51. *An Extension of the Macleod Equation.*

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It is suggested that the Macleod constant is a function of the critical temperature of a substance, and it has been established that for similar groups of substances, the critical temperatures, boiling points, and molar heats of vaporisation are connected with the parachor values by simple linear relationships. Divergence from these relationships is taken as evidence of association.

By utilising these generalisations, values for the various physical constants of certain elements have been calculated; parachor values so obtained exhibit close agreement with those suggested by Sugden from a study of the periodic variation of the parachor.

MACLEOD (*Trans. Faraday Soc.*, 1923, **19**, 38) has shown that the surface tension γ may be connected with the density of the liquid and of the vapour at the same temperature, D and d respectively, by means of the equation

$$\gamma = C(D - d)^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The constant C is unaffected by increase of temperature for normal liquids, but shows a slight and steady rise for associated liquids.

Fowler (*Proc. Roy. Soc.*, 1937, *A*, **153**, 229) has derived this equation in the form

$$\gamma = \frac{B}{4A^2T_c}\left(\frac{n}{V} - \frac{n'}{V}\right)^4 = \frac{B}{4mA^2T_c}(D - d)^4 \quad . \quad . \quad . \quad . \quad (2)$$

where n/V, n'/V represent the average molecular densities, m is the mass of the molecule, $A = 12n^2/V_c^2T_c$ is a constant for one particular substance, and B is an integral function whose evaluation for an individual element requires a precise knowledge of atomic dimensions, and of the interaction energy E_r for a pair of molecules. This equation has been shown to yield satisfactory values for the parachor values of argon and mercury, but its general application to a complete chemical group is rendered difficult owing to lack of precise data for the evaluation of B and A. It does indicate, however, that there may exist a simple connection between the parachor values, P, and the critical temperatures, T_c, of various elements.

Katayama (*Sci. Rep. Tôhoku Imp. Univ.*, 1916, **4**, 373) has suggested an equation of the form

$$\gamma[M/(D - d)]^{2/3} = k(T_c - T) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Elimination of γ between (1) and (3) gives for the Macleod constant

$$C = k(T_c - T)/M^{2/3}(D - d)^{10/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Mathias ("Le Point Critique des Corps Purs," 1904, p. 164) has shown that, in accordance with the law of rectilinear diameter, the critical density D_c may be calculated by means of the equation

$$D_c = M/V_c = (D - d)/2(2 - T/T_c) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It is not generally realised that this equation was suggested in a modified form by Thorpe

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and Rucker (J., 1884, **45**, 135), who demonstrated the exact nature of its application. Substituting for $(D - d)$ in equation (4), we have

$$C = k(T_c - T)/M^4[(4T_c - 2T)/V_c T_c]^{10/3} \quad \ldots \quad \ldots \quad (6)$$

This formula also indicates that the Macleod constant should be dependent on the critical temperature. Curiously enough, the above function does not vary appreciably when the values concerned are fairly remote from the critical point. In the following table k has been given the value 2·3, although it is well known that it varies slightly from substance. The experimental data are taken from Sugden ('' The Parachor and Valency,'' 1930, p. 27).

Benzene.

($T_c = 288·5°$; $V_c = 256·5$ c.c.)

t	20°	61°	90°	180°	210°	280°
$C^{1/4}$ (calc.)	2·634	2·634	2·630	2·52	2·190	1·520
$C^{1/4}$ (obs.)	2·638	2·647	2·646	2·641	2·657	3·372

The value for C given by equation (6) must be erroneous, for it predicts that the Macleod constant should become zero at the critical temperature whereas experimental results show that it tends to retain its normal value. Both this equation and Fowler's (*loc. cit.*) indicate that C should be a function of the critical temperature, and from a survey of the available data it is suggested that the Macleod equation be rewritten in the form

$$\gamma = [(T_c - \alpha)/MK]^4(D - d)^4 \quad \ldots \quad \ldots \quad (7)$$

in which M, the molecular weight, occurs to the fourth power as in (6). The constants α and K remain the same for one distinct chemical group and are probably configurational or cohesional functions characterising a particular type of molecule. Their values are determined from known data.

Sugden (*op. cit.*, p. 30) has defined the parachor as being given by $MC^{1/4}$, whence it follows that

$$P = (T_c - \alpha)/K \quad \ldots \quad \ldots \quad \ldots \quad (8)$$

i. e., the parachor for similar substances should be a linear function of the critical temperatures. This has been found to be the case for all the groups so far examined. The following equations have been derived from a graphical study of such groups.

Group.	Equation.	Group.	Equation.
Inert gases	$T_c = 3·7P - 48$	Methyl fluoride group ...	$T_c = 3·43P + 39$
Halogens, including BrCl, etc.	$T_c = 5·57P - 188$	Ethyl fluoride group ...	$T_c = 3·21P - 20$
Halogen acids	$T_c = 2·72P + 130$	Fluorobenzene group ...	$T_c = 2·33P + 63$

For a large number of substances it has been pointed out by Sugden (*op. cit.*) that the function P/V_c is approximately constant and has the value 0·77. This rule does not apply with the inert gases. In the following table it will be seen that, although the parachors decrease linearly with the critical temperatures, there is no precise connection between them and the critical volume; moreover, the critical volume of helium is greater than that of neon although the parachor value is less.

Substance.	P.	T_c, K.	V_c.	T_b, K.*	T_c/T_b.	P/V_c.
Helium	20·5	33·0°	57·7	4·1°	8·048	0·3553
Neon	25·0	44·3	41·7	27·1	1·634	0·5995
Argon	54·0	151	75·3	87·3	1·730	0·7171
Krypton	68·0	210	92·0	121·2	1·733	0·7391
Xenon	91·0	289·6	112·7	163·9	1·767	0·8076

* T_b is the boiling point.

The previous equations being accepted, the parachors of various substances can be calculated from their known critical temperatures. The following table shows the applicability of these relationships, P (S) being the values calculated from Sugden's atomic constants.

Substance.	T_c, K.*	P (calc.).	P (S).	Substance.	T_c, K.*	P (calc.).	P (S).
He	33·0°	21·9	20·5 †	Kr	210·0°	69·72	(68)
Ne	44·3	25·0	25·0 †	Xe	289·6	91·22	(91)
A	151·0	53·78	54·0 †	Rn	377·0	114·9	—
Cl	416·9	108·6	108·6	I	826·0	182·0	182·0
Br	575·4	137·0	136·0	F	99·4 ‡	—	51·4
HF	246·4 ‡	—	42·8	HBr	363·0	85·67	85·1
HCl	324·1	71·36	71·4	HI	424·0	108·1	108·1
C_6H_5F	559·0	212·9	215·7	C_6H_5Br	670·0	260·5	258·0
C_6H_5Cl	632·0	244·2	244·3	C_6H_5I	721	281·8	281·0

* Critical constants are taken from Lange's "Handbook of Chemistry and Physics," p. 897; Pickering, *J. Physical Chem.*, 1924, **28**, 97; and "International Critical Tables," Vol. III, p. 230.

† Experimental data (Sugden, *op. cit.*).

‡ Calculated from known parachor.

In the above table, the critical temperatures of fluorine and undissociated hydrogen fluoride, being unknown, have been calculated from the known parachor values. In the other cases the parachor values have been computed from existing data; those given for the first three inert gases are values determined at the Leiden laboratories. The values for krypton and xenon were suggested by Sugden from a study of the periodic variation of the parachor and agree very well with the calculated values. A probable value for radon appears to be 114·9
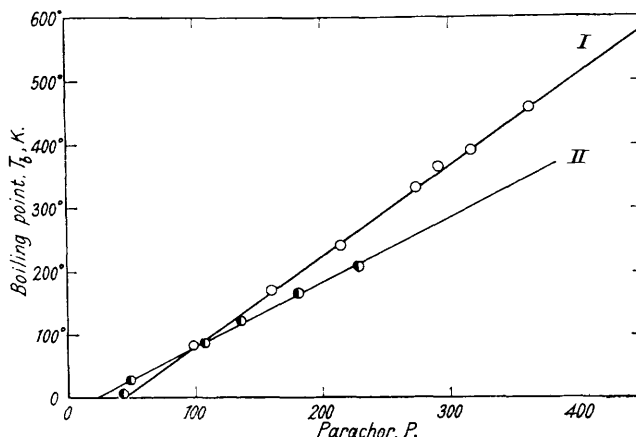
Where there is association, *e.g.*, as with hydrogen fluoride, there is a distinct departure from the linear relationship obeyed by the other members of the family. It is not possible, through lack of data, to apply these equations to many substances, but it has been observed that the plot of the boiling points, T_b, against the parachor values gives a relation which is as precise as when the critical temperatures are used. The graphs, I and II respectively, give the plot of the boiling points of the halogens (including halogen halides) and the inert gases against their respective parachor values as abscissæ.

This agreement suggests that there should be a very precise connection between the boiling points and the critical temperatures of chemically related elements, and this has been investigated by Pawlewski (*Ber.*, 1882, **15**, 460) and Guldberg (*Z. physikal. Chem.*, 1890, **5**, 374). The latter demonstrated that for closely related substances, the ratio T_c/T_b was very nearly constant. If we consider the two derived equations for the inert gases, *viz.*, $T_c = 3\cdot7P - 48$ and $T_b = 2\cdot07P - 24\cdot6$, and eliminate P it is apparent that a more accurate form of the Guldberg ratio would be $(T_c + \theta)/(T_b + \lambda)$, where θ and λ are constants. The two ratios are compared in the following table.

Substance.	T_c, K.	T_b, K.	T_c/T_b.	$(T_c + 48)/(T_b + 24\cdot6)$.
He	33·0°	4·1°	8·048	2·832
Ne	44·3	27·1	1·634	1·785
A	151	87·3	1·730	1·778
Kr	210	121·2	1·733	1·775
Xe	289·6	163·9	1·767	1·791

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The expected value for the constant is the quotient of the coefficients of P, *i.e.*, 1·786, and except with helium the fluctuation from this value is less than 1%.

By utilising the boiling point relation, an analysis has been made of the parachors of the alkali metals, whose boiling points fall regularly with increasing molecular volume. With Sugden's values for the parachors of sodium, potassium, and rubidium (*op. cit.*, p. 179), it will be found that a perfectly linear relationship is obtained with the boiling points, and if that of cæsium is accepted as 670°, a parachor value of 140 could be predicted for this substance. Sugden gives six values for this function derived from data concerning six different salts, and five of them are in the neighbourhood of this value. The sixth value, 153, is derived from the cæsium iodide, and in all cases iodides lead to higher values than other salts. It is suggested that $P = 140$ is the more correct value for cæsium, Sugden's provisional value being 150 ± 10. From the relationships now described, many others can be derived. For example, it is obvious by Trouton's law that a perfectly linear relation will exist between the parachor and the molar heat of vaporisation. This has been verified by the author, and an application of this relation to the data of Durrant, Pearson, and Robinson (J., 1934, 731) corroborates their conclusion that in the phosphine family arsine and stibine are normal liquids, whereas phosphine, and to a much greater extent ammonia, are associated.