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The Properties of Paraffins. II

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The square root in the formula of Boggia-Lera is derived in the case of the paraffins from Langmuir's ideas about the process of evaporation of liquids and van Laar's and van Arkel's rules about cohesion in liquids, combined with empirical expressions for the critical constants.

IN Part I we have investigated the validity of the formula of Boggia-Lera and extended its applicability to all polymethylene compounds. The formula was originally given as a purely empirical one and up to now we have used it as such. It is, however, desirable to ascertain its causes as these may give us some information about the limits of its applicability. The boiling point of a compound is a derived quantity, depending in a complicated way on a great many different properties, among which the heat of vaporization is by far the most important. For this reason we shall check our conclusions by comparing them with the known data for the paraffins, the only homologous series for which vapor pressure measurements are available. Another advantage of these compounds is the absence of large substituents or of appreciable electrical moments, as these might have a complicating influence on the thermal properties in the series. Table VII contains the data obtained by different investigators and the values we calculated from them. For our purposes we are not so much concerned with the absolute values of the heat of vaporization as with their differences. For this reason we calculated the average value for each compound between 11 mm and 760 mm pressure, these being the lowest and the highest pressure used by Krafft. The average values for the heat of vaporization are listed under Q_{av} . From these the heats of vaporization at the boiling point were obtained by the use of the well-known formula:¹

$$Q = Q_0(1 - T/T_c)0.4, \quad (1)$$

in which Q is the heat of vaporization and T_c the critical temperature, all temperatures being expressed in the absolute scale. The heat of vaporization at the boiling point was obtained by multiplying Q_{av} with the average of unity and the factor required to change the value of Q at 11 mm pressure to Q at the boiling point (Q_B), as calculated from formula (1). As this correction amounts to about 10 percent it is clear that the inaccuracy it introduces into Q_B is quite small.

To get an insight into the factors which determine the values of Q_B we must first consider what is known about the heat of vaporization of small and simple molecules. van Laar² has pointed out that for the attraction between two molecules only those atoms are important which are on the surface of the molecule. Atoms inside a molecule—like the carbon atom in CH_4 or CCl_4 —which are entirely surrounded by other atoms, are screened off so effectively that one need not take them into account when calculating cohesion forces. A great deal of work on this subject has been done by van Arkel and his co-workers,³ who studied a great variety of substances and lately even calculated the degree of screening quantitatively in some cases. In the case of larger molecules screening certainly will have the same effect, and in our case too, only those atoms of the paraffin molecule which are lying in the surface of the molecule can contribute to the intermolecular forces. This gives the three following variables on which the heat of vaporiza-

¹ R. M. Winter, *J. Phys. Chem.* **32**, 576 (1928). The same formula had already been used in a special case by Prud'homme (*J. de. chimie physique* **21**, 461 (1924)) with a different exponent. An expression of the same kind was given by van Laar for the internal heat of vaporization (*Zustandsgleichung von Gasen und Flüssigkeiten* p. 263). At higher temperatures formula (1) is quite accurate, but at very low pressures the agreement is not so good (Taylor

and Smith, *J. Am. Chem. Soc.* **44**, 2457 (1922)). This might be due to the method of calculation however.

² J. J. van Laar, *Zustandsgleichung von Gasen und Flüssigkeiten*, p. 199.

³ A. E. van Arkel, *Rec.* **51**, 1081 (1932); A. E. van Arkel and S. J. L. Snoek, *Rec.* **52**, 719 (1933); A. E. van Arkel *Rec.* **52**, 733 (1933); **53**, 246 (1934) and specially *Chemisch Weekblad* **31**, 470 (1934).

tion depends: 1. the composition of the surface of a molecule, 2. the size of the surface of a molecule, 3. the distance between the surfaces of two molecules.

The first factor does not give us any trouble with the paraffins. Because the composition of all paraffins is the same (except for the two final hydrogen atoms, which we may well neglect) the composition of their surface will be the same too. It may be that all the atoms causing the cohesion are hydrogen atoms, or there may be carbon atoms among them, but their proportion will be constant throughout the series, excepting the very first terms.

The shape of a molecule in a liquid is very complicated and irregular. Langmuir⁴ has given a great deal of consideration to this problem, paying special attention to the paraffin molecules. He points out that owing to the rotation around the C—C bonds the molecule can assume a great many different shapes. Whether it does so depends on the forces between its different parts. In the gas phase the attraction between the different methylene groups is so great that the

molecule will roll up into something approaching a sphere. In the liquid phase on the other hand, a group in the center of a rolled up molecule finds itself surrounded by the same methylene groups which adjoin it when it is stretched out between other molecules. Thus it takes no energy to change the shape of a molecule in a liquid consisting of the same kind of molecules and under these circumstances a molecule is not all curled up but only slightly curved. Kuhn has lately published several papers on this subject.⁵

Langmuir's conclusions are, of course, only approximately true as a methylene group in a certain molecule will more frequently turn its carbon atom towards a point inside a molecule and its hydrogen atoms towards a point outside.

It is clear that when a molecule evaporates its shape changes gradually as it moves out of the liquid into the gas phase. This process we cannot describe but the energy required for it is the same as that which must be supplied to give the molecule first the shape of a gaseous molecule in the liquid—which requires no energy—and afterwards transferring this—nearly spherical—mole-

TABLE VII.

SUBSTANCE	FORMULA C_nH_{2n+2} VALUE OF n	TEMPERATURE AT WHICH $p = 11$ mm IN DEGREES ABS.	BOILING POINT IN DEGREES ABS.	Q_{av} IN CAL.	Q_b FROM GAS AND FROM (1) IN CAL.	U_B IN CAL.	T_B^a T_c	U_{red} FOR $T = 0.716 T_c$ IN CAL.	U_{red} CALC. FROM (2) $1900 \times n^{\frac{1}{3}}$ IN CAL.	Q_B T_B	Q_B T_B CALC. FROM $16.0 \times n^{0.14}$
Propane ^a	3	161	229	4600	4200	3700	0.619	3300	4000	18.3	18.7
Butane ^a	4	194	273	5600	5200	4700	0.640	4300	4800	19.0	19.4
Pentane ^b	5	225	310	6900	6300	5700	0.658	5300	5500	20.3	20.0
Hexane ^c	6	249	342	7700	7100	6400	0.673	6000	6300	20.8	20.6
Heptane ^d	7	273	372	8600	7900	7200	0.689	6900	7000	21.2	21.0
Octane ^e	8	294	399	9200	8600	7500	0.701	7600	7600	21.6	21.4
Nonane ^f	9	313	423	10100	9200	8400	—	8300	8200	21.8	21.7
Decane	10	330	446	10600	9700	8800	0.716	8800	8800	21.7	22.1
Undecane	11	347	468	11300	10300	9400	—	9400	9400	22.0	22.4
Dodecane	12	364	488	12000	10900	9900	—	9900	10000	22.4	22.6
Tridecane	13	379	507	12600	11400	10400	—	10400	10500	22.5	22.9
Tetradecane	14	396	526	13400	12300	11200	—	11200	11000	23.4	23.1
Pentadecane	15	410	544	13900	12700	11600	—	11600	11500	23.4	23.4
Hexadecane	16	424	561	14600	13300	12200	—	12200	12100	23.7	23.6
Heptadecane	17	437	576	15200	13900	12700	—	12700	12600	24.2	23.8
Octadecane	18	448	590	15600	14300	13100	—	13100	13000	24.2	24.0
Nonadecane	19	459	603	16100	14700	13500	—	13500	13500	24.4	24.2

^a Values from Burrell and Robertson, J. Am. Chem. Soc. 37, 2188 (1915). Partly interpolated.

^b Values from Young, J. Chem. Soc. 71, 446 (1897). The temperature at which $p = 11$ mm is extrapolated, causing the figures for this substance to be less reliable. The boiling point is interpolated.

^c Values from Thomas and Young, J. Chem. Soc. 67, 1075 (1895). Interpolated.

^d Values from Young, J. Chem. Soc. 73, 675 (1898). Interpolated.

^e Values from Young, J. Chem. Soc. 77, 1145 (1900). Interpolated.

^f Values for nonane and higher hydrocarbons from Kraft, Berichtr. 15, 1145 (1882).

^g Values for T_B and T_c from van Laar, *Zustandsgleichung von Gasen und Flüssigkeiten*, p. 184. It has been assumed that the value for decane is also valid for the higher terms of the series.

⁴ I. Langmuir, in Alexander, *Colloid Chemistry I*, p. 525, and Third Colloid Symposium Monograph, p. 48 (1925).

⁵ W. Kuhn, *Kolloid Zeits.* 68, 2 (1934); *Zeits. f. physik. Chemie* A175, 1 (1936).

cule to the vapor. Langmuir tried to obtain a quantitative value for the heat of vaporization in this way, but that cannot be done. The internal heat of vaporization should be equal to the product of the surface of a molecule and the internal surface energy multiplied by the Avogadro number. There might be some doubt about the area of the surface of a molecule but at least the internal heat of vaporization should be proportional to the internal surface energy, except for a very small change due to the expansion of the liquid. This is by no means the case, as was shown by Whittaker.⁶ There can be little doubt, however, that the internal heat of vaporization of a paraffin is actually proportional to the surface of a molecule in its spherical shape if at least the distance between the surface of the molecule and that of the surrounding liquid is the same. (It is, of course, impossible to define exactly what should be considered to make up the surface of a molecule in a liquid, especially of one which is in a rolled-up state, which occurs hardly at all in the liquid, but we shall have to use the notion all the same.)

If all methylene groups in the liquid were entirely free to move independently, the average distance between two of them would always be the same in different liquids at a certain temperature. In a molecule, however, the methylene groups are only partially free to move and therefore two CH_2 groups in different molecules will be nearer to each other the larger the molecules are to which they belong, because the attraction between the other methylene groups tends to bring the groups under consideration nearer together too. So the temperature at which the distance between a molecule and the surrounding surface has a certain value, will be higher the larger the molecular weight is. At present it seems most logical to compare different substances at corresponding temperatures, which means, temperatures that are the same fraction of the critical temperature. That is usually done and it can easily be shown to be right in the simplified case of straight, cylindrical molecules lying parallel, with no free space at the ends, as follows:

⁶ Whittaker. Proc. Roy. Soc. **81**, 21 (1908). The same fact disproves the correctness of the formula of Stefan. (W. D. Harkins and L. E. Roberts, J. Am. Chem. Soc. **14**, 653 (1922).)

From the fact that the molecular volume of paraffins at the boiling point (which is approximately a corresponding temperature as seen from Table VII) is an additive property it follows that the intermolecular spaces make up a constant fraction of the total volume. If we increase the molecular weight the molecules only grow longer, without changing their other dimensions. The intermolecular spaces also change their total volume and their length in the same proportion, so the distance between two molecules remains the same.

The surface of a large, spherical molecule is proportional to the two-thirds power of its volume and, in the case of a paraffin, of its number of methylene groups (neglecting the final hydrogen atoms again). Thus we expect the internal heat of vaporization for different paraffins at a certain reduced temperature to be:

$$U_{\text{red}} = \text{const. } n^{\frac{2}{3}}. \quad (2)$$

In Table I M_{red} is calculated for $T = 0.716T_c$ from U_B by the use of formula (1) for comparison with the results obtained from formula (2) taking the constant to be 1900. It was assumed that the ratio of T_B and T_c was the same for decane and all the higher terms. This is certainly not true but the difference in U_{red} is probably only about 200 cal., which is not more than the error of the figures anyway. Considering that $Q = U + RT$ and that the power of U changes slightly if we make our comparison at the boiling points—which are not strictly corresponding temperatures—we get:

$$Q_B = \text{const. } n^{0.64}. \quad (3)$$

The change in U caused by the change in temperatures is quite small, and can be expressed as a factor representing a small power of n . Here the constant has the value 2250.

Now we still have to convert our formula for Q_B into one for T_B . The only exact way of connecting these two quantities is by the third law of thermodynamics, but for this method we do not have the required thermal data at present, nor do we know how to apply this law to large molecules. It is, however, a well-known fact that in general the Trouton quotient increases as a function of the boiling point. In our case we may expect this to be true too, and it would mean

that this quotient would be a function of n . The quotient changes only a little over our entire series and we may very well write it as a small power of n :

$$Q_B/T_B = 16.0 \cdot n^{0.14}. \quad (4)$$

Combining this with formula (3) we obtain as our final conclusion that T_B is proportional to the 0.50 power of n . Here we see the square root from the formula of Boggia-Lera come in more or less accidentally as the difference between two other powers of n .

It is also possible to give a proof for the value of the exponent in formula (4). Lacking the data needed for the use of the heat-theorem one has to use empirical expressions for the critical quantities. Although the factor A in the general vapor pressure equation

$$\ln p = -A/T + B \quad (5)$$

is not a constant, one may consider it to be one without introducing more than a very slight error, if one limits oneself to comparing the critical point and the boiling point; at least in the case of ordinary compounds like the paraffins.⁷ This means that we can replace A by Q_B/R and by substituting p_c and T_c , find

$$Q_B/T_B = Q_B/T_c + R \ln p_c. \quad (6)$$

Now we must express the critical quantities as functions of n in a suitable way. We shall use $T_c = 251 \times n^{0.39}$ and $\ln p_c = 4.54/n^{0.17}$. We might of course have made use of the fact that T_c/p_c is proportional to the critical volume and therefore to n , thus expressing p_c in T_c and n , but this would have complicated our calculations appreciably. Combining with formula (3) we find:

$$Q_B/T_B = 8.97 \times n^{0.25} + n^{8.99/0.17}. \quad (7)$$

The value of the first term on the right side of (7) increases slowly with n ; the value of the second term decreases. The first term, being the larger one and having the higher power in n , will outweigh the other one; so the value of Q_B/T_B is seen to increase very slowly with increasing term number. We can again try to find a product of a single small power of n to express the total value of (7), which is seen to be quite well represented by formula (4).

So we have derived the formula of Boggia-Lera for the paraffins excepting for the lowest members of the series. It is easily seen that the agreement at the beginning of the series may be greatly improved by adding a constant either to T or $n \times D$. Formula (3) could safely be extrapolated to higher values of n , but it seems very uncertain whether formula (4) could be extrapolated, as the accuracy of the empirical expressions on which it depends is very doubtful for larger molecules. For this reason it would not be safe to use the formula of Boggia-Lera for molecules with $n > 20$. These molecules are not very stable at the boiling point, however.

It is impossible to prove theoretically the validity of the formula of Boggia-Lera for other compounds, as there are not sufficient data available. We have pointed out, however, that, as a result of the formula of Boggia-Lera, the change in boiling point caused by the replacement of one end group by another one, decreases with the number of methylene groups in a molecule. Now if, on the other hand, we wish to take this former conclusion for an empirical fact, it can easily be shown to prove that for every series the term on the right side must have the same exponent and the factor next to n must have the same value. It also proves that if we want to use an additive term it cannot be added to T . Which leaves us only the original formula of Boggia-Lera, unless we want to use expressions of a more complicated kind.

⁷ van Laar, reference 2, p. 230.