160. *Physical Relationships amongst the Hydrides of Elements of the Fifth Group with Special Reference to Association in these Compounds.*

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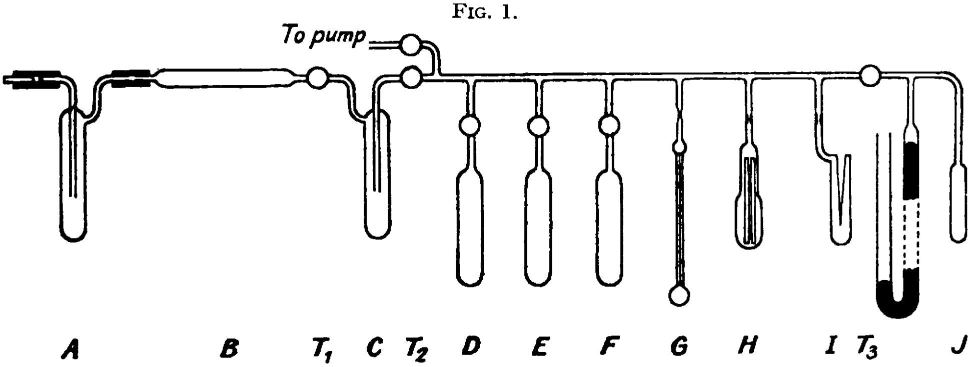
A recent investigation of the hydrides of the sixth-group elements (Robinson and Scott, J., 1932, 972) afforded interesting results; for instance, the association of water and hydrogen sulphide was clearly shown by comparison of the surface tensions. The work has now been extended to hydrides of elements of the fifth group, for which little data were available, and has demonstrated the association of ammonia and phosphine. The latent heats of vaporisation at the boiling point, when plotted against period number, show an upward inflexion corresponding to that in similar plots of the boiling point and the surface tension; this is attributed to association of the compounds, ammonia being bimolecular at the boiling point, and still more complex at lower temperatures, in accordance with its other relationships with water.

The values deduced for the parachors of these compounds from our liquid-density and surface-tension measurements indicate a positive anomaly in those of phosphine, arsine, and stibine; this finds a parallel in the negative anomaly in hydrogen chloride, bromide, and iodide, but the hydrides of the intermediate group sulphur, selenium, and tellurium are normal. An adequate explanation of this transition is discussed in the next paper, surveying the periodic relationships of the physical properties of the volatile hydrides in the light of new data.

EXPERIMENTAL.

Materials.—Commercial synthetic ammonia was, before fractionation, washed with 50% potassium hydroxide solution and dried over soda–lime, potash pellets, and, finally, freshly burned quicklime. It has been stated (Biltz, *Ber.*, 1894, **27**, 1258; Gutmann, *Annalen*, 1898, **299**, 267), contrary to the experience of Baker (J., 1893, **73**, 422), that phosphoric oxide is inadmissible as a drying agent for ammonia, since it reacts with it; but we found that if the ammonia is carefully dried over quicklime and the pentoxide is fresh and free from lower oxide, there is no reaction between the two compounds; with insufficiently dried gas, however, reaction occurs with formation of a semi-fluid mass and the evolution of much heat.

FIG. 1.



Phosphine, prepared from yellow phosphorus and potassium hydroxide solution in pure hydrogen, was passed through concentrated hydrochloric acid to remove liquid hydrogen phosphide, and then through aqueous potassium hydroxide. It was dried over fused calcium chloride, potash pellets, and phosphoric oxide, and condensed at about − 180° in a glass vessel in which it was sealed in a vacuum; it was then fractionated as required. Neither as liquid nor as gas was the purified material spontaneously inflammable when exposed to air.

Arsine was prepared in pure hydrogen by slowly dropping (2 hours) a solution of arsenious oxide (20 g., A.R.) in freshly boiled hydrochloric acid (250 c.c. acid; 50 c.c. water) on pure magnesium (50 g., stick or turnings) in a 750 c.c. round-bottomed flask cooled in water. The reaction products passed through aqueous potash into successive tubes (25 cm. long) containing potash pellets, fused calcium chloride, and phosphoric oxide, and thence to a vessel, immersed in liquid air, protected by a long guard-tube containing phosphoric oxide and leading to the fume shaft. 18 G. of magnesium were dissolved and 8 g. of almost pure arsine formed, which was at once transferred to the fractionating system (Fig. 1), where it was finally purified and distributed.

Stibine was prepared from freshly boiled, pure 4*N*-hydrochloric acid and an alloy made by heating to bright redness magnesium (coarse filings, 300 g.) and high-grade antimony (powder, 200 g.), in pure hydrogen, the pulverised alloy being added to the acid out of contact with air through a special hopper. A stream of pure hydrogen carried the stibine through a purifying train identical with that used for the arsine to a condensing vessel where 10 g. of stibine were collected for every 250 g. of alloy used. It was immediately transferred to the vacuum fractionating and distributing system (Fig. 1).

The vessel A, containing the preparation at − 180°, was connected through dry pressure tubing and a tube containing phosphoric oxide and the tap T_1 to the carefully dried system, which was then evacuated (0·0004 mm.) by opening T_1 to vessel A. All taps save T_1 were closed, and the liquid was distilled, with A in a bath at − 75°, through B into C, which was kept at − 180°. With T_1 closed, the material, now in an all-glass apparatus, was separated into fractions by distillation from a vessel 45° below the b. p. of the liquid into condensers at − 180°. After 5 minutes at the evaporating temperature, with T_2 closed, the liquid in C was allowed to distil into D by opening T_2 for ten seconds. T_2 was then closed for 5 minutes, and the process repeated until one-third of the material had been transferred. A middle third was similarly brought into E. The residue was collected in D. After having been deprived of small head fractions, the middle fraction was transferred to J, and tap T_3 closed. The vapour pressure of the liquid was ascertained at a series of temperatures by surrounding J with appropriate thermostatic baths, the purity of the specimen being demonstrated by the absence of change in the vapour pressure with the removal of successive head fractions. After these measurements, the material was appropriately distributed between the various vessels; G for density, H for surface tension, and I for m. p. and b. p. Details of the operations involved and of the methods employed in the various measurements have already been described (Mills and Robinson, J., 1927, **1823**; Pearson and Robinson, J., 1932, 652; Robinson and Scott, *ibid.*, p. 972), and only departures therefrom are here noted.

Density.—The pressures developed at room temperature by these hydrides when sealed up necessitated the use of thick-walled bulbs. This increased insulation of the liquid led to the adoption of thermostatic baths, in place of those in which the temperature was allowed to rise slowly: these proved so convenient that they have been used in all subsequent work. The bulbs were kept at the several temperatures until the readings were constant, usually in about 30 minutes. Furthermore, as a check against the effect of distortion through the high pressures, the Pyrex pyknometers were recalibrated after each experiment, but no perceptible change was detected.

Densities (g./c.c.) of liquid hydrides.

Phosphine.			Arsine.			Stibine.		
Temp.	Vol. (c.c.) of 0·5965 g.	*d.*	Temp.	Vol. (c.c.) of 1·3027 g.	*d.*	Temp.	Vol. (c.c.) of 0·5534 g.	*d.*
− 57·5°	0·8330	0·7161	0°	0·9014	1·445	0°	0·2574	2·150
− 60·2	0·8280	0·7204	− 10	0·8846	1·473	− 10	0·2536	2·182
− 69·0	0·8118	0·7348	− 20	0·8678	1·501	− 25	0·2483	2·229
− 71·5	0·8073	0·7389	− 30	0·8507	1·531	− 40	0·2431	2·276
− 87·4	0·7794	0·7653	− 40	0·8340	1·562	− 50	0·2396	2·310
			− 50	0·8174	1·594			
			− 60	0·8006	1·625			

Although McIntosh and Steele (*Phil. Trans.*, 1906, **205**, 99; *Z. physikal. Chem.*, 1906, **55**, 140) had measured the density of liquid phosphine, we repeated the measurement because their specimen had a slightly high vapour pressure (see Stock, Henning, and Kuss, *Ber.*, 1921, **54**, 1119; Henning and Stock, *Z. Physik*, 1921, **4**, 226). Our results (see below) were uniformly higher, and as a check we remeasured the coefficient of expansion on an independent sample; the two results, *viz.*, 0·002275 and 0·002269, agreed. Two independent samples of highly purified liquid arsine gave closely agreeing densities and almost identical coefficients of expansion, *viz.*, 0·00200 and 0·00195. The density of liquid stibine found by Stock and Guttmann (*Ber.*, 1904, **37**, 885), *viz.*, 2·26 at − 25° and 2·34 at − 50°, was slightly higher than ours, and we repeated our measurements on a second sample prepared from specially purified antimony kindly supplied by the Cookson Lead and Antimony Co. Ltd., Willington Quay-on-Tyne, through the courtesy of Mr. C. Cooper, M.Sc. Practically identical results were obtained, the coefficient of cubical expansion being 0·00140 between − 50° and 0°.

Table IV shows the molecular volumes of the compounds at their b. p.'s calculated from the present experimental data, and also the mean molecular diameters obtained by utilising the Hertz relationship (*Z. Elektrochem.*, 1921, **27**, 25): $\rho = (M/d)^{\frac{1}{3}} \times 102/42{\cdot}7 \times 10^9$.

Melting Points.—The m. p. of ammonia given in Table IV is generally accepted; that of phosphine is due to Olchewsky (*Monatsh.*, 1886, **7**, 372; *Anz. Akad. Krakau*, 1908, **375**, 483). Two independent specimens of arsine had m. p. −111·0° and − 111·5°; Olchewsky (*Monatsh.*, 1884, **5**, 127; *Phil. Mag.*, 1895, **39**, 188) gives – 113·5°. Similarly, two preparations of stibine melted at –89·7° and –90·3°; previous values are –91·5° (Olchewsky, *Monatsh.*, 1886, **7**, 371; *Ber.*, 1901, **34**, 3592) and – 88° (Stock and Doht, *Ber.*, 1902, **35**, 2270).

Boiling Points.—The b. p. of phosphine is given as – 87·4° (Henning and Stock, *Z. Physik*, 1921, **4**, 226), – 85° (Olchewsky, *loc. cit.*), and – 86·2° (McIntosh and Steele, *Phil. Trans.*, *loc. cit.*). Olchewsky (*loc. cit.*) found arsine to boil at – 54·8°, and Schlundt and Shaefer (*J. Physical Chem.*, 1912, **16**, 253) at *ca.* – 70°. Our value lies precisely on our $\log_{10}p$–$1/T$ curve and agrees with that deduced from Faraday's vapour-pressure measurements. Our value for stibine (– 17·1°/751·1 mm.) agrees with that of Stock and Doht (*loc. cit.*), *viz.*, – 17·0°/760 mm.

Vapour Pressure and Latent Heat of Vaporisation.—The accepted vapour pressure of ammonia has been used to calculate the molecular heat of vaporisation at the b. p. ($\lambda_{\text{b. p.}}$), and the results, together with those from direct measurement, give a mean value of 5·65 kg.-cal.; the derived Trouton's constant indicates association in the liquid. McIntosh and Steele (*loc. cit.*) and Briner (*J. Chim. physique*, 1906, **4**, 476) measured the vapour pressure of phosphine, but Stock found slightly lower values. From the mean values, $\lambda_{\text{b. p.}}$ is 3·85 kg.-cals., and Trouton's constant is normal.

TABLE I.

The vapour pressure of arsine and stibine.

Observers.	Temp., ° K.	Press., mm.	log *p*.	Observers.	Temp., ° K.	Press., mm.	log *p*.
		Arsine.				*Stibine.*	
D., P. & R.	180·5°	116·3	2·0656	D., P. & R. ...	212·7°	98·78	1·9948
,, ...	198·2	335·5	2·5256	,, ...	243·6	459·20	2·6620
,, ...	212·4	697·9	2·8438	,, ...	255·5	743·35	2·8712
,, ...	214·5	767·0	2·8848	,, ...	255·9	751·05	2·8756
F.	214·0	760	2·8808	S. & D.	256·0	760·0	2·8808
O.	218·2	*ca.* 760	2·8808				
S. & S.	203·0	*ca.* 760	2·8808				

D., P. & R = Present authors; F. = Faraday; O. = Olchewsky; S. & S. = Schlundt and Shaefer; S. & D. = Stock and Doht.

Table I gives the vapour-pressure data for arsine and stibine. The agreement between our results and those of Faraday (*Phil. Trans.*, 1845, **135**, 155) is noteworthy. The values for arsine may be expressed in a Nernst vapour-pressure equation of the form.

$$\log p = \frac{-\lambda_0}{4{\cdot}573}\cdot\frac{1}{T} + 1{\cdot}75 \log T - \frac{\varepsilon T}{4{\cdot}573} + c$$

[λ_0 = molecular heat of vaporisation at 0° K.; T = temp. (°K.) at which vapour pressure = p; ε and c are constants], yielding

$$\log p = -\ 787{\cdot}5/T + 1{\cdot}75 \log T - 0{\cdot}0000565T + 2{\cdot}4948$$

from which $\lambda_0 = 3{\cdot}602$ kg.-cals., $\varepsilon = 0{\cdot}0002584$, and

$$\lambda_{\text{b. p.}} = (\lambda_0 + 3{\cdot}5T_{\text{b. p.}} - \varepsilon T^2_{\text{b.p.}})(1 - p/\pi_0)$$

whence, neglecting p/π_0, which is small, $\lambda_{\text{b. p.}} = 4{\cdot}34$ kg.-cal. Trouton's constant is normal. From one of Nernst's relationships, the conventional chemical constant is given by the equation $i = 1{\cdot}33 \log T_{\text{b. p.}} - 0{\cdot}00098T_{\text{b. p.}} = 2{\cdot}8911$. For stibine,

$$\log p = -\ 1070/T + 1{\cdot}75 \log T - 0{\cdot}002416T + 3{\cdot}4083$$

from which $\lambda_0 = 4{\cdot}895$ kg.-cal., $\varepsilon = 0{\cdot}01105$, and $\lambda_{\text{b. p.}} = 5{\cdot}067$ kg.-cal.; Trouton's constant is again normal.

Surface Tension and Parachor.—The surface tension of ammonia was found by Berthoud (*J. Chim. physique*, 1918, **16**, 434; *Helv. Chim. Acta*, 1918, **1**, 84) to be 23·38 dynes/cm. at 11·1°, 18·05 at 34·05°, and 12·95 at 58·98°; we confirmed these (Table II), although, when extrapolated they disagree with Grunmach's value (*Ann. Physik*, 1901, **4**, 367).

As McIntosh and Steele's determination of surface tension (*loc. cit.*) may have been affected by the error in their liquid density (p. 732), we recalculated the values, using our own liquid densities. These results, together with those for arsine and stibine, not previously determined, are recorded in Table II.

Walden (*Z. physikal. Chem.*, 1909, **65**, 224) has shown that the surface tension of a liquid may be obtained with fair accuracy from the relationship

$$\gamma_{\text{b. p.}} = T_{\text{b. p.}}\ 2{\cdot}15 \log T_{\text{b. p.}}/MV_{\text{b. p.}}$$

The comparison between calculated and observed values (Table III) shows agreement except for ammonia, in which the considerable divergence is to be explained by association.

DISCUSSION AND SUMMARY.

The physical properties of the hydrides of the Group V B elements are collected in Table IV and in Fig. 2. The Ramsay–Shields constants, $K = d[\gamma(M/d)^{\frac{2}{3}}]/dt$, and the Trouton's constants indicate that, whereas arsine and stibine are normal liquids, phosphine and, to a much greater extent, ammonia are associated.

FIG. 2.

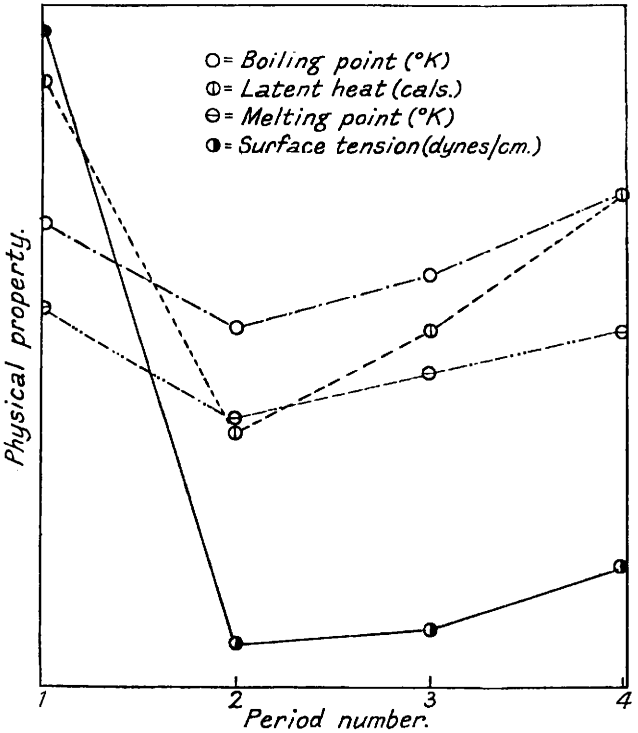


TABLE II.

The surface tensions and parachors of ammonia, phosphine, arsine, and stibine.

Series.	Temp.	*d.*	γ.	[*P*].	Temp.	*d.*	γ.	[*P*].
		Ammonia.				*Phosphine.*		
1	− 56·0°	0·7091*	39·15	60·06	− 87·4°	0·7652	20·4	94·61
2	− 51·7	0·7040*	38·30	60·16	− 93·1	0·7746	21·6	94·82
2	− 39·0	0·6879*	35·56	60·42	− 101·2	0·7881	23·0	94·62
1	− 34·0	0·6823*	34·39	60·42				
2	− 33·0	0·6814*	34·06	60·37				
		Arsine.				*Stibine.*		
	− 60·0	1·625	22·20	104·4	− 50·0	2·310	29·18	125·9
	− 58·8	1·621	21·98	104·4	− 40·0	2·276	27·67	125·9
	− 50·0	1·594	20·40	104·3	− 30·0	2·245	26·16	126·0
	− 40·0	1·563	18·60	104;3	− 20·0	2·213	24·64	126·0
	− 30·0	1·531	16·81	104·0	− 17·0	2·204	24·19	125·9
	− 20·0	1·502	15·08	103·6	− 10·0	2·182	23·13	125·8
					0·0	2·152	21·62	125·6

* Cragoe and Harper ("The specific volume of liquid ammonia," Washington, 1921).

TABLE III.

Surface tensions at the respective boiling points.

	NH_3.	PH_3.	AsH_3.	SbH_3.
$\gamma_{b.p.}$, obs.	34·25	20·59	21·98	24·19
$\gamma_{b.p.}$, calc.	49·06	20·33	22·31	23·40

TABLE IV.

The physical properties of the hydrides of the elements of Group V.

Compound.	NH_3.	PH_3.	AsH_3.	SbH_3.
Critical temp.	132·5°	52·0°	—	—
B. p.	− 33·3°	− 87·4°	− 58·5°	− 17·0°
$\lambda_{b.p.}$	5·65	3·83	4·34	5·08
M. p..	− 77·7°	− 132·5°	− 111·2°	− 88·5°
Liquid density at b. p.	0·681	0·765	1·621	2·204
Coeff. of expansion × 10^5	180	227	195	140
Mol. vol. at b. p.	25·00	44·50	48·11	56·62
Mol. diameter × 10^9	6·985	8·273	8·690	9·173
$d\gamma/dt$ (obs.)	0·211	0·178	0·180	0·151
K	− 56° to −39°, 1·40 − 39° to −33°, 1·59	1·79	2·10	1·87
Trouton's constant	23·56	20·63	20·26	19·80
Chem. const., *i*	2·931	2·841	2·891	2·951
Mean mol. parachor	60·39	94·65	104·2	125·9

The anomaly shown by ammonia with respect to the Walden relationship has definite significance, for our examination of the validity of the relationship for numerous liquids shows agreement of the order of ±0·5 dyne/cm. between the calculated and the observed values for all normal liquids, and, with the exception of hydrogen fluoride, a much higher calculated value for associated liquids.

The surface tensions of the elements, when plotted against the period number, show a slight upward inflexion at phosphine, and a pronounced one at ammonia (see Fig. 2). Similar inflexions are shown in the analogous graph for the boiling points, in conformity with Robinson and Scott's suggestion (*loc. cit.*) that both these properties, when thus plotted, give similar curves wherein anomalies arising from association are clearly shown. The associated nature of ammonia and phosphine being accepted, the inflexions in the plots of the molecular heats of vaporisation at the boiling point must also, as tentatively suggested by Paneth and Rabinowitsch (*Ber.*, 1925, **58**, 1147), be ascribed to the same cause; hence departure from linearity in this property can be safely accepted as evidence of association.

In view of the linear relationship between the period number and the boiling point and molecular heat of vaporisation in unassociated liquids, such as the chlorides and the alkyls of Group IV elements (Paneth and Rabinowitsch, *loc. cit.*), it seems reasonable to assume that extrapolation from the higher unassociated members of the series (in the present instance arsine and stibine) to the lower periods (phosphine and ammonia) should give values for the physical properties of the latter compounds which they would possess were they not associated. This has been done for ammonia with interesting results, the extrapolated physical constant being in every case almost exactly half the observed value. This ratio can hardly be accidental, for a similar one has been found for the surface tension of water (Robinson and Scott, *loc. cit.*); it indicates that at its boiling point ammonia is largely bimolecular.

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