716. *Studies in Co-ordination Chemistry. Part X.* The Vapour Pressure and Heats of Vaporisation of the Stannic Halides.*

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The development of some ideas concerning the stability of co-ordination compounds is outlined. We have determined the vapour pressures of stannic chloride, bromide, and iodide, using an all-glass membrane manometer (see *J.*, 1951, 3252) as a null instrument for the pressure measurement. Details are given of the methods used for the purification and handling in a vacuum of these compounds. For the three halides the vapour pressure–temperature relation is represented by the general equation $\log P = A - B/T$ over the temperature range investigated, A and B being different constants for each compound. The heats and entropies of vaporisation are calculated. The boiling points at atmospheric pressure are: $SnCl_4$, 113·9°; $SnBr_4$, 205·0°; SnI_4, 348·4°.

IN previous Parts of this series, complexes of certain transition metals with tertiary arsines were investigated (*J.*, 1950, 843, 848, 851, 857, 2061, 2071; 1951, 38, 2602). Arising out of this and other work dealing with the metal complexes of tertiary amines, phosphines, and arsines, some tentative generalisations have emerged concerning the nature of the metal–ligand bond in these compounds. It is suggested † that, other factors being equal (*e.g.*, steric effects being absent and the number of lone pairs of electrons on L being the same), the relative

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* Part IX, *J.*, 1951, 2602.

† The views now outlined have been described in greater detail by Nyholm (Thesis, London, 1950).

strengths of attachment of a series of ligands of the type LR_3 (L = N, P, As, etc.) or LR_2 (L = O, S, Se, Te) to a metal atom M is determined chiefly by two main factors:

(*a*) The product $\chi_L \times \chi_M$, where χ_L and χ_M are the effective electronegativities of the donor atom L of the ligand, and of the metal M, respectively. For covalent bonds, Gordy (*J. Chem. Physics*, 1946, **14**, 305) and Walsh (*J.*, 1948, 398) have suggested that the bond-force constant may be expressed as a function of the product of the electronegativities of the bonded atoms, and may be taken as a measure of bond strength. An extension of the idea to the co-ordinate link seems reasonable, especially since, once formed, there is really no difference between the two types of bond except that the charges on the atoms will be different. This would presumably alter the effective electronegativities of the two atoms as compared with a covalent bond.

(*b*) The possibility of double-bond formation between L and M involving *d* electrons of the metal M and either a *p* or one of the vacant *d* orbitals of the donor atom L (cf. Pauling, "Nature of the Chemical Bond," 2nd edn., 1940, p. 250; Syrkin, *Bull. Acad. Sci. U.R.S.S.*, Classe Sci. chim., 1948, 69; Syrkin and Dyatkina, "The Structure of Molecules," Butterworth, London, 1950, p. 347; Chatt, *J.*, 1949, 3340; 1951, 652; *Nature*, 1950, **165**, 637).

Thus, in a series of ligands of the Group V elements, of the type LR_3, it was suggested that for co-ordination with boron, aluminium, and other acceptor atoms which have no *d* electrons, the strength of attachment could be explained by the electronegativity effect alone; hence, for these metals the order of strength of attachment should be $NR_3 > PR_3 > AsR_3 > SbR_3$. Although it had been known for some time (Brown and Davidson, *J. Amer. Chem. Soc.*, 1942, **64**, 317) that, towards trimethylaluminium we have the relation $NMe_3 > PMe_3$, yet it was not until recently (Professor Herbert C. Brown, personal communication, 1950) that data for the whole series became available. Professor Brown found that, towards the trimethyl compounds of the Group III metals, the strength of attachment of the Group V ligands is $NR_3 > PR_3 > AsR_3 > SbR_3$, which can be explained as above. However, it would be expected that co-ordination with transition metals, such as nickel, should depend upon both factors since these metals have *d* electrons available and, with the exception of nitrogen, the Group V ligands have vacant higher *d* orbitals which could overlap with a filled *d* orbital of the metal atom to form a π-type bond. The composite bond would then consist of a σ component, decreasing in strength in the sequence N > P > As > Sb, and a π_{d-d} component whose contribution would be nil in the case of nitrogen but important for phosphorus and later elements. The contribution of this π component to the total strength of the bond would depend upon factors such as: (*a*) the relative availability of *d* electron pairs in metals containing a complete sub-shell of 10 *d* electrons (*e.g.*, Sn) and in those in which the *d* shell is incomplete (*e.g.*, Ni), the level of the *d* electrons in both cases being just below that of the bonding orbitals; (*b*) the relative overlaps of the two *d* orbitals, which is dependent upon their relative sizes (see Orgel in report of Co-ordination Chemistry Conference, Wilkins, *Nature*, 1951, **167**, 434). A theoretical investigation of the possible use of *d* orbitals for both σ- and π-bond formation in complex compounds has recently been carried out by Craig, Maccoll, Nyholm, Orgel, and Sutton (to be published shortly).

Further investigation of tertiary amine, phosphine, and arsine complexes is now being carried out in order to obtain quantitative data concerning their order of stability and so enable us to correlate the strength of attachment of the ligand with the nature of the donor atom of the ligand, the metal acceptor, and the ions or groups attached to the metal atom.

Experimentally, the investigation of the strength of attachment of tertiary amines, phosphines, and arsine to Group VIII metals is difficult, and as a start the tin complexes have been chosen for study because the dissociation products are volatile and hence dissociation is accompanied by an increase in pressure which can be measured. Quadrivalent tin readily forms complexes of the type $Sn(Hal)_4,2R_3P(As)$ (Allison and Mann, *J.*, 1950, 2915), and if it is assumed that the σ bonds make use of $5s5p^35d^2$ octahedral bond orbitals of the tin atom, then a filled 4*d* shell is available immediately below these; it was desired to ascertain whether these *d* electrons contribute materially to the strength of the binding of the ligands by forming double bonds.

For this investigation, accurate data were required for the vapour pressures of the tetrahalides, but as these are not to be found in the literature (see also Hildebrand, *J. Chem. Physics*, 1947, **15**, 727), the present investigation was undertaken, the further object being to use these data in the study of the relative stabilities of the tin complexes.

Young (*Sci. Proc. Roy. Dublin Soc.*, 1909—1910, **12**, 374; *J.*, 1891, **59**, 911) determined vapour pressures, specific volumes, and critical constants of the compounds of Group IV elements with the object of testing the validity of van der Waals's generalisations regarding "corresponding" pressures, temperatures, and volumes. Vapour-pressure measurements on stannic chloride were carried out by a dynamic method with a mercury manometer, the halide being in contact with the mercury of the manometer. Mündel (*Z. physikal. Chem.*, 1913, **85**, 435) studied small vapour pressures at low temperatures both experimentally and theoretically, measuring the vapour pressure of stannic chloride between −53° and −33°. The pressure measurements were made by means of a differential mercury manometer, which, by means of a micrometer screw, measures the difference in level of mercury in a U-tube. Again, however, these measurements were carried out with the halide in contact with mercury. Werthheimer (*Ber. deut. physikal. Ges.*, 1919, **21**, 692), in a theoretical paper, put forward a general form of the vapour-pressure equation. In testing this equation and deductions from it, Werthheimer used experimental data for several compounds, including stannic chloride in the range 30—319°. However, no references, or details of the experimental measurements, were quoted.

Apart from an isolated estimate of the boiling point of stanic bromide at 12 mm. mentioned by Anschütz and Reitter ("Die Destillation unter vermindertem Druck im Laboratorium," 2nd edn., Cohen, Bonn, 1895) we can find no record of vapour-pressure measurements for stannic bromide in the literature. These authors give b. p. 75·8—76·6°/12 mm. and 204·6—204·8°/760 mm., and for the iodide, b. p. 190—190·2°/16 mm. and 295°/760 mm. The only other reliable measurement of heats of fusion and vaporisation of stannic iodide was carried out by Negishi (*J. Amer. Chem. Soc.*, 1936, **58**, 2293) but the vapour-pressure measurements were over a limited range and the extrapolation was so large that the uncertainty in the boiling point could be appreciable.

The practical importance of vapour-pressure data prompted Stull (*Ind. Eng. Chem.*, 1947, **39**, 517, 514) to collect and systematise the available information for a large number of organic and inorganic compounds. All data for a given compound were collected, arranged, and plotted on a Cox chart (Cox, *ibid.*, 1923, **15**, 592; Davis, *ibid.*, 1925, **17**, 735; 1930, **22**, 380; Davis and Calingaert, *ibid.*, 1925, **17**, 1287). A median line was drawn so that it fits the points consistently and temperature values were "read back" at different pressures. The results were then presented in systematic tabular form. The data available for the stannic halides were meagre, in some cases having been measured at two temperatures only. Thus, since the method of analysis is a graphical one, the personal error is an unknown factor and to a fair extent this method of analysis is no better than the data used in its design.

It must be emphasised that in previous work, except that of Negishi (*loc. cit.*), no precautions were taken to avoid contact between the stannic halides and mercury. Young (*loc. cit.*) stated that mercury was attacked by stannic chloride even at low temperatures. According to Dumas (*Ann. Chim. Phys.*, 1862, **33**, 358) stannic chloride reacts with mercury to give both mercurous and stannous chlorides. Moreover, no precautions to exclude moisture were mentioned although the stannic halides hydrolyse readily in moist air, the ease of hydrolysis increasing from the iodide through the bromide to the chloride, which fumes in moist air. The hydrated chloride and bromide usually make ground joints stick together firmly, thus making it impossible to use any stopcocks or ground joints in the main system unless these are rejected afterwards. Stannic iodide decomposes readily in the presence of even small amounts of oxygen or water in the neighbourhood of its boiling point. The great affinity of the halides for water presented the main difficulty in their purification and handling in vacuum, and it was considered desirable to mention in some detail the apparatus and technique used since this largely affects the purity of the compounds and hence the accuracy of the measurements.

EXPERIMENTAL.

Purification and Handling of the Tetrahalides.—Stannic chloride. Chemically pure stannic chloride was further purified by distillation under vacuum in the apparatus shown in Fig. 1A. A flask *c* was provided with a long neck, bent as shown in the diagram; close to the bulb were sealed two side tubes *b* and *d*. A special all-glass seal *e*, separately shown in Fig. 1B, connected the flask *c* to a series of flasks *A*, *B*, *C*, and *D*; the last of these was connected to another seal *k*, the open end of which was sealed to the adapter *l* with a multi-head rotating receiver *m*. The special seals are small, thin-walled capillary tubes sealed in wider tubes in such a manner that the bent capillary tube can be broken at will by means of a small magnetic hammer enclosed in glass. Stannic chloride was introduced through the inlet *a*, which was then sealed off. The flask *c* was cooled in liquid air and thoroughly evacuated through *b*, which was then sealed off. The bulb was heated in an oven at 100° for 12 hours, whereby a white, crystalline sublimate, probably the hydrate, was formed at the cold bent neck which was kept projecting outside the oven. The flasks *A*, *B*, *C*, and *D* were evacuated through *j*, the bulbs and connecting tubes being kept, during the evacuation, as hot as possible to expel any adsorbed water vapour, and finally *j* was sealed off. The flask *c* was now connected to the rest of the apparatus simply by breaking the capillary tube of the special seal *e*, the magnetic hammer being used. The more volatile part of the liquid was then distilled into *A* by cooling *A* in liquid air. The flask was then sealed off at the constriction *f*, and the contents of *A* rejected. The greater part of the stannic chloride was distilled into *B* in the same way. Two more distillations were carried out, the material being collected in *D*. Each time a residue was left in the flasks, which were sealed off at the constrictions *g*, *h*, and *i* as soon as each distillation was completed. The multihead receiver *m* attached to the adapter *l* was then evacuated and out-gassed through *n*, which was then sealed off. The capillary of the seal *k* was broken and samples of the purified stannic chloride were collected in the receiving tubes. These were previously slightly drawn down and scratched by a file to facilitate breaking them.

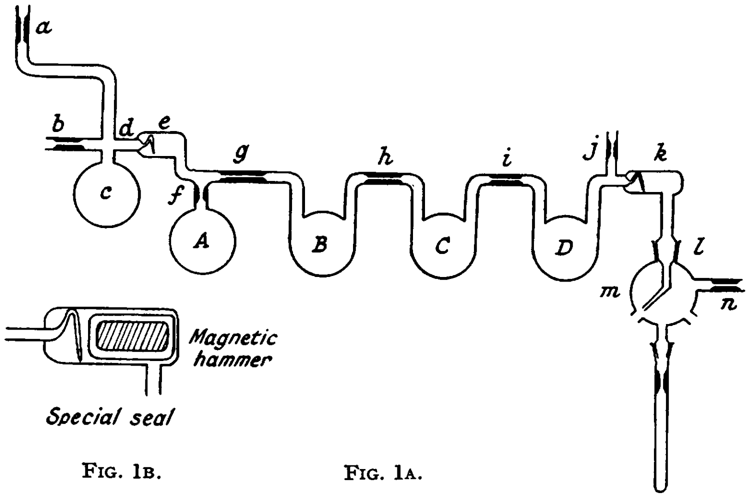
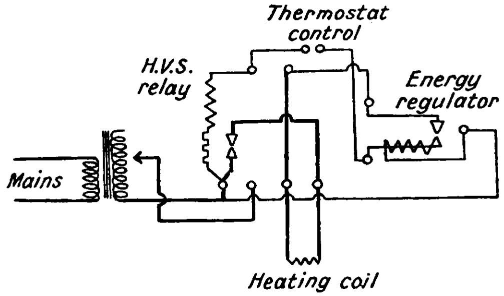


FIG. 1B. FIG. 1A.

Stannic bromide. A B.D.H. product was further purified by fractional distillation under partial vacuum, a Vigreux type column about 30 cm. long being used. Since the m. p. of stannic bromide is slightly above room temperature, it was necessary to warm the receiver with a small flame to prevent the solid from blocking the tubes. The receiving part was exactly the same as that used for stannic chloride, and the same precautions were taken.

Stannic iodide. A B.D.H. product was recrystallised three times from carbon tetrachloride. The crystals were dried in a current of dry air at 120° and finally under vacuum. They were then sublimed and sealed under vacuum in sample tubes (see Fitzgerald, *J. Amer. Chem. Soc.*, 1907, **29**, 1693).

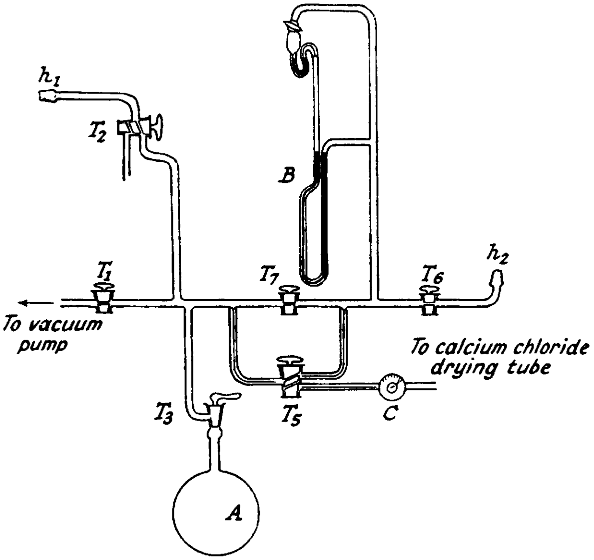
FIG. 2.



The thermostat was made of an aluminium-bronze alloy, which was chosen for its high thermal conductivity and heat capacity. It has a high m. p. and when electrically heated shows no sign of oxidation. The block, a 12″ × 15″ cylinder, had a 2″ × 10″ hole in the centre to take the reaction flask. The block was heated by two nichrome coils; one, an 85-ohms coil, was included in the control circuit, and the second, a 50-ohm coil, was connected directly to the mains through a variable resistance. The latter coil helped in reaching the required temperature rapidly and was immediately switched off when the temperature was within 5° of the required value. For the accurate control of temperature a thermostat regulator was used in combination with a Sunvic energy regulator type TYB and a Sunvic hot-wire vacuum switch type F 102—3M used as a relay. This standard control circuit is illustrated in Fig. 2. Temperature measurements were carried out by means of chromel–alumel thermocouples calibrated against one whose elements had been calibrated by the National Physical Laboratory.

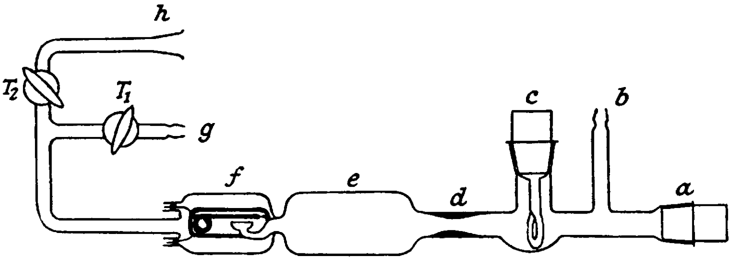
Temperature measurements, recorded by a Cambridge thermocouple potentiometer, were within ±0·1°. Vapour-pressure measurements were carried out by means of an all-glass membrane manometer (see p. 3252). The main vacuum line shown in Fig. 3 consists of a mercury manometer *B*, the closed end of which was provided with a U-type loop and cut-off stopcock (Gilmont, *Ind. Eng. Chem.*, *Anal.*, 1948, **20**, 474). A two-way capillary tap T_5 was connected to the line by a length of capillary tubing, and its free end was connected to a needle valve *C* which ended with a calcium chloride drying-tube, thus allowing dry air to balance the pressure to be measured. A 5-litre flask *A* was connected through the tap T_3; this was used as a vacuum reservoir, in case it was needed whilst carrying out a run, for the pump was always stopped to prevent any vibrations, which affected the glass-membrane manometer. Taps T_1, T_2, T_4, and T_6 were inserted to facilitate manipulation and to separate any part of the vacuum line when necessary.

FIG. 3.



When carrying out a run, a tube containing the sample was thoroughly cleaned, dried, and introduced through the ground joint at *a* in the apparatus shown in Fig. 4, where it was held in position by the strong loop-hole of the vacuum breaker *c*. The whole part shown in Fig. 4 was connected to the main line by means of the ground joint *h* through the socket h_1 (see Fig. 3) and inclined at an angle of about 20° to the horizontal with the right-hand side uppermost. This inclination was usually sufficient to allow the sample tube to glide easily to the reaction flask *e*. The tubes *b* and *g* were connected together with pressure tubing, and the apparatus was evacuated on both sides of the diaphragm at the same time, a two-stage Speedivac pump being used. The reaction flask was out-gassed, then cooled by ether–solid carbon dioxide. The sample tube was then broken under vacuum simply by turning the tap *c*; meanwhile evacuation was continued. Slight tapping was sometimes necessary to cause the sample tube to fall into the reaction flask. The flask was then cautiously sealed off at the previously made constriction *d*. This step requires care because any fault may lead to the breaking of the glass-membrane manometer. Taps T_1 and T_2 were closed, and the apparatus released from the main line and inserted vertically in the constant-temperature zone of the high-temperature thermostat, while the joint *h* was again connected to the main line at h_2 (see Fig. 3). Evacuation was continued, tap T_2 was opened to the main line and finally the pump was stopped. The block was heated to the required

FIG. 4.



temperature and kept thereat for at least ½ hour. At every temperature two pressure measurements were recorded; one, p_1, was taken when approaching the temperature from below by heating the block to that temperature; the other reading p_2 was approached from the higher temperature by heating to some temperature above that required and allowing the block to cool to the required value. The zero reading of the manometer was checked over the whole range both before and after a run to ensure that it had remained constant.

RESULTS AND DISCUSSION.

The samples used in this investigation are undoubtedly very pure in view of the technique used for their purification. A comparison between the boiling points found for the tetrahalides in this investigation and the values obtained by other investigators, corrected to one atmosphere, are given in Table I.

TABLE I.

Compound.	Author(s).	B. p.	Compound.	Author(s).	B.p.
$SnCl_4$	Andrews [a]	112·9°	$SnBr_4$	Carnelly and O'Shea [e]	201·0° (uncorr.)
	Thorpe [b]	113·9		Preis and Rayman [f]	203·3
	Young [c]	114·1		Bond [d]	206·5
	Bond [d]	112·6		Rader [g]	206·7
	This investigation *	113·9		This investigation *	205·0
SnI_4	Rader [g]	346·0			
	Negishi [h]	348·0			
	This investigation *	348·4			

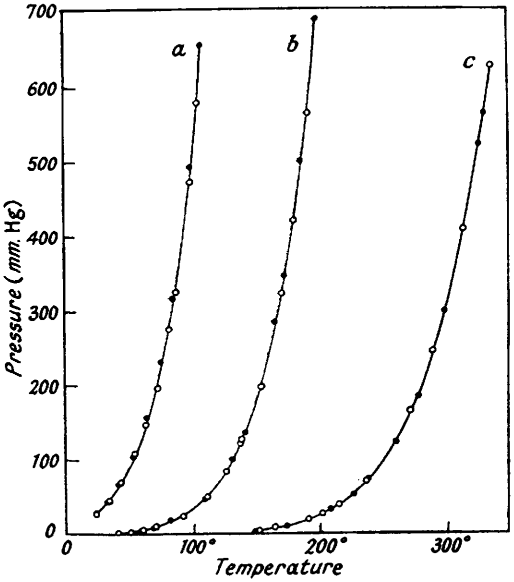
[a] *Chem. News*, 1847, **25**, 61. [b] *J.*, 1880, **37**, 331. [c] *Loc. cit.* [d]. *J. Amer. Chem. Soc.*, 1926, **48**, 348. [e] *J.*, 1878, **33**, 55. [f] *Annallen*, 1884, **223**, 324. [g] *Z. anorg. Chem.*, 1923, **130**, 325. [h] *Loc. cit.*

* Estimated boiling points are considered as correct to ± 0·2°.

TABLE II.

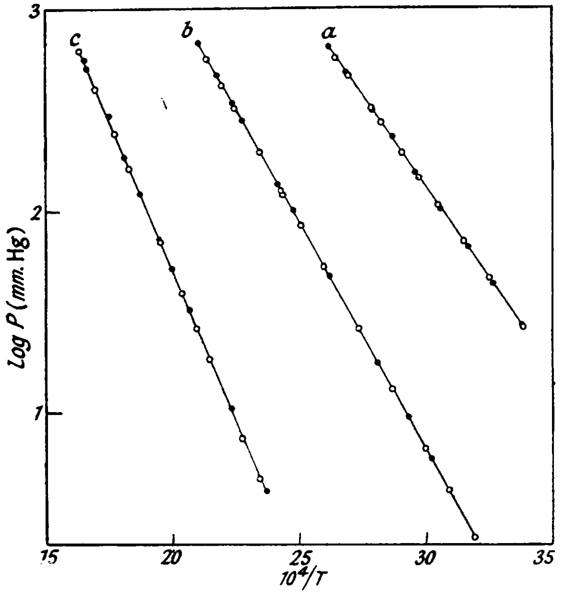
	Temp.	p_1, mm.	p_2, mm.	$P_{obs.}$	$P_{calc.}$	$P_{calc.} - P_{obs.}$		Temp.	p_1, mm.	p_2, mm.	$P_{obs.}$	$P_{calc.}$	$P_{calc.} - P_{obs.}$
				Vapour pressure of stannic chloride.									
(1)	22·5°	26·5	26·5	26·50	26·50	0·00	(2)	23·2°	27·4	27·2	27·30	27·41	0·11
	34·8	46·9	46·7	46·80	46·80	0·00		33·5	44·1	44·1	44·10	44·12	0·02
	44·4	70·6	70·7	70·65	70·63	—0·02		42·8	66·1	66·0	66·05	66·07	0·02
	54·7	107·1	107·2	107·15	107·13	—0·02		53·4	101·9	101·7	101·80	101·76	—0·04
	62·9	146·3	146·4	146·35	146·39	0·04		64·5	155·4	155·5	155·45	155·02	—0·43
	70·9	195·8	195·6	195·70	195·70	0·09		75·5	230·3	230·4	230·35	230·14	—0·21
	80·9	274·4	274·4	274·40	274·74	0·07		84·7	314·1	314·0	314·05	313·69	—0·36
	85·7	324·1	324·1	324·10	324·12	0·02		98·8	490·0	490·0	490·00	489·32	—0·68
	97·6	471·7	471·6	471·65	471·65	0·09		108·5	653·3	653·2	652·25	652·23	—1·02
	104·3	577·3	577·3	577·30	577·34	0·04							
				Vapour pressure of stannic bromide.									
(1)	40·0°	2·4	2·4	2·40	2·39	—0·01	(2)	57·8	5·8	5·9	5·85	5·86	0·01
	50·3	4·1	4·0	4·05	4·06	—0·01		68·0	9·4	9·4	9·40	9·40	0·00
	60·4	6·7	6·6	6·65	6·63	—0·02		82·8	17·7	17·8	17·75	17·78	0·03
	74·9	13·0	13·1	13·05	13·07	0·02		108·6	47·9	47·9	47·90	48·01	0·11
	92·5	26·2	26·2	26·20	26·26	0·06		130·3	100·1	100·2	100·15	100·30	0·15
	111·5	53·1	53·2	53·15	53·24	0·09		140·3	137·1	137·2	137·15	137·25	0·10
	125·3	85·2	85·1	85·15	85·25	0·10		165·5	283·9	283·8	283·85	283·85	0·00
	136·5	122·0	122·0	122·00	122·04	0·04		173·2	348·5	348·4	348·45	348·66	0·21
	137·9	127·4	127·3	127·35	127·47	0·12		185·7	479·6	479·6	479·60	479·84	0·24
	152·6	197·7	197·8	197·75	197·79	0·04		199·8	689·6	689·6	689·60	689·75	0·15
	170·5	324·5	324·5	324·50	324·72	0·22							
	180·5	420·8	420·9	420·85	421·02	0·17							
	192·3	563·8	564·0	563·90	563·90	0·00							
				Vapour pressure of stannic iodide.									
(1)	152·4	4·7	4·8	4·75	4·75	0·00	(2)	148·6	4·1	4·1	4·10	4·11	0·01
	165·5	7·7	7·7	7·70	7·69	—0·01		174·2	10·5	10·4	10·45	10·43	—0·02
	192·0	18·7	18·7	18·70	18·71	0·01		209·9	32·3	32·4	32·35	32·27	—0·08
	203·1	26·3	26·4	26·35	26·37	0·02		226·9	52·3	52·3	52·30	52·26	—0·04
	2616·6	39·2	39·2	39·20	39·19	—0·01		239·6	73·3	73·3	73·30	73·35	0·05
	237·1	70·6	70·5	70·55	70·53	—0·02		260·1	122·6	122·6	122·60	122·57	—0·03
	272·5	164·1	164·2	164·15	164·10	—0·05		278·4	187·5	187·5	187·50	187·67	0·17
	290·2	243·4	243·3	243·35	243·61	0·26		299·9	299·2	299·3	299·25	299·16	—0·09
	315·1	407·5	407·5	407·50	407·38	—0·12		327·6	518·7	518·8	518·75	518·80	0·05
	337·6	625·6	625·6	625·60	625·46	—0·14		332·0	563·8	563·7	563·75	564·00	0·25

FIG. 5.



a, $SnCl_4$. *b*, $SnBr_4$. *c*, SnI_4. ○ *First run.* ● *Second run.*

FIG. 6.



a, $SnCl_4$. *b*, $SnBr_4$. *c*, SnI_4. ○ *First run.* ● *Second run.*

The vapour-pressure data for the three halides are given in Table II. Results are given for two runs on each compound. Pressures are considered to be accurate to better than ±0·2 mm. In the tables p_1 and p_2 have the meaning given above, and $P_{obs.}$ represents the mean value of p_1 and p_2. The variation of $P_{obs.}$ with temperature is shown in Fig. 5. In Fig. 6, values of log $P_{\text{obs.}}$ are plotted against $1/T$. The vapour pressure–temperature relationships for the three compounds are represented by the following equations :

stannic chloride, $\log P = 7{\cdot}59676 - 1824{\cdot}9/T$
stannic bromide, $\log P = 7{\cdot}63048 - 2270{\cdot}8/T$
stannic iodide, $\log P = 7{\cdot}66607 - 2973{\cdot}9/T$

These equations were derived empirically by the method of least squares. The two last columns in Table II give the pressures calculated from the equations and the differences between observed and calculated value. Only in one case is the deviation more than 1 mm. and in most cases the agreement is better than 0·3 mm.

By assuming that the molal volume of the liquid is negligible compared with that of the vapour, and that the perfect-gas laws apply to the vapour phase, one can put the Clausius–Clapeyron equation in the simple form, $\Delta H = -\boldsymbol{R}\mathrm{d}(\ln p)/\mathrm{d}(1/T)$, where ΔH is the heat of vaporisation in calories per mole and $\boldsymbol{R}$ is taken as 1·987 cal. deg.$^{-1}$ mole^{-1}. By use of this equation the heats of vaporisation of the tetrahalides have been calculated; these are given in Table III, which also shows the value of the entropy of vaporisation in each case.

TABLE III.

Heats and entropies of vaporisation of the stannic halides.

	ΔH, cal./mole.	ΔS, cal./mole/degree.
$SnCl_4$	8,350	21·6
$SnBr_4$	10,390	21·7
SnI_4	13,610	21·9

Our value for the latent heat of vaporisation of stannic chloride, namely, 32·1 cal./g., is in reasonably good agreement with the value of 32·6 cal./g. obtained by calculation by Hammick (*Phil. Mag.*, 1922, **44**, 590), who used the expression $\lambda_{\text{vap.}} = \lambda_{\text{ex.}} + H + h$, where $\lambda_{\text{vap.}}$ is the heat of vaporisation at the normal boiling point, $\lambda_{\text{ex.}}$ is the heat of expansion, H is the heat due to the change of internal energy of the substance occurring during the transformation from the liquid to the vapour phase, and h is the heat of association. For stannic iodide, our value of 13,610 cal./mole agrees satisfactorily with that given by Negishi (*loc. cit.*), namely, 13,650 cal./mole.

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