975. *Dependence of Physical Properties on Atomic Size and Atomic Number. Part V.* Boiling Points of Halides.*

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In a sequence of halides the b. p. is a linear function of the surface area of the halogen atoms in the molecule. The b. p.s of two similar sequences are also linearly related. A generalised scheme giving linear correlation between b. p.s of any sequence of halides and those of the halogens is presented.

SOMAYAJULU[1] has empirically shown that in any sequence of compounds of the general formula RX_n, where X is a halogen and R any atom or atomic group, the boiling point is linearly related to the sum of the effective atomic numbers (Z') of the halogen atoms in RX_n, the value of Z' being empirically taken as 9, 17, 22, and 30 for F, Cl, Br, and I respectively, in place of their true atomic numbers (Z) of 9, 17, 35, and 53 respectively. Thus

$$T_b = a \sum Z' + b \qquad (1)$$

a and b being constants for any particular sequence.

The above relation is highly successful and consistent in describing the boiling-point trend in many series of compounds, such as interhalogens, tetrahalides of silicon and carbon, and many other halides. The objection due to the arbitrary nature of Z' can be overcome by using the square of the atomic radius (*i.e.*, a fraction of surface area) in place of Z', this giving[2] similar correlation with T_b. The present paper demonstrates the validity of such simple inter-relations and their consequence, and the general validity of all such relations for a wide variety of sequences.

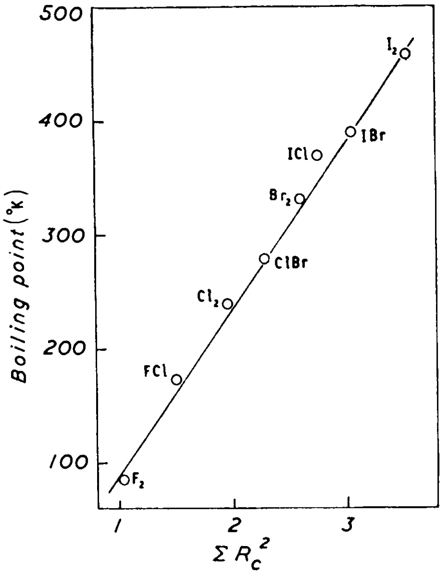

FIG. 1. *Boiling point as a function of the surface area for the halogens and diatomic interhalogens.*

Boiling Point and Atomic Size.—In the halogen series,[2] Z' is proportional to R_c^2 where R_c is the covalent atomic radius of the halogen atom. Substituting this value of Z' in equation (1), we immediately obtain

$$T_b = a_1 \sum R_c^2 + b \qquad (2)$$

where a_1 and b are constants, *i.e.*, in a sequence of similar compounds containing halogens, the boiling point is linearly related to the sum of the squares of the covalent radii of the

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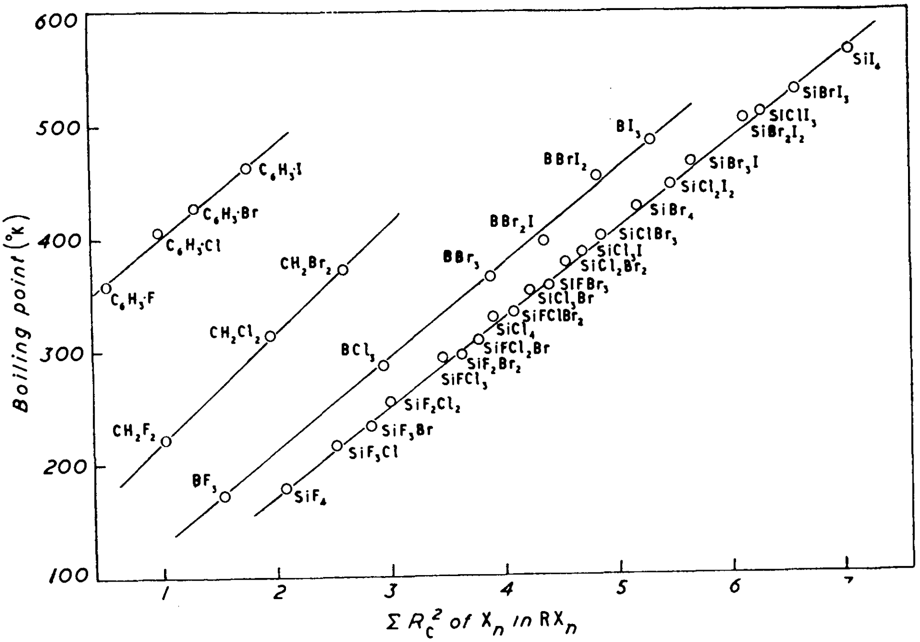
* Parts I—IV are considered to be, respectively, refs. 1 and 2, *J. Chem. Phys.*, 1957, **26**, 807, and *J.*, 1957, 2540.

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

[2] Somayajulu and Palit, *ibid.*, p. 262.

halogen atoms in the molecule (Figs. 1 and 2). The values of R_c used for the halogens are by Schomaker and Stevenson,[3] namely 0·72, 0·99, 1·14, and 1·33 Å respectively, for F, Cl, Br, and I.

FIG. 2. *Boiling point as a function of the surface area for phenyl halides, methylene halides, boron trihalides, and silicon tetrahalides.*



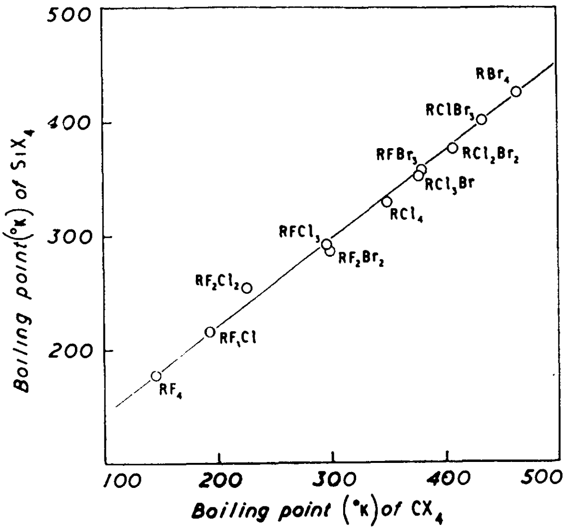


FIG. 3. *Boiling point of silicon tetrahalides as a function of boiling point of carbon tetrahalides.*

Fig. 1 demonstrates the validity of relation (2) for the halogens and interhalogens, X_2. In all cases where Somayajulu's relation is valid,[1] eqn. (2) would also be applicable and graphs of the type of Fig. 1 would be obtained. We give in Fig. 2 a few representative graphs for four typical sequences of the type RX, RX_2, RX_3, and RX_4, represented by phenyl halides, methylene halides, boron trihalides, and silicon tetrahalides.

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[3] Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

Correlation between T_b of Two Sequences.—If eqn. (1) [or (2)] is valid, T_b of two sequences of the same type would be linearly related, *i.e.*,

$$T_b' = \alpha T_b'' + \beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where α and β are constants. Thus, we find the simple result that T_b of halides of, say, carbon would be linearly related to that of any other sequence of halides, say, of silicon, provided they contain the same number of halogen atoms in the molecule and corresponding members of the two sequences are compared. The validity of this is shown by Fig. 3. We can thus predict the boiling point of an unknown silicon halide from that of the corresponding carbon halide and *vice versa.*

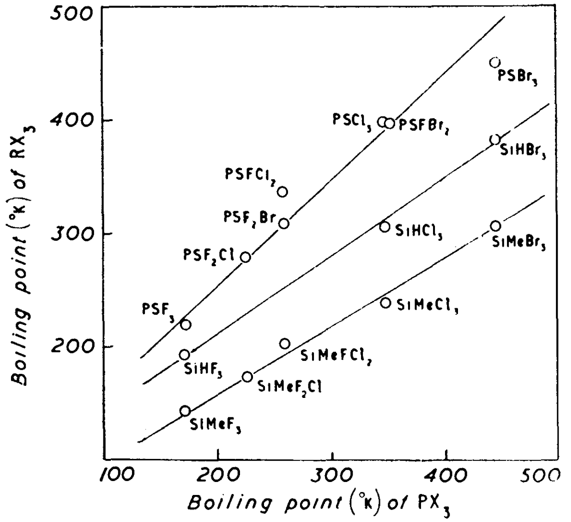

FIG. 4. *Boiling point of the sequences* PSX_3, $SiHX_3$, *and* $SiMeX_3$ (T_b − 100) *versus boiling point of* PX_3.

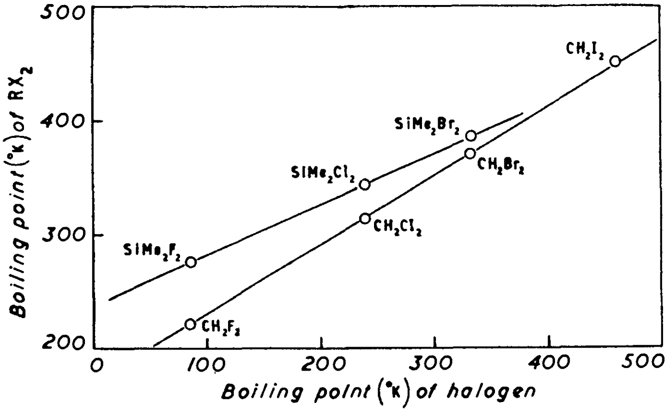

FIG. 5. *Boiling point of* CH_2X_2 *and* $SiMe_2X_2$ *versus boiling point of* X_2.

For three trihalide series, phosphorus trihalides being taken as the basis for comparison, Fig. 4 shows that eqn. (3) is fairly held, and that even in such complicated compounds as phosphorus thiohalides it is valid.

In Fig. 5, T_b of the simplest carbon dihalides, plotted against that of the halogens (no b. p. data for mixed dihalides are available), again shows the relation to be valid, and we conclude that the boiling-point trend of the halogens is somehow maintained in combination. Similar remarks apply to the boiling points of dimethylsilicon dihalides.

Fig. 6 shows that eqn. (3) fairly well represents the behaviour of some monohalogen derivatives. From the method of derivation of eqn. (3) we can use T_b for pure halogens as our basis for comparison, for monohalides as for dihalides, so here also we conclude that the boiling-point trend of the pure halogens somehow persists in their monohalogen derivatives.

A remarkable feature of Figs. 3—6 is that, though the intercepts vary widely, the variation of the slope, α, is small and its value is not far from unity, which shows that a and a_1 are of the same order of magnitude for all sequences. The much lower (almost half) slope in Fig. 6 is only an apparent exception to this, because here we compare a monohalogen series with the diatomic pure halogens. It is surprising that these general trends in the boiling points of halogen compounds has not been earlier observed except for a few cases. For example, the boiling points of halides are [4, 5] linear with the polarisability of the halogens, and the boiling points of halide sequence of rare-gas structure are [6] linear with the boiling points of the corresponding rare gases. Very recently Macdiarmid [7] has noted that the boiling points of dimethylsilicon dihalides are linear with those of the corresponding carbon compounds. These observations fit in with our more general relations discussed here and previously.

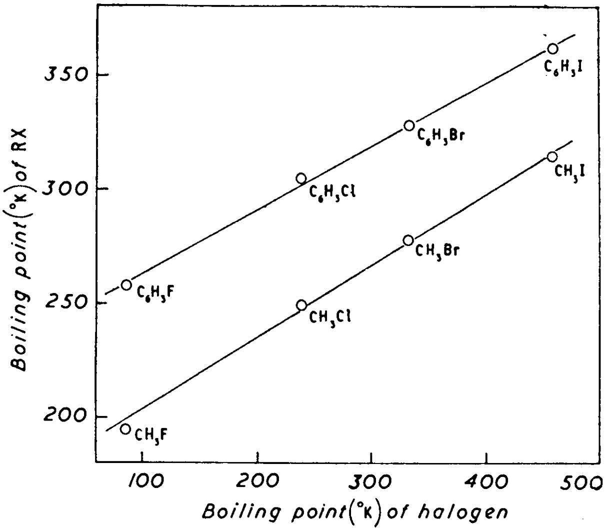

FIG. 6. *Boiling point of* CH_3X *and* C_6H_5X *versus boiling point of* X_2.

A Generalised T_b versus T_b *Plot.*—Eqn. (3) can be graphically represented in a more general way. From the linear form of the foregoing equations, a fictitious set of boiling points (°K), *viz.*, half the T_b of F_2, Cl_2, Br_2, and I_2, can be allotted to F, Cl, Br, and I and such boiling points properly summed can be used as the abscissa in a generalised T_b *versus* T_b plot for comparison with those of any sequence of halogen compounds containing the same number of halogen atoms. This has been done in Fig. 7 for many sequences of halogen compounds. All sequences show linearity, the slope of the lines being not far from unity for all of them. The intercept depends among other factors on the mass and structure of the molecules. Such diagrams are useful in predicting the order of boiling points of a given sequence of halogenated compounds, and, knowing the values of any two, those of the others. This is worth while, as there are 4, 10, 20, and 35 compounds in any sequence of RX, RX_2, RX_3, and RX_4 type respectively.

Boiling Point and Z'.—Though eqns. (2) and (3), being free from the objection of

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[4] Huckel, " Structural Chemistry of Inorganic Compounds," Vol. II, Elsevier, New York, 1951.

[5] Van Arkel, " Molecules and Crystals," 2nd Edn., Butterworths Scientific Publications, London, 1947.

[6] Carlson, *Ber.*, 1925, **58**, 1747.

[7] Macdiarmid, *Quart. Rev.*, 1956, **10**, 208.

arbitrariness of Z' value, appear to be of more fundamental significance than eqn. (1), we do not consider them any better for the following reasons. First, not only are the same values of S, where $Z' = Z - S$, consistently used for halogens, but the same values cause good correlations in sequences of elements of other groups of the Periodic Table. Secondly, not only T_b but also many other properties of various sequences are correlated simply[1] with Z'. Thirdly, the most important argument for using Z' values is that the sequence relations discussed here are all linear, so it is immaterial whether the summation in $\sum Z'$ or $\sum R_c^2$ concerns only the halogen atoms in the molecule or the whole molecule, and our choice of the former is a mere convenience. In a homologous series, however, T_b is often related linearly [8] to $\sqrt{\sum Z}$ or $\sqrt{\sum Z'}$ of the whole molecule, and in such cases relations of the type of eqn. (2) or (3) are either inapplicable or difficult to apply. We have therefore explored below the validity of eqn. (1), but clearly wherever eqn. (1) is found to be applicable, eqns. (2) and (3) and also the generalised plot are necessarily valid.

FIG. 7. *Boiling point of* SiH_3X, $SiMe_2X_2$, BX_3, *and* CX_4 versus *boiling point of* X, X_2, X_3, *and* X_4 *respectively.*

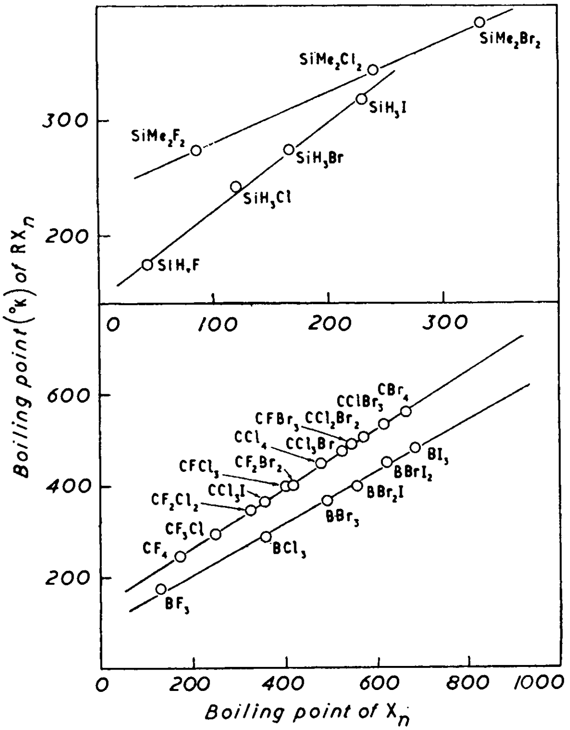
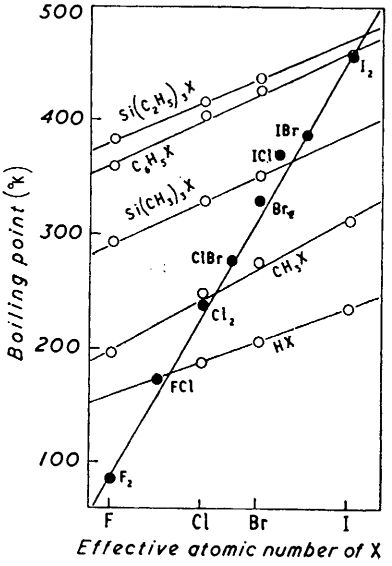


FIG. 8. *Boiling point of* X_2, HX, CH_3X, $SiMe_3X$, C_6H_5X, *and* $Si(C_2H_5)_3X$ versus *effective atomic number of* X.



Boiling Points of Halides of the Type RX.—We have plotted in Fig. 8 the boiling points of halides of this type against Z'. In each case a straight line is obtained in conformity with the relation given by Somayajulu.[1] Among the hydrogen halides, hydrogen fluoride, which is associated, is an exception by boiling at a higher temperature than expected. From the observed T_b for hydrogen fluoride, and assuming eqn. (1) to be valid for HX, we have calculated the apparent $\sum Z$ for HF and thence its average degree of association, which comes out at 4·5. Unfortunately, no method is available for independent verification of this value.

We have also plotted in Fig. 8 the boiling points of the halogens and the interhalogens of AB type, and all of them fall fairly well on a straight line. Our equations are only

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[8] Somayajulu and Palit, *J.*, 1957, 2540.

FIG. 9.

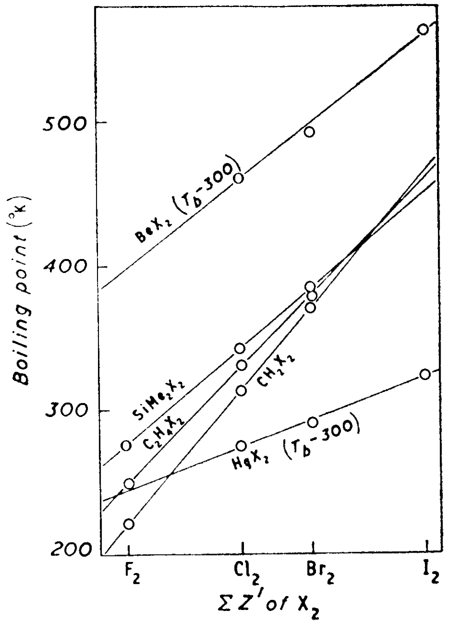

FIG. 10.

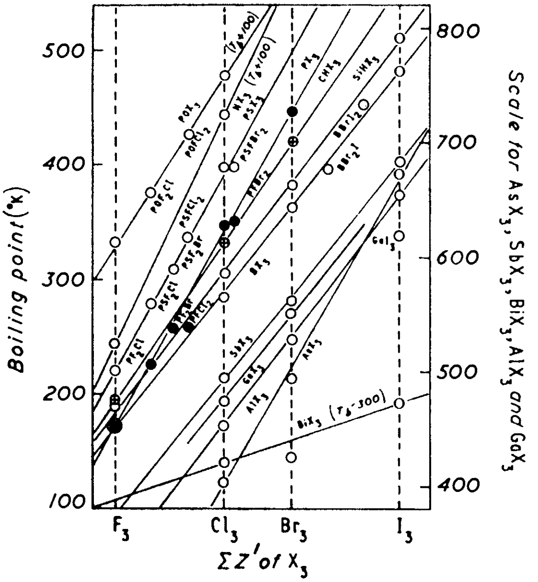

FIG. 11.

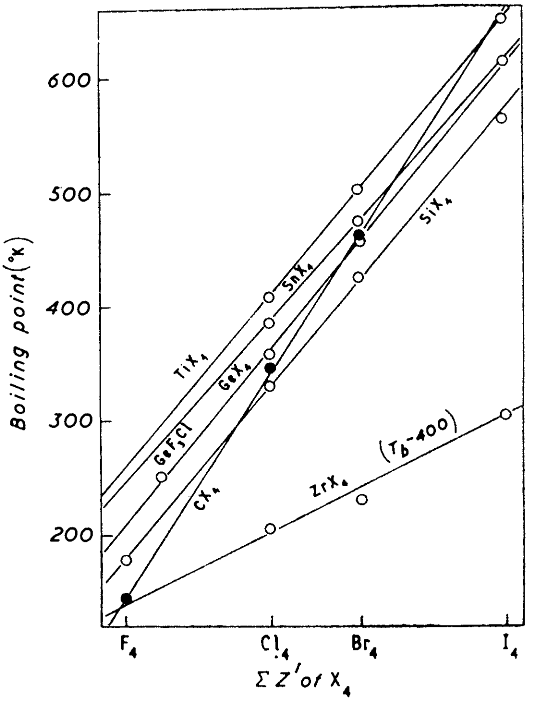

FIG. 9. *Boiling point of* BeX_2, $SiMe_2X_2$, CH_2X_2, *sym*-$C_2H_4X_2$, *and* HgX_2 versus *the sum of the effective atomic numbers of the* X_2 *part.*

FIG. 10. *Boiling point of* POX_3, NX_3, PSX_3, PX_3, CHX_3, $SiHX_3$, BX_3, SbX_3, GaX_3, AlX_3, AsX_3, *and* BiX_3 versus *the sum of the effective atomic numbers of the* X_3 *part.*

FIG. 11. *Boiling point of* TiX_4, SnX_4, GeX_4, SiX_4, CX_4, *and* ZrX_4 versus *the sum of the effective atomic numbers of the* X_4 *part.*

approximate ones, but they illustrate unmistakably the existence of a definite trend, occasional departure, especially in fluorine compounds, being not uncommon. However, the slight departure from linearity with FCl and ICl may be due to a small percentage of ionic character in the bond.

Boiling Points of Halides of the Type RX_2.—Fig. 9 shows the boiling points of various dihalides of this type. In all cases (except HgF_2 and BeF_2 which are ionic) fairly good straight lines are obtained. It is remarkable that Be and Hg, which form predominantly covalent halides, behave normally whereas Cd and Zn (not shown), which form ionic halides, behave anomalously.

Boiling Points of the Halides of the Type RX_3.—The trihalides of B, Al, Ga, N, P, As, Sb, Bi, CH, SiH, PO, and PS obey our equation fairly closely (Fig. 10). The metals and metalloids, however, show occasional anomalies, particularly their fluorides, and this is ascribed to the fact that they are either polar or associated, or tend to decompose on boiling.

Boiling Points of the Halides of the Type RX_4.—For the boiling points of tetrahalides plotted against Z', Fig. 11 shows that each sequence gives a straight line. The diagram for silicon tetrahalides has already been published.[1] The boiling points of the titanium tetrafluoride and stannic fluoride are, however, too high for our equations, presumably owing to association or polarity. The boiling point of zirconium tetrafluoride is not available.

Discussion.—We have established the existence of definite trends in the boiling point of halogen compounds, a ready explanation of which is, however, not available. As we believe, however, that the attractive force at the surface of all halogen atoms is the same, the boiling point, which measures the total intermolecular force, increases linearly with the area of the halogen atoms in similar molecules. We are in favour of such a simple explanation because Z'/R_c^2 is constant [2] for all halogens and since Z' appears to be the net nuclear charge, *i.e.*, nuclear charge operating outside an atom after partial screening by the

TABLE 1. *Boiling points of halides* (°K).

Sequence of halides	X = F	X = Cl	X = Br	X = I	*a*	*b*
X_2	85·16 (85·00)	238·56 (237·00)	331·94 (332·00)	457·57 (S) (484·00)	9·50	−86·00
HX	292·56 (158·03)	188·16 (188·19)	207·16[d] (207·04)	237·76 (237·20)	3·77	124·10
CH_3X	195·16 (199·09)	249·46 (245·01)	277·76 (273·71)	315·76 (319·63)	5·74	147·40
C_6H_5X	359·16 (362·03)	405·26 (401·42)	429·36 (426·04)	461·76 (465·43)	4·92	124·20
$Si(CH_3)_3X$	289·56[a] (288·53)	330·16[a] (329·09)	353·16[a] (354·44)	— (395·00)	5·07	242·90
$Si(C_2H_5)_3X$	383·16[a] (382·08)	416·66[a] (417·44)	439·66[a] (439·54)	— (474·90)	4·42	342·30
CH_2X_2	221·56[b] (222·66)	313·26 (311·78)	370·96 (367·48)	453·16(D) (456·60)	5·57	122·40
$Si(CH_3)_2X_2$	275·86[a] (275·86)	343·36[a] (343·38)	385·46[a] (385·58)	— (453·10)	4·22	199·90
s-$C_2H_4X_2$	248·46[c] (248·14)	330·46 (330·22)	383·16 (381·52)	452·16 (463·60)	5·13	155·80
HgX_2	923·16 (543·72)	577·16 (575·56)	595·16 (595·46)	627·16 (627·30)	1·99	507·90
BeX_2	— (692·82)	761·16[d] (757·32)	793·16[c] (797·62)	863·16[c] (862·10)	4·03	620·30
BX_3	172·16 (146·20)	285·66 (280·60)	363·76 (364·60)	483·16 (499·00)	5·61	− 5·00
AlX_3	1564·16[d] (S) (325·51)	453·16[d] (S) (451·03)	528·16[d] (529·48)	655·16 (655·00)	5·23	184·30
GaX_3	— (385·42)	474·36[d] (480·46)	552·16[d] (539·86)	629·16[d] (634·90)	3·96	278·50
NX_3	144·16[d] (144·16)	344·16[d] (344·08)	— (469·03)	— (668·95)	8·33	−80·75
PX_3	172·16[d] (165·65)	347·86[d] (337·25)	446·06 (444·50)	— (616·10)	7·15	−27·40
AsX_3	— (225·77)	403·36[e] (396·41)	494·16[e] (503·06)	676·16 (673·70)	7·11	33·80
SbX_3	592·16[d] (375·09)	494·16[d] (491·97)	561·16[d] (569·79)	683·16(Ca) (686·67)	4·87	243·60
BiX_3	— (678·52)	720·16 (713·56)	726·16 (735·46)	773·16(D) (770·50)	1·46	639·10
CHX_3	190·96[c] (189·64)	334·36 (334·12)	423·56 (424·44)	— (568·92)	6·02	27·10
$SiHX_3$	192·96 (192·43)	306·16 (307·39)	382·16 (379·24)	493·16 (494·20)	4·79	63·10
$Si(CH_3)X_3$	242·96[a] (240·28)	339·36[a] (342·04)	406·66[a] (405·64)	— (507·40)	4·24	125·80
POX_3	233·36[c] (230·50)	378·46[c] (376·90)	466·16 (468·40)	— (614·80)	6·10	65·80
PSX_3	220·26[d] (220·25)	398·16 (399·05)	448·16(D) (510·80)	— (689·60)	7·45	19·10
CX_4	145·16[c] (146·58)	349·96 (341·46)	462·66 (463·26)	— (658·14)	6·09	−72·70
SiX_4	178·16[d] (178·00)	330·73 (330·00)	426·16 (425·00)	563·16 (577·00)	4·75	− 7·0
GeX_4	236·76[d] (206·40)	359·66 (368·00)	459·66 (469·00)	648·16 (630·60)	5·05	24·60
SnX_4	978·16 (246·48)	387·26 (386·64)	475·16 (474·24)	613·16 (614·40)	4·38	88·80
TiX_4	557·16 (261·94)	409·56 (410·42)	503·16 (503·22)	650·36[d] (651·70)	4·64	94·90
ZrX_4	— (534·62)	604·16[d] (598·46)	630·16[d] (638·36)	704·16[d] (702·20)	2·66	462·80

For references, see Table 2, on following page.

electron cloud, Z'/R_c^2 is the net electrical force at the surface of a halogen atom, and so this force becomes equal for all halogen atoms. This equality being assumed, the above explanation fits well with the facts and also explains why the rate of increase in boiling point is approximately the same for all types of halide.

All boiling-point data for the halides used are collected in Tables 1 and 2 and their sources indicated. We have also calculated the boiling points on the basis of Somayajulu's equation (eqn. 1) and presented the calculated values in parentheses for each compound. The calculated values seldom differ much from the observed values except for the highly associated fluorides. It being remembered that the compounds considered are not usually purely covalent, but partially ionic in some cases, the agreement reached without the consideration of the dipole–dipole interactions and other factors is remarkable.

TABLE 2. *Boiling points of halides* (°K).

	Type RX_4							
SiX_4	F_3Cl	216·16[d] (216·00)	F_2Cl_2	254·16[d] (254·00)	FCl_3	292·16[d] (292·00)		
	F_3Br	231·46[a] (239·75)	F_2Br_2	286·86[a] (301·50)	FBr_3	356·96[a] (363·25)		
	Cl_3Br	353·16 (353·75)	Cl_2Br_2	377·16 (377·50)	$ClBr_3$	401·16[d] (401·25)		
	Cl_3I	386·56 (391·75)	Cl_2I_2	445·16 (453·50)	ClI_3	508·16 (515·25)		
	Br_3I	465·16 (463·00)	Br_2I_2	503·16 (501·00)	BrI_3	528·16 (539·00)		
	FCl_2Br	308·56[a] (315·75)	$FClBr_2$	333·66[a] (339·50)				
CX_4	F_3Cl	193·16[b] (195·26)	F_2Cl_2	245·16[b] (243·98)	FCl_3	297·26[b] (292·70)		
	F_3Br	— (225·71)	F_2Br_2	298·16 (281·02)	FBr_3	380·16 (384·05)		
	Cl_3Br	377·26 (371·87)	Cl_2Br_2	408·16 (402·32)	$ClBr_3$	433·16 (432·77)		
	Cl_3I	415·16 (420·59)	Cl_2I_2	— (499·76)	ClI_3	— (578·93)		
GeX_4	F_3Cl	252·86[c] (246·80)	F_2Cl_2	270·36[d] (287·20)	FCl_3	310·66[c] (327·60)		
	Type RX_3							
PX_3	F_2Cl	225·86[d] (222·85)	F_2Br	258·06[d] (258·40)	FCl_2	259·31[d] (280·05)	FBr_2	351·56[d] (351·55)
POX_3	F_2Cl	276·46[d] (279·30)	Cl_2Br	410·76 (407·40)	FCl_2	326·06[d] (328·10)	$ClBr_2$	438·16(Ca) (437·90)
PSX_3	F_2Cl	279·46[d] (279·85)	F_2Br	308·66[d] (307·10)	FCl_2	337·86[d] (339·45)	FBr_2	398·46[d] (403·95)
BX_3	Br_2I	398·16[c] (409·40)	BrI_2	453·16[c] (454·20)				
$Si(CH_3)X_3$	F_2Cl	272·66[a] (274·20)	FCl_2	302·66[a] (308·12)				
	Type X_2							
X_2	FCl	172·36[c] (161·00)	ICl	370·56[c] (360·50)	ClBr	278·16[d] (284·00)	IBr	389·16[c] (408·00)

D, Decomposes; S, Sublimes; Ca, Calculated.

All boiling-point data are taken from the International Critical Tables unless otherwise indicated.

[a] Post, "Silicones and Other Organic Silicon Compounds," Reinhold Publishing Corporation, New York, 1949. [b] Bigelow, *Chem. Rev.*, 1947, **40**, 51. [c] Hodgman, "Handbook of Physics and Chemistry," Chemical Rubber Publishing Co., Ohio, 1949. [d] Sidgwick, "Chemical Elements and Their Compounds," Vols. I and II, Clarendon Press, Oxford, 1950. [e] Landolt–Börnstein Tabellen.

We have also recorded the slopes and intercepts of eqn. (1) for all the above sequences in Table 1. Since the ratio R_c^2/Z' is a constant, 0·5845 Å², for halogens, the constant a' in eqn. (2) can be obtained by multiplying a by 0·5845.

One remarkable feature of the slope a is that it continually increases with the period number of R in RX_n; for example among the sequences BeX_2, BX_3, CX_4, NX_3, and X_2 it is 4·0, 5·6, 6·1, 8·3, and 9·5 respectively. The slope decreases with increase in atomic number of R in any group. These observations indicate that the electronegativity of the elements and period number are important factors in determining the boiling point.

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