

161. *The Volatile Hydrides. Part I. Periodicity as a Means of correcting and supplementing Determined Physical Properties. Part II. The Parachor, the Molar Volume at Absolute Zero, and the Electronic Structure and Properties of Compounds.*

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PART I.

FROM a survey of the physical properties of certain volatile hydrides, Paneth and Rabinowitsch (*Ber.*, 1925, **58**, 1145) concluded that (i) in any periodic group, melting points, molar heats of vaporisation, and molar volumes vary directly with the period number of the parent elements, and (ii) the difference in the values of the physical constants of contiguous members of a group tends to be the same as that between the corresponding inert gases. By using the new and corrected data now available, these deductions, originally based on limited evidence, have been shown to be valid, and equally applicable to surface tension. Their utility in evaluating undetermined properties is illustrated by recent measurements on stibine and arsine, of which the former had a molar heat of vaporisation of 5.08 kg.-cals., and the latter a molar volume of 48.11 c.c. (Durrant, Pearson, and Robinson, this vol., p. 735), in excellent agreement with the predictions of Paneth and Rabinowitsch, *viz.*, 5 kg.-cals. and 48 c.c. With the aid of the generalisations we have deduced probable values for certain physical properties of krypton, xenon, radon, methane, silane, germane, stannane, bismuthine, and, their existence being assumed, of the hydrides of polonium, lead and eka-iodine (at. no. 85). Surface tensions may be calculated from the Walden formula, $\gamma_{b.p.} = T_{b.p.} \times 2.15 \log T_{b.p.}/MV_{b.p.}$, using extrapolated values of the molecular volumes and boiling points, and are in good agreement with figures obtained from extrapolation as shown in Tables VI and VIII.

The extrapolated molar heats of vaporisation give Trouton's constants of the correct order (for an unassociated volatile hydride, 20.5) for every compound, *viz.*,

SiH ₄ .	GeH ₄ .	SnH ₄ .	PbH ₄ .	BiH ₃ .	PoH ₂ .	(Eka-I)H.
18.94	19.78	20.36	20.85	19.56	20.06	20.88

Departures from linearity when physical properties are plotted against period, tentatively ascribed to association, are definitely related to this cause, and data for the higher unassociated members of a group give, by extrapolation, values ascribable to the unimolecular form of the first member. Data so obtained for ammonia, water, and hydrogen fluoride are recorded in Table I, with, for comparison, the observed values for the ordinary

TABLE I.

Observed and calculated physical data for ammonia, water, and hydrogen fluoride.

	Ammonia.			Water.			Hydrogen fluoride.		
	Obs.	Calc.	Ratio.	Obs.	Calc.	Ratio.	Obs.	Calc.	Ratio.
B. p., ° K.	239.7	131.5	1.82	373.0	156.5	2.38	292.5	140.0	2.09
M. p., ° K.	196.0	117.8	1.66	273.0	177.0	1.54	181.0	110.0	1.65
Molar heat of vaporisation	5.65	2.86	2.00	9.67	3.80	2.55	6.00	3.04	1.97
Surface tension	34.25	17.56	1.95	58.9	26.7	2.21	8.65	21.10	0.41
Molar volume	25.00	31.09	0.80	18.81	23.5	0.80	20.95	21.30	0.98

associated species. The ratios of these values indicate that certain physical properties of the individual compounds are affected in equal proportion by association, exceptions being the melting point, which is probably more controlled by the structure of the solid than by the nature of the liquid, and the molecular volume.

Hydrogen fluoride is exceptional with regard to the last two properties, for whereas the first three indicate a degree of association at least equivalent to that of ammonia, the surface tension is actually below rather than above the anticipated value. This has led us to conclude that association in hydrogen fluoride involves ring formation, *e.g.*,

$F \begin{array}{c} \nearrow H-F \searrow \\ \leftarrow H \leftarrow F \rightarrow \\ \searrow H \end{array}$. The pronounced polarity expected in the simple molecule, or indeed in an open-chain molecule, would then be absent, and the surface orientation in the liquid correspondingly altered. A ring structure, moreover, reasonably accounts for the relatively high molecular volume, which is anomalous if linear co-ordination only be assumed. By decreasing the number of particles per unit of surface, this volume effect should, in turn, further reduce the surface tension. These two anomalous properties are of further significance (see Part II).

FIG. 1.
Freezing points.

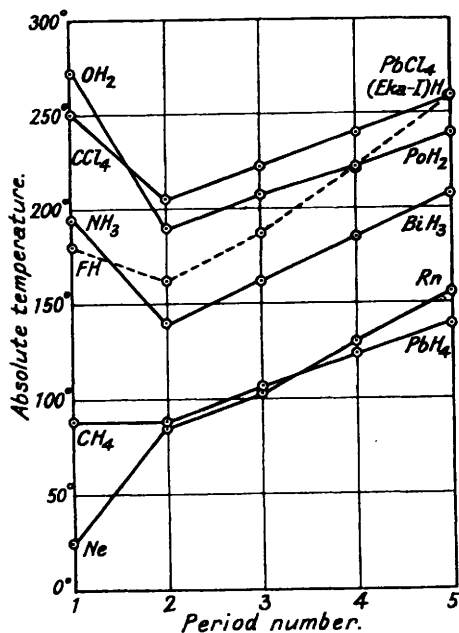
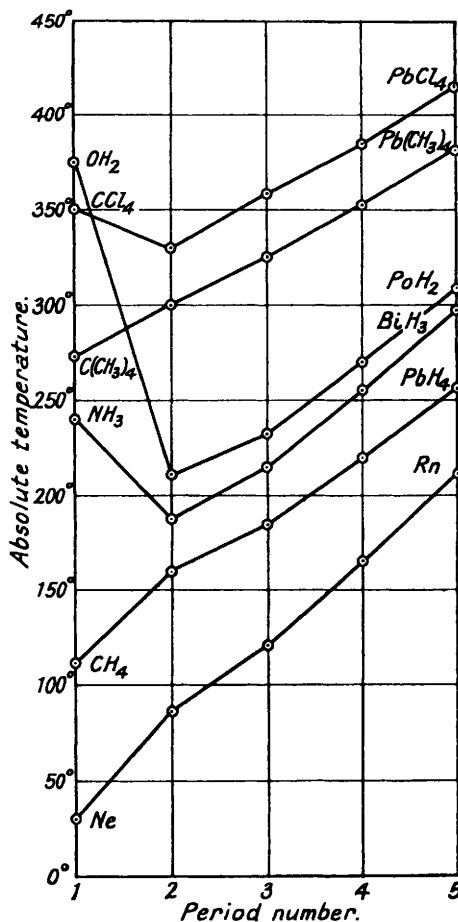


FIG. 2.
Boiling points.



Physical Constants of the Volatile Hydrides and Inert Gases.

The sources of the data are denoted as follows :

A, Paneth and Rabinowitsch, *loc. cit.* (where earlier references may be found); B, Robinson and Scott, J., 1932, 972; C, Durrant, Pearson, and Robinson, *loc. cit.*; D, Pearson and Robinson, this paper; E, Simons and Bouknight, *J. Amer. Chem. Soc.*, 1932, **54**, 129; F, Simons, *ibid.*, 1924, **46**, 2179; G, Steele, McIntosh, and Archibald, *Z. physikal. Chem.*, 1906, **55**, 145.

Figures placed in parentheses in the tables have been obtained by extrapolation.

Melting and Boiling Points.—The thermal constants are recorded in Table II and plotted in Figs. 1 and 2, together with data for the chlorides, methyls, and inert gases. Since Whytlaw-Gray and Ramsay's m. p. for radon (*Z. physikal. Chem.*, 1910, **70**, 116)

TABLE II.

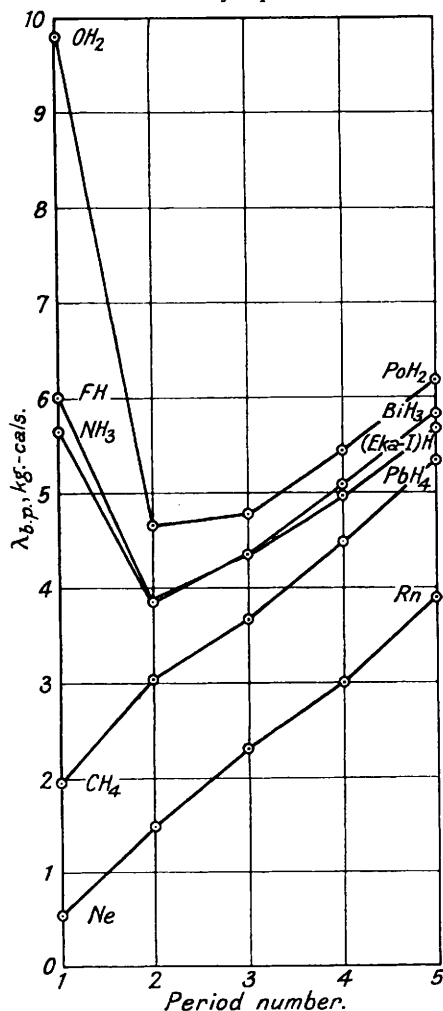
Melting points and boiling points ($^{\circ}\text{K}$).

CH_4	89° 111.7	NH_3	196° 239.7	OH_2	273° 373	FH	181° 292.5	Ne	25° 28
SiH_4	88 161	PH_3	140 185.7	SH_2	190 212.5	ClH	161.5 188	A	85 87.2
GeH_4	108 184.5	AsH_3	161.8 214.5	SeH_2	207 231.5	BrH	186 204.3	Kr	104 121.3
SnH_4	123 221	SbH_3	184 256.0	TeH_2	222 270	IH	222 237	Xe	130 165.0
PbH_4	(138) (256.5)	BiH_3	(206.2) (297.5)	PoH_2	(237) (308.5)	(Eka-I)H	(258) (270)	Rn	(155) (211)

Sources: Groups IV and VII, A; Group VI, B; Group V, C.

may be high (cf. Paneth and Rabinowitsch, *loc. cit.*), we have adopted, arbitrarily, 150°K ., the value anticipated from analogy with the linear increase of the unassociated Group IV alkyls and chlorides.

FIG. 3.
Molar heats of vaporisation.



Molar Heat of Vaporisation at the Boiling Point.—The molar heats of vaporisation are given in Table III and Fig. 3. Recorded data are very discrepant, but in many cases numerous individual determinations have been made, and we have, therefore, taken means, rejecting only Cederberg's results because they are uniformly much higher than those of other workers. (Paneth and Rabinowitsch took only values deduced from vapour-pressure measurements, but these are liable to a considerable error from traces of impurity, as is evident in much of the earlier work.) For hydrogen telluride, Bruylants' results have been preferred to those of Stein (J., 1931, 2134), for the latter give the unusual value of 16.4 for Trouton's constant and show a curvature and erratic values when $\log p$ is plotted against $1/T$. Guntz's measured value, 7.2 kg.-cals., for hydrogen fluoride has been rejected in favour of 5.999 kg.-cals. calculated by us from the vapour-pressure measurements of Simons (*J. Amer. Chem. Soc.*, 1924, 46, 2179), which we regard as trustworthy since they satisfy the usual Nernst equation.

Molecular Volumes.—The molecular volumes are recorded in Table IV and Fig. 4.

In extrapolating, account was taken of the uncertainty in the data for radon (Rutherford, *Phil. Mag.*, 1909, 17, 723; Whytlaw-Gray and Ramsay, *loc. cit.*), and since the increment (calculated from Sugden and Garner's data, J., 1929, 327, 1298) between tetraethyl-lead and tetraethyltin is precisely the 8.9 units anticipated from linear extrapolation of krypton and xenon, we have preferred to use the value 51 in place of the observed 44.5.

Surface Tensions.—Of the surface tensions, recorded in Table V and Fig. 5, those with an asterisk were calculated from the molar volumes in Table IV and the boiling points in Table II, by using the Walden formula (p. 736). When compared with the values from

TABLE III.

Molar heat of vaporisation at the boiling point (kg.-cals.).

CH ₄	1.95	NH ₃	5.65	OH ₂	9.67	FH	6.00	Ne	0.55
SiH ₄	3.05	PH ₃	3.83	SH ₂	4.66	ClH	3.88	A	1.5
GeH ₄	3.65	AsH ₃	4.34	SeH ₂	4.71	BrH	4.34	Kr	2.3
SnH ₄	4.50	SbH ₃	5.08	TeH ₂	5.45	IH	4.99	Xe	3.0
PbH ₄	(5.35)	BiH ₃	(5.82)	PoH ₂	(6.19)	(Eka-I)H	(5.64)	Rn	3.9

Sources: Group IV, C; HF, E; remainder A.

FIG. 4.

Molar volumes at the boiling point.

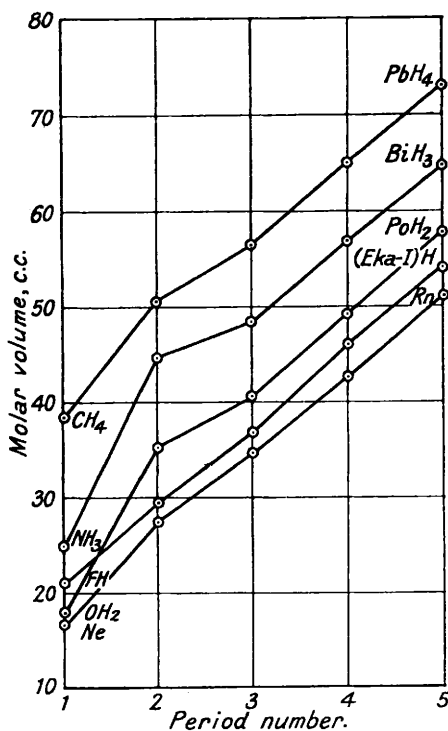


FIG. 5.

Surface tension.

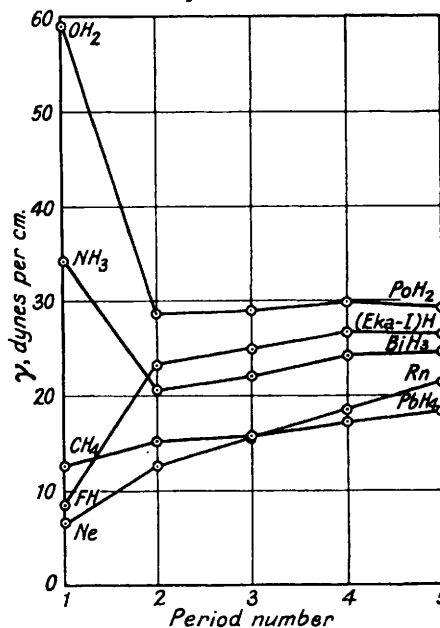


TABLE IV.

Molecular volumes.

CH ₄	38.39	NH ₃	25.00	OH ₂	18.81	FH	20.95	Ne	16.8
SiH ₄	50.55	PH ₃	44.50	SH ₂	35.25	ClH	29.64	A	28.5
GeH ₄	(56.65)	AsH ₃	48.11	SeH ₂	40.54	BrH	37.60	Kr	34.6
SnH ₄	(64.85)	SbH ₃	56.62	TeH ₂	49.06	IH	45.75	Xe	42.6
PbH ₄	(73.25)	BiH ₃	(64.50)	PoH ₂	(57.46)	(Eka-I)H	(54.30)	Rn	(51.0)

Sources: Group VI, B; Group V, C; Group VII, D, E, and G; Group IV, F.

TABLE V.

Surface tensions at the boiling point.

CH ₄	12.80	NH ₃	34.25	OH ₂	58.9	FH	8.65	Ne	6.665
SiH ₄	15.11	PH ₃	20.59	SH ₂	28.7	ClH	23.15	A	12.77
GeH ₄	(15.80)	AsH ₃	21.98	SeH ₂	28.9	BrH	24.90	Kr	15.84
SnH ₄	(17.17)	SbH ₃	24.19	TeH ₂	30.0	IH	26.80	Xe	18.64
PbH ₄	(18.13)	BiH ₃	(24.52) *	PoH ₂	(28.9) *	(Eka-I)H	(26.21) *	Rn	(20.66)

Sources: Group VII, BrH, D; ClH and IH, G.

extrapolation of the surface tensions of lower members of the respective groups agreement is satisfactory (Table VI). The values obtained by either of the methods are evidently sufficiently accurate for the calculation of the parachor.

TABLE VI.

Compound.	BiH ₃ .	PoH ₂ .	(Eka-I)H.
γ , calculated	24.52	28.89	26.21
γ , extrapolated	26.40	31.10	28.70

PART II.

It is known that the parachor of an element varies slightly with the compound of which the surface tension is measured. Even in simple cases, free from ambiguity as to the general nature of the bonds (covalent, co-ordinate, or electrovalent), such variations are apparent, and appreciating this, Mumford and Phillips (J., 1929, 2112) recalculated the parachors of a number of elements in a way which made the variations more marked. Other evidence of these apparent alterations in molar volume had previously been obtained by Huggins (*Physical Rev.*, 1923, **23**, 205; 1926, **28**, 1086) from the X-ray examination of crystals, by Trautenberg and Phillips (*Physikal. Z.*, 1921, **22**, 587) from the stopping power of gases for α -particles, and by Moles (*Anal. Fis. Quim.*, 1927, **25**, 204) and Biltz (*Z. anorg. Chem.*, 1929—1933) from molar volumes at absolute zero.

The parachor of hydrogen in the volatile hydrides appeared to present the possibility of a quantitative study of this particular phenomenon in a group of closely related simple compounds for which many reliable data were available. To realise this it was necessary to have, for reference, a series of representative values for the parachor in truly covalent compounds. Although accurately determined for many elements on a number of different substances, there are certain elements for which it is based solely on a few or divergent experimental results. Even admittedly rougher values have, however, shown some marked periodicities (Sugden, *op. cit.*), with, nevertheless, certain striking discrepancies. As redeterminations could not be made for all elements, with inadequate existing data, the values have been smoothed (a process which in no case involved a change of more than 2 units). The result is in Table VII, wherein the values of only silicon, phosphorus, selenium,

TABLE VII.

Parachors of the elements.

C		N		O		F		Ne
4.8	7.7	12.5	7.5	20.0	5.0	25	0.0	25
23.6		26.7		23.2		29.3		29.0
Si		P		S		Cl		A
28.4	10.8	39.2	9.0	48.2	6.1	54.3	-0.3	54.0
10.6		11.1		12.8		13.7		14.4
Ge		As		Se		Br		Kr
39.0	11.3	50.3	10.7	61.0	7.0	68.0	0.4	68.4
18.2		18.4		19.0		22.0		21.6
Sn		Sb		Te		I		Xe
57.2	11.5	68.7	11.3	80.0	10.0	90.0	0.0	90.0
19.0		18.5		18.5		18.7		18.7
Pb		Bi		Po		Eka-I		Rn
76.2	11.0	87.2	11.3	98.5	10.2	108.7	0.0	108.7

antimony, and iodine have been changed from those given by Sugden (*op. cit.*), *viz.*, Si from 27.8 to 28.4; P from 38.2, a mean of only three determinations, to 39.2, by neglecting the very discrepant value of Morgan and Daghlien (*J. Amer. Chem. Soc.*, 1911, **33**, 657); Se from 62.5 to 61.0; Sb from 66.0 (2 determinations) to 68.3; and I from 91 to 90, actually the mean of the experimental determinations. In the case of krypton, xenon, and radon, for which experimentally determined surface tensions and molar volumes are not available, the extrapolated values given in Part I were used to calculate the parachor; the results for the first two are close to those suggested by Sugden, *viz.*, 68 and 91 respectively. The

values for germanium, bismuth, polonium, and eka-iodine were selected in accordance with the values for contiguous elements.

The parachors of the hydrides set out in Table VIII were derived from experimental determinations of liquid density and surface tension, exceptions being the hydrides of germanium, tin, bismuth, and eka-iodine, on which determinations were impracticable, and for which we have used the extrapolated values (Part I).

TABLE VIII.

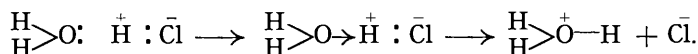
Parachors of the volatile hydrides.

Compound	CH ₄	SiH ₄	GeH ₄	SnH ₄	PbH ₄
Parachor of compound	72·63	99·65	112·9	132·0	151·2
Parachor of H in compound	16·96	17·81	18·5	18·7	18·7
Compound	NH ₃	PH ₃	AsH ₃	SbH ₃	BiH ₃
Parachor of compound	60·4	94·5	104·2	125·9	144·9
Parachor of H in compound	16·0	18·4	18·1	19·0	19·2
Compound	OH ₂	SH ₂	SeH ₂	TeH ₂	PoH ₂
Parachor of compound	52·1	81·7	94·5	115·2	134·5
Parachor of H in compound	16·1	16·8	16·8	17·6	18·0
Compound	FH	ClH	BrH	IH	(Eka-I)H
Parachor of compound	35·78	67·38	81·26	104·7	124·5
Parachor of H in compound	10·28	13·08	13·26	14·7	15·8

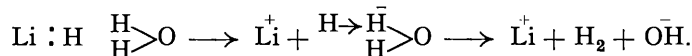
The results show conclusively that the apparent volume of the hydrogen atom (parachor) varies with the nature of the element to which it is bound, from 10·28 in the halogen hydride, HF, to 19·20 in the metallic hydride, H₃Bi. These differences are ascribed to a change in the electrochemical nature and the size of the second atom. The parachor of hydrogen is low in its halides, corresponding to the strongly electron-acquisitive character of the halogen, is very probably high (judged by molecular volume) in the alkali-metal hydrides, corresponding to the tendency shown by these metals to lose an electron, and is normal in methane where the electron sharing is equal. In the combining elements the increment per electron decreases as the shell approaches completion Si ^{10·8} → P ^{9·0} → S ^{6·1} → Cl ^{-0·3} → A. The slight alteration resulting from the addition of the ultimate electron (halogen → inert gas) is noteworthy.

As the number of electron shells increases the parachor increment per electron increases, O ^{5·0} → F, S ^{6·1} → Cl, Se ^{7·0} → Br, Te ^{10·0} → I, evidently through an increase in the screening effect.

The decrease in the parachor of hydrogen from halogen to alkali-metal hydride accords well with the current electronic theory and supports the hydrolytic view of ionisation. In halides, the hydrogen having evidently lost control of its electron readily accepts two from a donor atom and ionisation follows :



On the other hand, hydrogen in lithium hydride, already strongly negative by reason of an electron acquired from the lithium, co-ordinates with one of the hydrogen atoms of water and decomposition with the liberation of hydrogen follows :



A similar cause accounts for the facilitation of the dissociation of the hydrides of the heavier members of Groups V and VI (e.g., SnH₄, BiH₃, SbH₃, TeH₂) by moisture and for the difficulty experienced in their preparation. Moreover, ionisation in general is influenced by the magnitude of the negative charge on the central donor atom in the solvent which, apart from the halogens, would be large only in water and ammonia; these are excellent ionising solvents.

The problem of association is also simplified, being in the hydrides necessarily restricted

to those of Groups V, VI, and VII, for only these compounds possess a donor atom; moreover, since, as in ionisation, the probability of association taking place depends on the charge on the donor, it should be considerable in ammonia, water, the hydrogen halides (diminishing from the fluoride to the iodide), and present, but very small, in hydrogen sulphide and phosphine. This accords precisely with the experimental observations recorded in previous communications (Robinson and Scott, J., 1932, 972; Durrant, Pearson, and Robinson, preceding paper).

An interesting relationship is to be found between the parachors of the volatile hydrides and their molecular volumes at absolute zero. Biltz and Ruff, and their respective co-workers, have carried out an exhaustive series of researches (*Z. anorg. Chem.*, 1926—1933) on the latter property. Both schools have treated this as a constitutive function, but, whereas Biltz finds the ratio $MV_{b.p.}/MV_0$ to vary from 1.42, for liquids boiling at 100° , to 1.32, for liquids boiling at -50° , Ruff regards it as constant at 1.412, the value predicted by Lorentz. In the volatile hydrides, we find that $MV_{b.p.}/MV_0$ is constant for the members of each periodic group but differs from group to group:

Group	IV.	V.	VI.	VII.	VIII.
$MV_{b.p.}/MV_0$	1.25	1.27	1.33	1.35	1.24

By means of the appropriate group ratio, MV_0 has been calculated from $MV_{b.p.}$ (Table IV) for compounds lacking experimental data, and Table IX, wherein the results are collected, shows a general periodicity similar to that displayed by the parachor.

TABLE IX

Molecular volumes at absolute zero.

CH ₄	30.71	NH ₃	19.68	OH ₂	14.15	FH	15.52	Ne	14.0
SiH ₄	40.78	PH ₃	35.04	SH ₂	26.50	ClH	23.70	A	23.4
GeH ₄	45.32	AsH ₃	37.87	SeH ₂	30.48	BrH	27.30	Kr	26.3
SnH ₄	(51.88)	SbH ₃	44.59	TeH ₂	36.88	IH	35.00	Xe	34.9
PbH ₄	(58.60)	BiH ₃	(50.79)	PoH ₂	(43.20)	(Eka-I)H	(40.23)	Rn	(41.8)

From these data emerges another relationship, *viz.*, that $[P]/MV_0$ is a constant characteristic of each group, the few associated members being excluded (Table X). Molecular volume at absolute zero thus proves, as anticipated by Sugden (J., 1927, 1780, 1786; 1929, 1055), to be generally a less reliable criterion of the relative volume occupied by a molecule than the parachor, which, by the $\gamma^{1/4}$ factor, allows for association or intermolecular attraction. It may thus be understood why, *e.g.*, the atomic volume of hydrogen deduced by Biltz and Lemke (*Z. anorg. Chem.*, 1932, 203, 326, Table 5) should appear greater in hydrogen bromide than in the selenide or in stibine, which would otherwise be difficult to explain. Despite the fact that molecular volume at absolute zero concerns the solid,

TABLE X.

Ratios: Parachor/(volume at absolute zero).

Group	IV.	V.	VI.	VII.	VIII.
Period 1	2.42	3.00	3.70	2.32	1.80
„ 2	2.40	2.70	3.08	2.80	2.31
„ 3	2.50	2.73	3.09	3.10	2.60
„ 4	2.54	2.80	3.11	3.00	2.57
„ 5	2.56	2.85	3.13	3.00	2.61

and that at the boiling point the liquid, association in the latter produces no corresponding effect in the ratio $MV_{b.p.}/MV_0$, and therefore, association must affect each property equally. On the other hand, the constant value of $[P]/MV_0$ for the unassociated liquids of each group is indicative that each is a function of the same physical property, most probably the true molecular volume.

SUMMARY.

Part I.—A complete survey of the physical properties of the volatile hydrides has been made and it is established (a) that in any group the melting points, boiling points,

molar heats of vaporisation, molar volumes, and surface tensions vary directly with the period numbers of the parent elements, (b) that the difference in the values of the physical constants of contiguous members of a group tends to be the same as that between the corresponding inert gases, and (c) that departure from linearity when a physical property is plotted against period is due to association. With the aid of these generalisations, values for the undetermined physical constants of krypton, xenon, radon, and the hydrides of carbon, silicon, germanium, bismuth, polonium, and eka-iodine have been ascertained.

Part II.—It is demonstrated that the parachor of hydrogen in volatile hydrides has a different value according to the element to which it is united, being smallest in the halogen hydrides and greatest in the metallic hydrides. The variation is related to known differences in the chemical properties of the various hydride types, and is shown to accord well with a hydrolytic mechanism of ionisation. A survey of all the existing data has shown that the ratio $MV_{b.p.}/MV_0$ is constant for each periodic group, whilst a comparison between parachor and MV_0 indicates that, for associated liquids, the former provides the more reliable means of comparing molecular dimensions.

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