.9$$

$$\text{and} \quad 6C + 6H = 11.73$$

$$\text{or} \quad H = 0.3616$$

$$\text{and} \quad C = 1.593$$

I will still give a few values calculated in the meantime, viz. propylbenzene, calculated with benzene and  $CH_2 = 2.76$ , equal to 20.01,  $\frac{T_k}{p_k}$  being equal to 19.772, and chlorobenzene with  $Cl-H = 2.185$  calculated at 13.915 and found 14.18.

But all the nitriles appear to give much too high values of  $\frac{T_k}{p_k}$ , and so for  $b$ , and are associating in a high degree. Even benzonitril, but this nitril in a less degree than the others.

**Astronomy.** — "*Investigation of the inequalities of approximately monthly period in the longitude of the moon according to the meridian observations at Greenwich*". *Addendum*. By J. E. DE VOS VAN STEENWIJK. (Communicated by Prof. E. F. v. D. SANDE BAKHUYZEN).

Professor BATTERMANN and Prof. ERNST BROWN have both been so kind as to point out to me, in letters to Prof. BAKHUYZEN, that BROWN's theoretical value, quoted by me, for the motion of the moon's perigee (p. 140), which was taken from *Monthl. Not.* **64** 532, does not quite agree with his final result, which was published by him in *Memoirs R. A. S.* **59**, 94 (comp. also *Monthl. Not.* **70**, 3). If we use the value assumed by me for the ellipticity of the earth 1:297.5, then the theoretical result for the sidereal motion in a Julian year for 1850 becomes **146435"16**, so that my result from the observations **146435"31** is now only 0"15 greater, against 0"26 formerly.