494. *Boiling Points of Homologous Liquids.*

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The equation $T_b = a\sqrt{(\Sigma Z)} + b$ has been found to represent the boiling points of many homologous series, *e.g.*, *n*-alkyl fluorides, chlorides, bromides, iodides, acids, amines, aldehydes, ketones, *n*-alkyl-benzenes, *-cyclo*hexanes, and *-cyclo*hex-1-enes, where ΣZ is the atomic number sum and a and b are constants characteristic of any particular series. For *n*-alkanes, *n*-alkenes, and *n*-alkynes the above equation is not applicable, but T_b is found to be related linearly to the cube root of ΣZ; for alcohols, thiols, esters, and ethers T_b is related approximately linearly to ΣZ.

The boiling points of a series of compounds, especially halides of similar structure and having an equal number of atoms in the molecule, have been successfully correlated with the atomic number of the varying atoms in the series.[1] We now attempt to correlate the boiling points of a homologous series by using atomic number as the independent parameter. We now suggest the empirical relation (1) between the boiling point, T_b, in any homologous series and the sum of the atomic numbers of the atoms in the molecule (ΣZ), a and b being constants.

$$T_b = a\sqrt{(\Sigma Z)} + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Aldehydes, Ketones, Acids, Primary, Secondary, and Tertiary Amines and Halides.—We illustrate equation (1) with eight homologous *n*-alkyl series in Fig. 1 (bromides and iodides not shown). The plot of T_b against the square-root of ΣZ gives straight lines agreeing with the equation, except for occasional slight departure for the first member of a series.

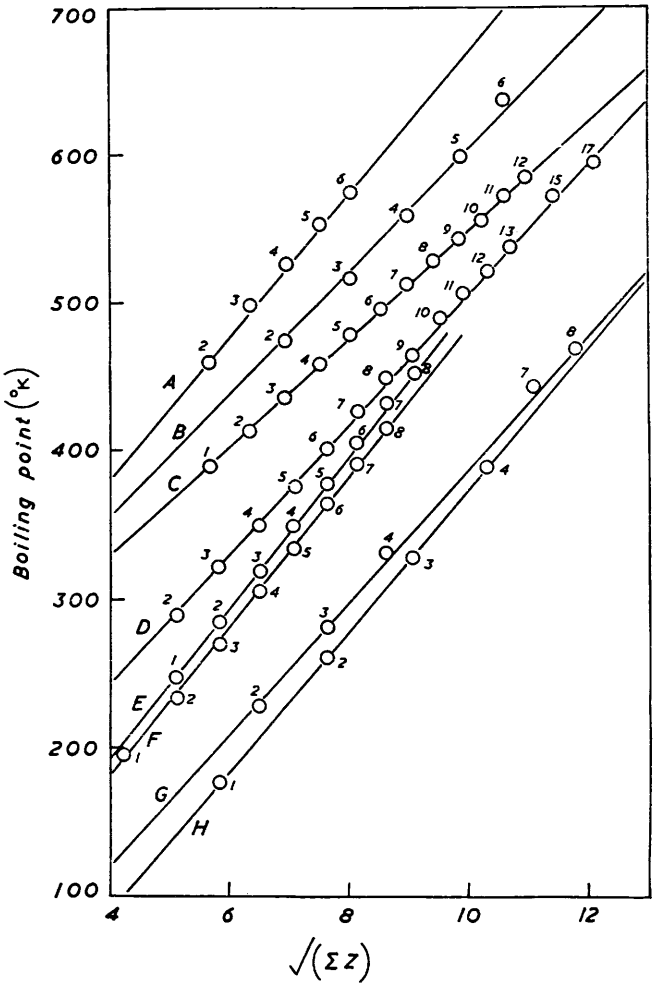
The least-square values of a and b are compiled in the Table (1—13). The slopes for all the series are of the same order of magnitude, those for the halides being the highest and that for the fatty acids the lowest. It is remarkable that the value of a lies within such a narrow range for these various types of compounds. With regard to the value of b, the boiling point corresponding to zero atomic number, the highly electronegative elements, *viz.*, the halides, lead to the lowest values and the carboxylic acids the highest; the value of b decreases continuously from primary through secondary to tertiary amine. Since the variation in slope among the different homologous series is small, it is clear that the intercept (b) plays the more important part in determining boiling point.

	Homologous Series	a	b	p		Homologous Series	a	b	p
1.	*n*-Alkyl fluorides	51·31	− 26·70[1]	½	11.	*n*-Alkyl-benzenes	46·88	52·57	½
2.	,, chlorides	52·06	− 17·05	,,	12.	,, *-cyclo*hexanes ...	49·54	9·16	,,
3.	,, bromides	57·54	−102·5	,,	13.	,, *-cyclo*hex-1-enes	47·24	34·10	,,
4.	,, iodides	61·10	−164·0	,,	14.	*n*-Alkanes	154·40	−223·90	⅓
5.	,, aldehydes	48·87	36·85	,,	15.	*n*-Alk-1-enes	154·45	−222·10	,,
6.	,, ketones	44·11	67·20	,,	16.	*n*-Alk-1-ynes	144·44	−168·78	,,
7.	,, acids	36·17	188·0	,,	17.	Normal alcohols	2·44	288·0	1
8.	,, primary amines...	45·43	55·56	,,	18.	*n*-Alkyl ethers	3·58	157·10	,,
9.	,, secondary amines	46·52	28·10	,,	19.	,, acetates	2·76	220·80	,,
10.	,, tertiary amines ...	47·95	− 5·05	,,	20.	*n*-Alkanethiols	3·87	178·0	,,

[1] Somayajulu, *Indian J. Phys.*, 1956, **30**, 258.

Hydrocarbons.—For simple hydrocarbons, *viz.*, alkanes, alkenes, and alkynes, the simple square-root plot apparently gives two straight lines intersecting near C_{10} in all cases (Fig. 2). We do not, however, attach any special importance to this, as good straight lines

FIG. 1. *Boiling points of* n-*alkyl derivatives.*



A, R·CHO (T_b + 150°); *B*, R_2CO (T_b + 100°); *C*, R·CO_2H; *D*, R·NH_2; *E*, RCl; *F*, RF; *G*, R_2NH (T_b − 100°); *H*, R_3N (T_b − 100°).
In all Figures the numerals against each point represent the number of carbon atoms in the alkyl group.

are obtained by changing the exponent to 1/3 as is shown in Fig. 3. It appears that the general relation is of the form,

$$T_b = a(\Sigma Z)^p + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

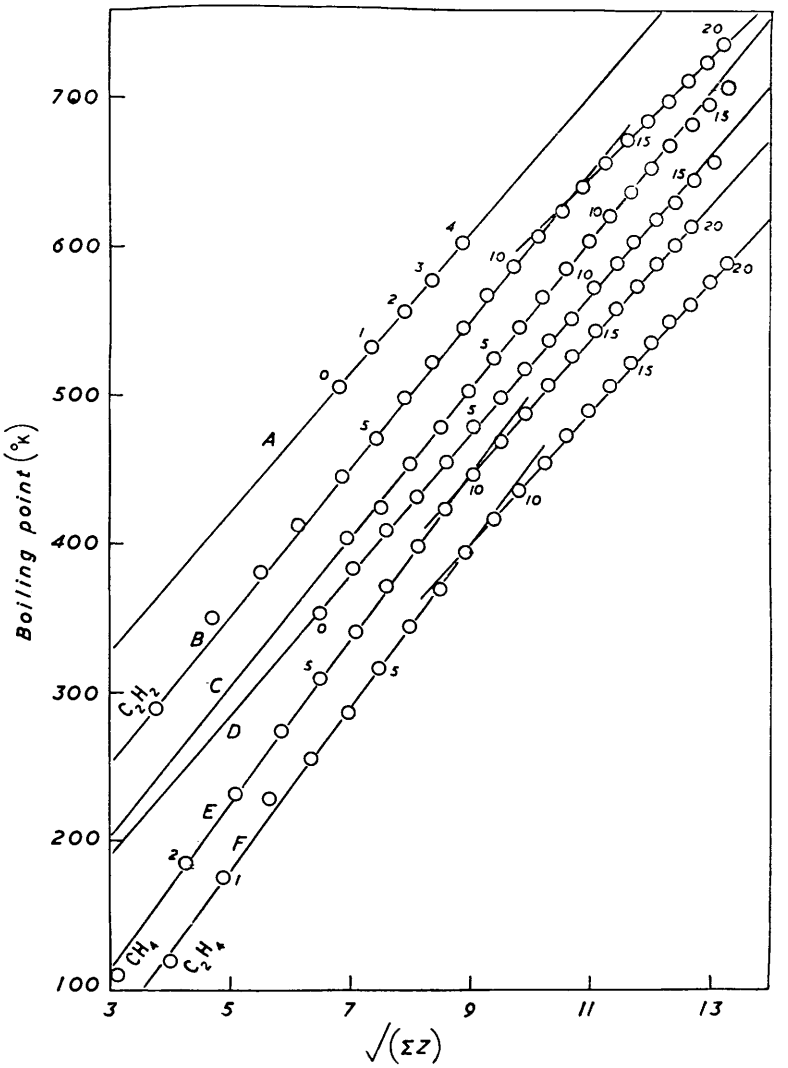
where p is usually 1/2 but differs from this value for simple aliphatic hydrocarbons and a few other series. However, for other hydrocarbon series, *viz.*, alkyl-benzenes, *-cyclo*-hexanes, and *-cyclo*hexenes, the square-root relation is quite good (Fig. 2), though a slight change of exponent makes it even better. The values of the constants a and b and of the exponent p are also collected in the Table.

Comparison with Previous Equations.—Several equations have already been suggested

to correlate the boiling point with either the molecular weight or the number of carbon atoms as the variable parameter; our suggestion of atomic number is novel. A summary of these equations has been given by Partington [2] and the situation has been lately discussed by Varshni.[3] The most successful is that of Boggio-Lera [4]

$$T_b^2 = AM + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

FIG. 2. *Boiling points of hydrocarbons.*



A, Alkyl*cyclo*hexenes ($T_b + 150°$); *B*, alkynes (treated as alkylacetylenes) ($T_b + 100°$); *C*, alkyl*cyclo*hexanes; *D*, alkylbenzenes; *E*, alkanes (treated as alkylmethanes); *F*, alkenes (treated as alkylethylenes) ($T_b - 50°$).

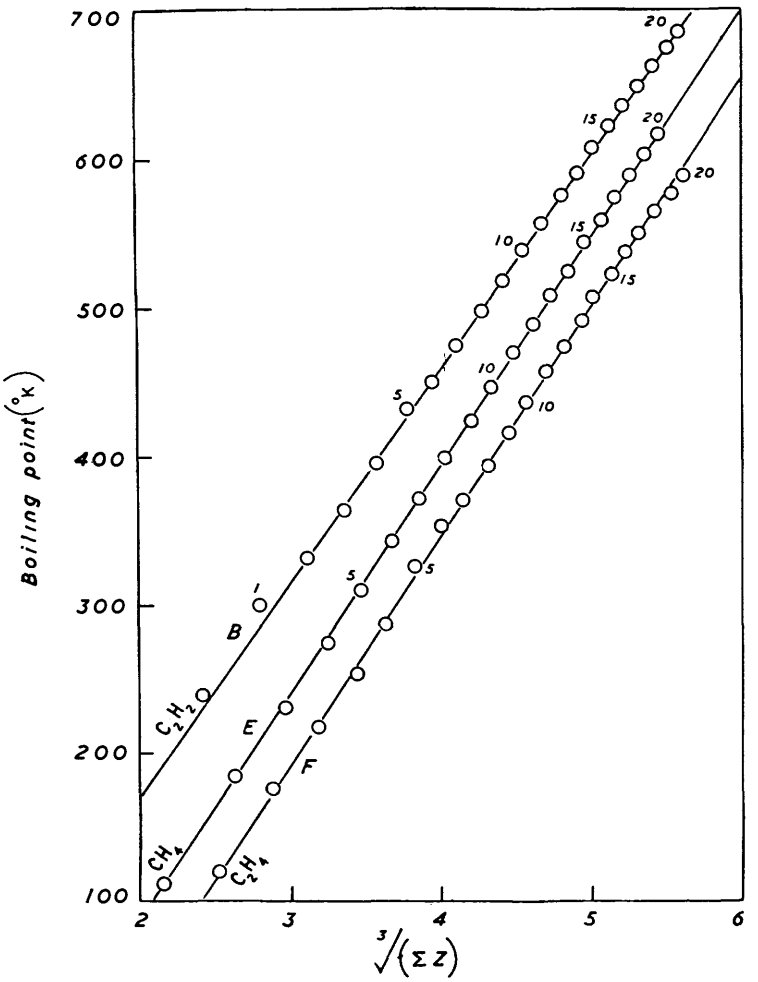
where M is the molecular weight. This equation evidently is in essence similar to ours and gives good correlation in many cases. We have compared Boggio-Lera's equation

[2] Cf. Partington, " An Advanced Treatise on Physical Chemistry," Vol. II, Longmans, Green and Co., London, 1951, pp. 275—303.
[3] Varshni, *J. Indian Chem. Soc.*, 1953, **30**, 169; 1955, **32**, 211.
[4] Boggio-Lera, *Gazzetta*, 1899, **29**, 441.

with ours and have found that in the twenty series studied by us Boggio-Lera's equation is as good as ours in 7 cases, inferior in 3 cases (series 11, 12, and 13 of the Table), and wrong in 10 cases (series 8—10 and 14—20). We do not, therefore, favour an equation of the form of Boggio-Lera's even with atomic number as the variable parameter (*i.e.*, T_b^2 linear in, say, ΣZ).

Other equations which have attracted attention are by Nekrassov,[5] who has attempted

FIG. 3. *Boiling points of linear hydrocarbons.*



B, Alkynes (treated as alkylacetylenes) (T_b + 50°); *E*, alkanes (treated as alkylmethanes); *F*, alkenes (treated as alkylethylenes) (T_b + 50°).

to correlate T_b with some structural constants (a simple graphical plot shows its weakness) and by Van Arkel,[6] which correlates T_b with the molar volume of halides. Somayajulu [1] has shown that for halides atomic number effectively correlates the boiling points and no molar-volume data are necessary. The boiling point for halides from this standpoint will be dealt with in greater detail in a later communication.

Alcohols, Thiols, Ethers, and Esters.—So far we have dealt with practically all mono-substituted alkanes except the above four series, which do not obey the square-root

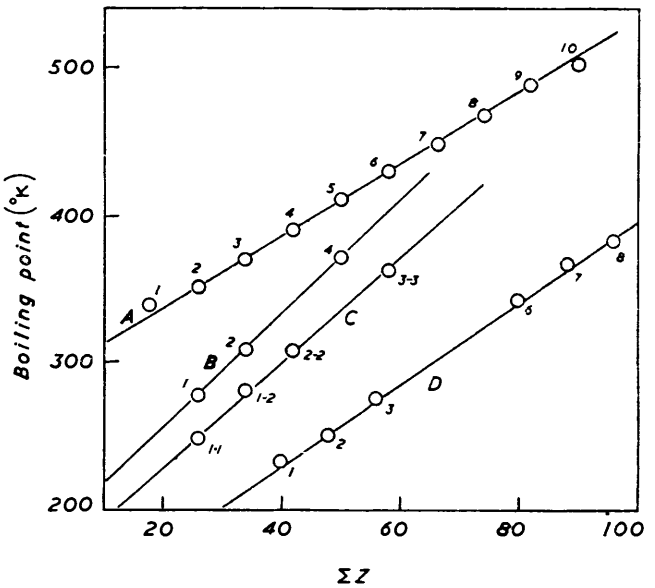
[5] Nekrassov, *Z. phys. Chem.*, 1929, *A*, **141**, 378; 1930, *A*, **148**, 216.
[6] Van Arkel, *Rec. Trav. chim.*, 1932, **51**, 1081; 1933, **52**, 719, 733; 1934, **53**, 91, 146.

relation but an equation of the form of eqn. 2 with $p = 1$ (Fig. 4). This relation is rather approximate and is essentially the same as is already known that in such series T_b is more or less linear with M. It is surprising that these simple compounds should behave so differently from the rest. The values of the constants a and b for these four series have been also collected in the Table.

Boiling Point and Other Properties.—Since we have correlated T_b with ΣZ and since the latter has been correlated [1, 7] with many physical properties, it follows that T_b will be simply related to such properties. One of the most evident is molar refraction, R, which is well known to be linear with ΣZ for a homologous series.

Some other physical properties depending on boiling point can also be correlated with atomic number. Thus from Trouton's rule, and also from Guldberg's rule, the heat of

FIG. 4. *Boiling points of alcohols, thiols, ethers, and esters.*



A, R·OH; *B*, R·SH; *C*, R′·O·R″; *D*, $CH_3 \cdot CO_2R$ ($T_b - 100$).

vaporisation and the critical temperature should both be linear with $\sqrt{(\Sigma Z)}$ in a homologous series. Also, from the semi-theoretical equation recently developed by Palit [8] that log ηM is linear with T_b, log ηM should be linear with $\sqrt{(\Sigma Z)}$.

From our present work it seems that the possibility of expressing boiling point as an additive function of properties of the atoms or groups present in a molecule seems to be rather remote, and that the atomic-number sum ΣZ (equal to the number of electrons in a molecule) is a fundamental property of an organic molecule and many of its physical properties are a function of it.

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[7] Somayajulu and Palit, *Indian J. Phys.*, 1956, **30**, 262.
[8] Palit, *J.*, 1956, 2740.
[9] "Selected values of physical and thermodynamic properties of hydrocarbons and related compounds," American Petroleum Institute Research Project, Carnegie Press, Pittsburgh, 1953.
[10] Rodd, "Chemistry of Carbon Compounds," Vol. I, Elsevier, New York, 1953.
[11] Hodgman, "Handbook of Physics and Chemistry," Chemical Rubber Publ. Co., Ohio, 1948.