201. *Relationships between the Parachor Values and the Physical Constants of Homologous Series.*

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Relationships are put forward connecting the parachor values with the critical temperatures and boiling points of substances in homologous series. The silicoparaffins obey a relation having the same numerical constants as the corresponding hydrocarbons. Associated substances such as the alcohols and acids do not obey these relations.

By utilising these generalisations certain doubtful atomic parachors have been calculated, and various physical constants predicted.

The connexion between these relations and the co-volume factor of the van der Waals equation is discussed, the parachor being regarded as a true comparative measure of molecular volume.

It has been shown (Lewis, this vol., p. 261) that for chemically similar molecules containing the same number of atoms, the parachor values, P, are connected with the critical temperatures, T_c, and the boiling points, T_B, by means of the equations

$$P = (T_c + \alpha_c')/k_c' = (T_B + \alpha_B')/k_B' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The critical temperatures for the lower members of the saturated and the unsaturated hydrocarbon series have been determined by various authors, but few data are available for the higher members. Though all the substances in such series exhibit great similarity in chemical properties, yet equation (1) cannot be expected to apply because the number of atoms in each successive molecule increases in an arithmetical progression.

It has been found that for such a homologous series, the parachor values are given with precision by the exponential function

$$P = e^{(T_c + \alpha_c)/k_c} = e^{(T_B + \alpha_B)/k_B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the exponent being similar in type to the terms in (1), though $\alpha_c \neq \alpha_c'$ and $k_c \neq k_c'$.

In the equations (2), k_c and k_B are universal constants applicable to all the hydrocarbons, but α_c and α_B increase in value with degree of unsaturation, remaining constant for one definite series. Fig. 1 gives the plot of the logarithms of the parachor values against the critical temperatures and the boiling points of the paraffins (*A* and ***a***), the olefins (*B* and *b*), and the acetylenes (*C* and *c*). The linear nature of the relationship is apparent, and the parallelism of the lines denotes the universal constancy of k_c and k_B. Some slight curvature is observable at octane in the boiling-point graph of the saturated paraffins, but the critical-temperature curve for this same series is absolutely linear.

The aromatic homologous series, benzene, toluene, etc. (*D* and *d*), yields a line which has the same value for $dT_B/d \log P$ as with the aliphatic hydrocarbons, indicating that ring formation does not affect the generality of application of equation (2). From this equation it is possible to calculate various unknown physical constants from a knowledge of the parachor values. The literature contains few data for the benzene series. The general equation $T_c = k_c \log P - \alpha_c$ being assumed, it is possible to calculate the value of α_c, because $T_c = 561{\cdot}5°$ K. for benzene, and k_c is equal to $dT_c/d\log P = 551$ for the paraffins; α_c is thus found to be 716, and on applying this result to toluene ($P = 246{\cdot}1$), the critical temperature is easily calculated to be 599° K., which is within 1% of the experimental figure, 593·6° K. (Int. Crit. Tables, Vol. 3, p. 230).

FIG. 1.

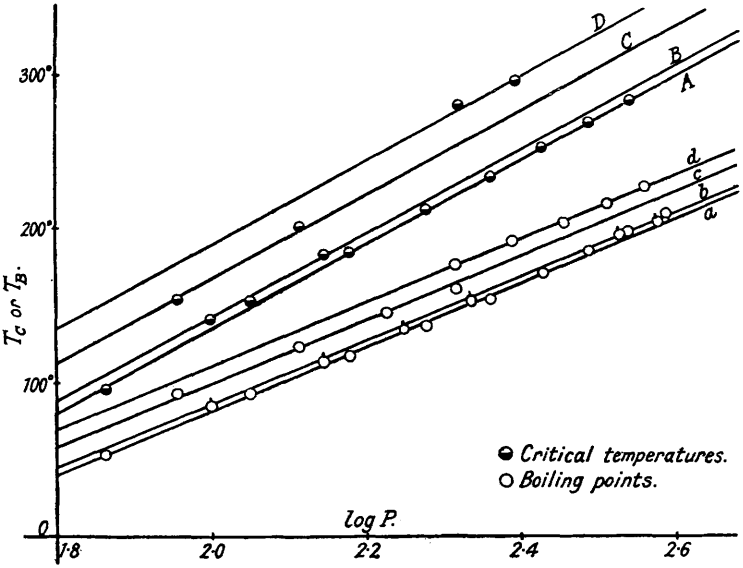


Table I gives the values for the critical temperatures of various hydrocarbons, etc., which have been computed in this manner. Where it is possible to compare the calculated values with known experimental figures, the agreement is all that can be expected. The remaining calculated values should prove a useful check on future experimental determinations.

As far as can be ascertained, the carbon and the silicon series fall approximately on the same line of the graph, indicating the importance of configuration in determining the application of equation (2). That this similarity of behaviour does not extend to equation (1) is shown by comparison (Table II) of the chemically similar halides of these substances. Similar differences in equations are found when the silicochloroform group is compared with the organic chloroform group, the equations being respectively $T_B = 1{\cdot}51P + 7$ and $T_B = 2{\cdot}19P - 70{\cdot}4$. In Table II, the atomic parachor for silicon has been taken as 28·7, obtained as follows. Sugden (*op. cit.*, p. 182), from a comparison of data for three substances, took 57·9 as being the most probable value for the parachor for tin. In this periodic group the parachor for carbon, $P = 4{\cdot}8$, is also known with accuracy, and utilising these figures it is possible to arrive at fairly exact figures for the atomic parachors of the related elements because such groups obey equation (1). The computed values are in Table III, the related hydrides being considered.

TABLE I.

Substance.	P.	T_B, obs.	T_c, obs.	T_c, calc.	$\frac{T_c + a_c}{T_B + a_B}$.	$\frac{T_c}{T_B}$.
Paraffin Series, C_nH_{2n+2}.						
CH_4	73·2	111·7°	190·5°	195°	1·308	1·760
C_2H_6	112·2	187·0	305·1	298	1·326	1·631
n-C_3H_8	151·2	235·0	368·6	369	1·326	1·568
n-C_4H_{10}	190·2	274·0	426·3	424	1·332	1·555
n-C_5H_{12}	229·2	310·0	470·0	468	1·328	1·520
n-C_6H_{14}	268·2	342·0°	507·8°	506°	1·324	1·485
n-C_7H_{16}	307·2	371·4	539·8	539	1·318	1·454
n-C_8H_{18}	346·2	398·5	569·0	567	1·315	1·427
n-C_9H_{20}	385·2	422·7	—	593	—	—
$T_c = 551 \log P - 832$; $T_B = 416 \log P - 670$.						
Silicon Series, Si_nH_{2n+2}.						
SiH_4	97·1	161·0	269·5	263	1·318	1·674
Si_2H_6	160·0	258·0	—	382	—	—
Si_3H_8	222·9	326·0	—	462	—	—
Si_4H_{10}	285·8	353	—	522	—	—
$T_c = 551 \log P - 832$; $T_B = 416 \log P - 670$.						
Olefin Series, C_nH_{2n}.						
C_2H_4	101·2	170·0	282·6	283	1·324	1·662
C_3H_6	140·2	224·8	364·5	359	1·337	1·621
C_4H_8	179·2	268·0	—	419	—	—
C_5H_{10}	218·2	313·0	—	465	—	—
n-C_8H_{16}	335·2	397·0	—	568	—	—
$T_c = 551 \log P - 824$; $T_B = 416 \log P - 664$.						
Acetylene Series, C_nH_{2n-2}.						
C_2H_2	90·4	188·0	309·0	311	1·314	1·640
CMe⋮CH	129·4	249·5	401·0	398	1·311	1·605
CEt⋮CH	168·4	291·0	—	462	—	—
CPr⋮CH	207·4	321·0	—	511	—	—
$T_c = 551 \log P - 765$; $T_B = 416 \log P - 630$.						
Benzene Series.						
C_6H_6	207·1	353·2	561·5	561·5	1·324	1·590
PhMe	246·1	384·0	593·6	599·0	1·316	1·546
PhEt	285·1	409·5	—	637	—	—
PhPr	324·1	431·0	—	667	—	—
PhBu	363·1	453·6	—	694	—	—
$T_c = 551 \log P - 716$; $T_B = 416 \log P - 611$.						

References to Table I: Sugden, "The Parachor and Valency," 1930; Int. Crit. Tables, Vol. 3, p. 230; Pickering, *J. Physical Chem.*, 1924, **28**, 97; Pearson and Robinson, J., 1934, 738; Hodgman–Lange, "Handbook of Chemistry and Physics," 1930, p. 897.

TABLE II.

Substance.	P.	T_B, obs.	T_B, calc.
SiF_4	131·5	—	150·8°
$SiCl_4$	245·9	330·6°	331·6
$SiBrCl_3$	259·6	353·0	353·2
$SiBr_2Cl_2$	273·3	377·0	374·9
$SiBr_3Cl$	287·0	413·5	396·5
$SiBr_4$	300·7	426·0	418·8
$SiICl_3$	282·6	386·5	389·5
SiI_4	392·7	563·0	563·5

$T_B = 1{\cdot}58P - 57$.

Substance.	P.	T_B, obs.	T_B, calc.
CF_4	107·6	—	113·3°
CCl_4	222·0	349·0°	349
CBr_4	276·8	462·0	462
CI_4	368·6	—	651·4

$T_B = 2{\cdot}06P - 108{\cdot}4$.

TABLE III.

Substance.	T_B, ° K.	P (calc.).	ΣP(H).	Atomic parachor, calc.
CH_4	111·7	73·2	68·4	4·8
SiH_4	161·0	97·1	68·4	28·7
GeH_4	184·5	108·5	68·4	40·1
SnH_4	221·0	126·3	68·4	57·9
PbH_4	256·5	143·4	68·4	75·0

Ramsay and Shields's results (J., 1893, **63**, 1089) indicate that the atomic parachor of silicon is 12, but Sugden (*loc. cit.*) suggests that the more probable value is 25, derived from the work of Mills and Robinson (J., 1927, 1823). From a study of the periodic variation of the parachor with group number, Pearson and Robinson (*loc. cit.*) suggest the value 28·4, in good agreement with that calculated from the b. p.'s of the hydrides. Similarly, the calculated value for lead differs very slightly from the value determined by Sugden (J., 1929, 327) from a study of tetraethyl-lead, *viz.*, $P(\text{Pb}) = 76{\cdot}2$. Equation (2) also suggests that a very exact relationship should exist between the critical temperatures and boiling points of substances in homologous series, a connexion which is to be anticipated because the function T_c represents the upper limit of the boiling point as the pressure is indefinitely increased. Guldberg's ratio T_c/T_B (*Z. physikal. Chem.*, 1890, **5**, 374), though remaining constant for related elements, decreases with increasing length of hydrocarbon chain. Elimination of log P between the two equations

$$T_c = k_c \log P - \alpha_c \text{ and } T_B = k_B \log P - \alpha_B$$

yields a modified form of the relation, *i.e.*, $(T_c + \alpha_c)/(T_B + \alpha_B) = k_c/k_B$, which is applicable to both the aliphatic and the aromatic series provided the corresponding values of α_c and α_B be employed. The constancy of this ratio is indicated in the penultimate column of Table I, the theoretical value being the quotient of the coefficients of log P, *i.e.*, 1·324, and the variation shown from this value is negligibly small. By its use, it is obviously possible to calculate the critical temperature of any hydrocarbon provided the b. p. is known. Consideration of the monohalogen derivatives of the paraffins is interesting because they yield illustrations of the chemically related types, CH_3F, CH_3Cl, etc., which obey equation (1), and also of homologous series of the type CH_3F, C_2H_5F, etc., which have critical temperatures varying exponentially with the molar volumes and thus obey equation (2).

The linear relations of type (1) obeyed by the chemically related substances are included in Table IV. It is curious that, in these cases, the coefficients of P yield a practically constant ratio, and the value given by the halogen acids for this ratio is in good agreement with that obtained from the organic halogen derivatives. The linear equations in parentheses were obtained with the help of relation (2), there being insufficient critical temperatures known to derive them from experimental figures. When data for these homologous series are considered, the b. p.–log P graphs for the chlorides, bromides, etc., are parallel, and the five available critical temperatures strongly suggest that these physical constants will vary similarly with increasing parachors.

TABLE IV.

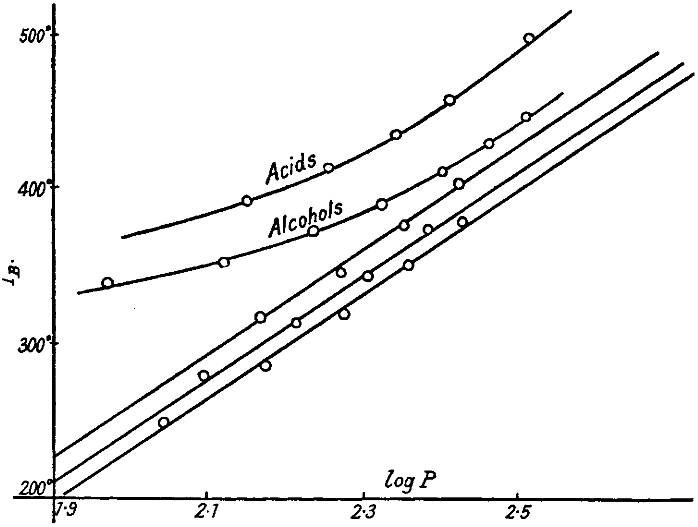
Substance.	P.	T_B, obs.	T_B, calc.	T_c, obs.	T_c, calc.	Substance.	P.	T_B, obs.	T_B, calc.	T_c, obs.	T_c, calc.
CH_3F	81·8	—	197·8°	317·9°	317·8°	C_3H_7F	159·8	—	276·2°	422·0°	422·0°
CH_3Cl	110·4	249·3°	249·3	416·1	415·4	C_3H_7Cl	188·4	319·5°	319·5	503·0	503·3
CH_3Br	124·1	277·5	274	—	462·3	C_3H_7Br	202·1	344·5	340·3	—	544·0
CH_3I	147·1	315·5	315·5	—	541	C_3H_7I	225·1	375·4	375·3	—	612·0
$T_c = 3{\cdot}42P + 38$; $T_B = 1{\cdot}80P + 50{\cdot}6$; ratio of coeffs. = 1·900.						($T_c = 2{\cdot}89T - 40$); $T_B = 1{\cdot}52P + 33{\cdot}1$; ratio of coeffs. = 1·90.					
C_2H_5F	120·8	241·0	240·4	—	367·1	C_4H_9F	198·8	—	310·1	—	454·0
C_2H_5Cl	149·4	285·2	285·0	460·2	460·2	C_4H_9Cl	227·4	350·5	350·3	—	525
C_2H_5Br	163·1	312·0	310·8	504·0	504·0	C_4H_9Br	241·1	374·0	370·0	—	563
C_2H_5I	186·1	345·3	349·0	—	577·7	C_4H_9I	264·1	402·6	402·6	—	631
$T_c = 3{\cdot}21P - 19{\cdot}6$; $T_B = 1{\cdot}66P + 40$; ratio of coeffs. = 1·933.						($T_c = 2{\cdot}70P - 87$); $T_B = 1{\cdot}42P + 27{\cdot}5$; ratio of coeffs. = 1·900.					
HF	42·8	—	149·9	—	246·4	HBr	85·1	206·7	206·2	363·0	361·5
HCl	71·4	188·0	188·0	324·1	324·3	HI	108·1	237·0	236·7	424·0	424·1
$T_c = 2{\cdot}72P + 130$; $T_B = 1{\cdot}33P + 93$; ratio of coeffs. = 2·04.											

Pearson and Robinson (*loc. cit.*, p. 741) have clearly shown that the strong electron-acquisitive nature of the halogen may considerably affect the parachor value of the group to which it is bound (cf. Mumford and Phillips, J., 1929, 2112). Some abnormalities may thus be expected in the halide series owing to a variable hydrogen parachor, but for the purposes of this paper, the parachor of hydrogen is regarded as invariant, and the physical constants of the series are assumed to vary in accordance with equation (2), which was obeyed so well by the hydrocarbons. On the basis of this variation, and by a combined use of equations (1) and (2), the critical constants of these substances have been calculated and are given in the table. The logarithmic constants employed are given below.

Homologous series.	k_c.	k_B.	a_c.	a_B.
Fluorides	350	312	351	405
Chlorides	350	312	300	390
Bromides	350	312	270	377
Iodides	350	312	217	361

In the region studied, the above constants agree extremely well with known data, though the tendency to curvature as the carbon chain elongates is more pronounced for the halides than for the saturated paraffins. For associated substances, very pronounced curvature is observed even when the chains are relatively short, and Fig. 2 shows the curvature exhibited by the monohydric alcohols and monobasic acids as contrasted with the parallel lines given by the halides.

FIG. 2.



From a comparison of parachor values with molecular areas as given by Herzfeld (" Handbuch der Physik," Vol. 22, p. 409, Springer, Berlin), Sugden (*op. cit.*) has shown that the parachor values give an excellent comparative idea of the collisional areas of various molecules. It should therefore be borne in mind that any equations connecting the parachor with certain physical constants may be indicative of an exact relationship between those constants and the true molecular volumes. That molar volumes affect the gas laws is implied in van der Waals's well-known relation, where b is a function of the molecular volume and is usually referred to as the co-volume. It was thought probable that this function might be related to the physical constants in the manner which has been found to apply to the parachor.

In this connexion the following facts are interesting. Sugden (*op. cit.*, p. 32) has shown that for methane the ratio $P^{\frac{1}{2}}/\pi R^2$ is equal to $2{\cdot}27 \times 10^{16}$, where R is the true collisional radius of the molecule. This numerical constant is found to be practically invariant for all molecules. If the value of this constant is accepted as being general for the paraffin series, it is possible to calculate the collisional radius R from the parachor, and hence the molecular volume ($= 4/3\ \pi R^3$). At *N.T.P.*, 1 c.c. of any gas contains $2{\cdot}7 \times 10^{19}$, molecules, and the total molar volume $V_m = 2{\cdot}7 \times 10^{19} \times 4/3\ \pi R^3$ c.c. per c.c. of gas. It will be observed from Table V that the co-volume b, when divided by the total molar volume, yields a quotient which is very approximately 4, thus roughly corroborating the general view that b is four times the volume of the molecules. Since V_m has been derived from the parachor, the constancy of this ratio also indicates the close connexion between this function and the molar volume.

TABLE V.

Substance.	$b \times 10^3$.	$V_m \times 10^4$.	b/V_m.	$-\log b$.	$-\log b$ (calc.).
Methane	1·91	4·350	4·390	2·719	2·718
Ethane	2·848	6·662	4·270	2·5452	2·501
Propane	3·770	8·978	4·200	2·4237	2·380
Butane	5·472	11·28	4·840	2·2618	2·2700
Pentane	6·516	13·60	4·800	2·1861	2·188
Hexane	7·747	15·90	4·860	2·1110	2·114

The b values also obey an equation of the form $b = e^{(T_c + a)/k}$, which is identical with (2), for the values of log b in the last column of Table V have been calculated from the critical temperatures by means of the relation $T_c = 525 \log b + 1618$. Similarly the b values of chemically related substances obey equation (1), as demonstrated below for the inert gases and the monohalogen derivatives of benzene.

Substance.	T_c.	$b \times 10^6$ (obs.).	$b \times 10^6$ (calc.).
He	33·00°	1058	692
Ne	44·3	763	763
A	151·0	1437	1420
Kr	210·0	1776	1786
Xe	289·6	2279	2279

$T_c = 161800b - 79{\cdot}1.$

Substance.	T_c.	$b \times 10^6$ (obs.).	$b \times 10^6$ (calc.).
C_6H_5F	559·0°	5742	5741
C_6H_5Cl	632·0	6485	6486
C_6H_5Br	670·0	6872	6873
C_6H_5I	721·0	7395	7394

$T_c = 98000b - 3{\cdot}6.$

In the last series, agreement is excellent, but helium exhibits some anomaly. This is to be expected because it possesses a unique electronic configuration which probably greatly modifies its general physical characteristics. Agreement is so good in the more normal of the inert gases that if the critical temperature of radon is taken as 104° (377° K.), the b value for this gas may be predicted to be 0·002819.

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