# S 26. Physical Properties of Triphenyl Compounds of Group VB Elements.

# By M. V. FORWARD, S. T. BOWDEN, and W. J. JONES.

The temperature variation of density, vapour pressure, and surface tension of the liquids have been measured, and the molecular volume, latent heat of vaporisation, and Kleeman-Macleod constants have been determined. The invariability of the latter constants over a wide range of temperature shows that the compounds behave as normal liquids.

The solid-liquid equilibria of binary systems of the compounds have been examined, and it is shown that the type of equilibrium may be related to the difference between the parachors of the components. The eutropic series is found to be non-ideal. In an examination of the isosterism of the CH group with the atoms of the elements of Group VB, it is concluded that factors other than the weight of the groups are involved in isomorphism. The equilibria between tetraphenyltin and each of the triphenyl compounds have been determined, and earlier measurements have been corrected.

No systematic study of the physical properties of liquid triphenyl compounds of the elements of Group VB has hitherto been made, although a few measurements of the density and surface tension over limited ranges of temperature have been carried out by Pascal (*Compt. rend.*, 1913, **156**, 1905) and by Walden and Swinne (Z. physikal. Chem., 1912, **79**, 713), respectively. In the present work it is found that the variation of density with temperature is normal for a range of 200° above the m. p., but triphenylbismuthine begins to decompose at 180°. It will be evident from the data in Table I that Pascal's values of the molecular volumes,  $V_{20°}$ , of the solid are less regular than the estimated molecular volumes,  $V_b$ , of the liquid at the boiling point. If Kopp's values (Annalen, 1855, **96**, 153) are taken for the atomic volumes of carbon (11·0) and hydrogen (5·5), the approximate atomic volumes of the elements of Group VB in this type of compound are: N, 16·5; P, 29·5; As, 34·5; Sb, 40·5.

#### TABLE I. V 20°. $V_b$ . L. B. p. С. [P].213 29716,090 364° 32·1 Triphenylamine ..... $\mathbf{584}$ 219 310 17,000 384 Triphenylphosphine ..... 28.7607 Triphenylarsine ..... Triphenylstibine ..... 234315 18,090 378 17.1622 234321 19,880 37710.5635Triphenylbismuthine ..... **4**·81 650

The vapour pressures of the liquids exhibit normal variation over the range 200—300°, and the values at a particular temperature are in the order NPh<sub>3</sub>> PPh<sub>3</sub>> AsPh<sub>3</sub>> SbPh<sub>3</sub>, but there is little difference between the vapour pressures of the phosphine and the arsine. If p is the vapour pressure and T the absolute temperature, the plot of log p against 1/T is nearly a straight line for each compound. The values of the average latent heat of vaporisation, L in calories per mole, as calculated from the slope of the line, are recorded in Table I. Approximate estimates of the b. p. at 760 mm. as found from the vapour-pressure curves are also given in Table I. Haeussermann (*Ber.*, 1901, **34**, 40) gave 347-348°, and Boldyreff (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1869) 365°, as the b. p. of triphenylamine.

The surface tensions of triphenylphosphine and triphenylstibine have been determined over a range of about 60° by Walden and Swinne (*loc. cit.*), but their values are uniformly lower than those found in the present work. For a range of 100° above the m. p., the surface tensions of the amine, phosphine, arsine, and stibine vary almost linearly with temperature, and a similar relation obtains with the bismuthine from the m. p. to the decomposition temperature. The relation between surface tension and density of unassociated liquids has been given by Kleeman (*Phil. Mag.*, 1911, **21**, 99) and Macleod (*Trans. Faraday Soc.*, 1923, **19**, 38), and for the triphenyl compounds we find that the Kleeman-Macleod constant  $[C = \gamma/(D - d)^4$ , where  $\gamma$  is the surface tension, *D* the density of the liquid, and *d* that of the vapour] does not vary appreciably over the range examined. This constancy indicates that the liquids are normal in so far as they do not exhibit change of association with temperature. In these compounds the parachor constants for the elements of Group VB, as calculated from Sugden's value for the phenyl group, 190.0 ("The Parachor and Valency", Routledge, 1930, p. 181), and from Vogel's value, 188.3 (*J.*, 1948, 654), are as follows :

	N.	Р.	As.	Sb.	Bi.
Sugden	13.9	37.4	$52 \cdot 2$	$65 \cdot 4$	80.4
Vogel	19.0	42.5	57.3	70.5	85.5

The atomic parachors given by Sugden (op. cit.) are: N, 12.5; P, 37.7; As, 50.1; Sb, 66.0; Bi, 80.



Ordinates represent temperature and abscissæ moles %.

The extent to which the triphenyl compounds are miscible with one another in the solid state has been ascertained from the phase diagrams representing the solid-liquid equilbrium. Of the ten possible binary systems, Pascal (*loc. cit.*) has investigated six systems by the cooling-curve method, and we have now examined the other systems and have re-determined the solidus and liquidus curves of the triphenylamine-triphenylarsine system. The precision of the measurements has been increased by the use of highly purified components, and the difficulty which Pascal experienced in determining the course of the solidus curve has been largely obviated by application of the thaw-melt method. The equilibria are presented graphically in the first two columns of the diagram. The systems may be classified into types in accordance with the scheme proposed by Roozeboom (*Z. physikal. Chem.*, 1899, **30**, 385).

Triphenylamine and triphenylphosphine are completely miscible in the solid state (Type III). The amine and the arsine form partially miscible solid solutions (Type V); the eutectic mixture corresponding to 79% AsPh<sub>3</sub> melts at 49.8° and not at 45.5° as recorded by Pascal, while the mutual solubilities of the compounds are lower than those found by him. The amine and the stibine also form partially miscible solid solutions (Type V) which contain 4.7% and 99.3%. respectively, of the latter at  $43 \cdot 3^{\circ}$ ; the eutectic composition corresponds to  $77 \cdot 5\%$  of the stibine. Similar equilbria are exhibited by the amine and the bismuthine; the eutectic mixture contains 75% of the latter and melts at  $62.5^{\circ}$ . Since the miscibility gap extends from 4.3 to 87.5% of bismuthine, the solid solubility of the amine in the bismuthine is greater than in the stibine. Triphenylphosphine and triphenylarsine form partially miscible solid solutions (Type IV). The phosphine and the stibine give rise to a continuous series of solid solutions (Type III), and the solid solution containing 67.5% of stibine has the lowest m. p.  $(39^{\circ})$  of the series. The phosphine and the bismuthine form partially miscible solid solutions (Type V). Triphenylarsine and triphenylstibine form a continuous series of solid solutions (Type III), and the arsine and the bismuthine form partially miscible solutions (Type V). Triphenylstibine and triphenylbismuthine give rise to partially miscible solid solutions (Type IV); solid solutions containing 48.5% and 38.8% of the bismuthine, respectively, are in equilibrium with liquid phase containing 33.9% of this at the peritectic temperature,  $62.4^{\circ}$ . If, with Pascal, we assume that the formation of a continuous series of solid solutions (Type III) is possible only when the components exhibit complete isomorphism, it may be concluded that the members of the following systems are truly isomorphous: triphenylamine, triphenylphosphine; triphenylphosphine, triphenylstibine; triphenylarsine, triphenylstibine. Moreover, the narrowness of the miscibility gap in the two Type IV systems (triphenylphosphine, triphenylarsine; triphenylstibine, triphenylbismuthine) indicates that the departure from complete isomorphism is slight. In the other systems (Type V) the miscibility gap is wide and the conditions leading to isomorphism are correspondingly limited. If the mean percentage difference,  $\Delta[P]$ , between the parachors  $[P]_1$  and  $[P]_2$  of the two components is defined by  $200([P]_1 - [P]_2)/([P]_1 + [P]_2)$ , the magnitude of this quantity corresponds to the type of phase diagram in this particular eutropic series as indicated herewith:

Type IV:	$\Delta[P] =$	1.95 -	2.18
Type III :	$\Delta[P] =$	2.55 -	4.50
Type V :	$\Delta[P] =$	4·72 —	10.9

It is not possible to correlate the type of phase diagram and the recorded molecular volumes of the solids.

According to Drew and Landquist (J., 1935, 1480) it would be expected that in an ideal eutropic series (where the valency angles of the eutropic elements are the same and the compounds are closely isomorphous) corresponding compounds would melt at temperatures lying near together, and a mixture of all the corresponding compounds would melt within this range. From a study of the m. p.s of the triphenyl compounds, they concluded that N and Bi are divergent from the other elements and that only P and As are compatible with one another. On a similar basis we find that Sb and Bi are also compatible with one another, and further, in agreement with Drew and Lanquist, that the relationship between the Group V elements is not nearly so close as that between the Group IV elements.

In an attempt to account for the isomorphism of organic compounds, Grimm, Günther, and Tittus (Z. physikal. Chem., 1931, 14, B, 169) assumed that isosteric groups can replace one another so that the corresponding compounds are miscible in the solid state. Although this assumption was not confirmed by these workers, we have further examined the matter in view of the statement by Bradlow, Vanderwerf, and Kleinberg (J. Chem. Educ., 1947, 24, 433) that only isosteric groups not differing greatly in molecular weight can replace one another without causing marked differences in the physical properties of the compounds. Since the group CH is

isosteric with the atoms of the elements of Group V, we have examined the phase equilbria of triphenylmethane with each of the triphenyl compounds of the Group VB elements. The types of equilbrium are represented in the third column of the diagram. It is the arsine (with higher molecular weight than the phosphine and amine) which is completely miscible with triphenylmethane in the solid state, and it is to be concluded, therefore, that factors other than the weight of the isosteric groups govern the solid solubility of these compounds.

In the phase diagram given by Cambi (*Atti R. Accad. Lincei*, 1912, **21**, i, 776) for tetraphenyltin and triphenylstibine, the liquidus curve on the stibine side coincides with the horizontal part of the solidus. This representation, however, is incorrect owing to the presence of impurity in the stibine which he used. The phase equilibria of tetraphenyltin with each of the triphenyl compounds of the elements of Group VB are shown in the fourth column of the diagram. It is evident that the components exhibit little, if any, solubility in the solid state, and that the composition of the eutectic undergoes a regular antibatic variation with the m. p. of the triphenyl compound.

### EXPERIMENTAL.

#### (All thermometer readings are corrected.)

Preparation of Materials.—Triphenylphosphine was prepared from phenylmagnesium bromide and phosphorus trichloride (Pfeiffer and Pietsch, Ber., 1904, **37**, 4621; Sauvage, Compt. rend., 1904, **139**, 675); after crystallising twice from light petroleum and five times from ether-alcohol, it had m. p. 80-5°. The arsine was prepared by the action of the same Grignard reagent on arsenic trichloride, and after a series of crystallisations from the above solvents, it melted at 60-8°. The stibine was obtained by the procedure described by Harris, Bowden, and Jones (J., 1947, 1569), and after repeated crystallisation from ether-alcohol, it had m. p. 55°. After a similar purification process the bismuthine (Pfeiffer and Pietsch, *loc. cit.*) melted at 78.5°. These m. p.s are uniformly higher than those recorded by earlier workers but agree closely with the values found by Drew and Landquist (J., 1935, 1480). Pure specimens of triphenylamine (m. p. 127.5°), triphenylmethane (m. p. 92.0°), and tetraphenyltin (m. p. 225.9°) were available.

Density Determinations.—The pyknometer consisted of a glass bulb (2 c.c. capacity) fused to a graduated capillary tube, and the volume corresponding to each scale division was found by calibration with water. The dry pyknometer containing the molten organic compound was immersed in a mechanically-stirred bath of castor oil, and the volume occupied by the substance at different temperatures was determined in the usual manner. All weighings were corrected for buoyancy. The densities in g./c.c. are given in Table II. The variation of density with temperature is represented by the following equations:

Triphenylamine :	$D_{4^{\circ}}^{l^{\circ}} = 1.1185 - 0.0008036 t$
Triphenylphosphine :	$D_4^i = 1.1335 - 0.0007457 t$
Triphenylarsine :	$D_{4^{\circ}}^{t} = 1.2994 - 0.0008628 t$
Triphenylstibine :	$D_{4^{\circ}}^{i^{\circ}} = 1.4564 - 0.0009426 t$
Triphenylbismuthine :	$D_{4^{\circ}}^{i_{\circ}} = 1.7633 - 0.001224 t$

# TABLE II.

Temp.	NPh <sub>3</sub> .	PPh <sub>3</sub> .	AsPh <sub>3</sub> .	SbPh <sub>3</sub> .	BiPh₃.	Temp.	NPh <sub>s</sub> .	PPh3.	AsPh <sub>3</sub> .	SbPh <sub>3</sub> .	BiPh <sub>3</sub> .
80°			1.2304	1.3810		180°	0.9739	0.9993	1.1439	1.2865	1.5429
100		1.0589	1.2131	1.3621	1.6409	200	0.9578	0.9844	1.1266	1.2676	
120		1.0440	1.1958	1.3432	1.6164	220	0.9417	0.9694	1.1093	1.2478	
140	1.0060	1.0291	1.1785	1.3243	1.5919	240	0.9256	0.9546	1.0920	1.2298	
160	0.9900	1.0142	1.1612	1.3054	1.5674	260	0.9095	0.9397	1.0747	1.2109	

Vapour-pressure Measurements.—The vapour pressure of the liquids was measured by the isoteniscope method (Smith and Menzies, J. Amer. Chem. Soc., 1910, 32, 1412), the modification described by Chipman and Peltier (Ind. Eng. Chem., 1929, 21, 1106) being used. The measurements were carried out in an atmosphere of dry nitrogen, and the isoteniscope, which was immersed in a mechanicallystirred bath of castor oil, was vigorously shaken before each reading of the pressure. The results (in mm.) are recorded in Table III. The variation of vapour pressure with absolute temperature is represented by the following equations:

Triphenylamine :	$\log \phi =$	8.413 -	3524	T
Triphenylphosphine :	$\log \phi =$	8.539 -	3717	T
Triphenylarsine :	$\log p =$	8.954 -	3953	T
Triphenylstibine :	$\log \phi =$	9.578 -	4350	T

The average latent heats of vaporisation as computed from the slopes of the lines are given in Table I.

				Tabl	E III.				
Temp.	NPh <sub>3</sub> .	PPh3.	AsPh <sub>3</sub> .	SbPh <sub>3</sub> .	Temp.	NPh <sub>3</sub> .	PPh3.	AsPh <sub>3</sub> .	SbPh <sub>3</sub> .
200°	9.6				260°	62.8	37.4	34.9	26.0
210	13.3	$7 \cdot 2$			270	<b>83</b> ·0	<b>49</b> ·9	47.2	36.6
220	18.4	10.0	8.7		<b>280</b>	109.5	66·1	63.9	51.1
230	25.7	14.2	12.5	8.8	290	142.6	87.0	$85 \cdot 2$	
240	$34 \cdot 9$	20.2	17.8	12.4	300	183.8			
250	47.1	27.5	$25 \cdot 2$	18.1					

Surface-tension Measurements.—The capillarimeter (Bowden, J. Physical Chem., 1930, 34, 1866) consisted of two capillary tubes of radii 0.033 cm. and 0.058 cm., fused to quill tubing (radius 0.35 cm.) which formed the wider limb of the instrument. The molten substance was introduced into the apparatus through a small funnel which was preheated to a temperature 10° above the m. p. of the compound. The capillarimeter was maintained at the required temperature in a bath of castor oil, and the difference between the capillary rise in the two tubes was measured by a travelling microscope reading to 0.001 cm. Adequate precautions were taken to ensure the formation of fresh liquid surfaces in the capillary tubes and to effect thorough wetting of the walls before each reading. The surface tension was calculated from the equation given by Sugden (J., 1921, **119**, 1483). The results are listed in Table IV, where D represents the density of the liquid,  $\gamma$  the surface tension in dynes per cm., C the Kleeman-Macleod constant, and [P] the parachor.

				Tabl	E IV.				
Temp.	D.	γ.	С.	[P].	Temp.	D.	γ.	С.	[P].
	Tri	phenylam	ine.			Tri	phenylars	ine.	
135.8° 169.7 195.9 224.5	1.0096 0.9824 0.9614 0.9384 Triph 1.0585	33.5 29.7 27.4 25.0 enylphosj 36.1	32·2 31·9 32·0 32·2 Mea phine. 28·7	584.5 582.9 583.7 584.5 an 583.9 607.4	$79.6^{\circ} \\ 100.6 \\ 131.3 \\ 156.3 \\ 195.8 \\ 220.6 \\ 241.5 \\ $	1.2307 1.2126 1.1861 1.1647 1.1307 1.1091 1.0911	$\begin{array}{c} 39{\cdot}2\\ 36{\cdot}4\\ 33{\cdot}8\\ 31{\cdot}4\\ 28{\cdot}1\\ 25{\cdot}9\\ 24{\cdot}0 \end{array}$	17·1 16·8 17·1 17·1 17·2 17·1 17·0 Mec	$\begin{array}{c} 622 \cdot 5 \\ 620 \cdot 3 \\ 622 \cdot 5 \\ 622 \cdot 3 \\ 623 \cdot 5 \\ 622 \cdot 8 \\ 621 \cdot 2 \\ 021 \cdot 2 \\ 021 \cdot 2 \\ 022 \cdot 2 \\$
129·4 164·2	1.0370 1.0111	33·3 30·2	28·8 28·9	607·6 608·1		Tri	phenylstil	oine.	III 022 2
194·7 226·0	0.9883 0.9649 Triphe	27.5 24.7 enylbismu	28.8 28.6 Me: thine.	607.8 606.0 an 607.4	$76.0 \\ 131.5 \\ 163.2 \\ 193.0$	$     \begin{array}{r}       1 \cdot 3847 \\       1 \cdot 3324 \\       1 \cdot 3026 \\       1 \cdot 2745     \end{array} $	$38 \cdot 1$ $33 \cdot 3$ $30 \cdot 4$ $28 \cdot 0$	$   \begin{array}{r}     10.4 \\     10.6 \\     10.6 \\     10.6   \end{array} $	633·5 636·6 636·5 637·3
$98.5 \\ 133.9 \\ 155.0$	1.6427 1.5993 1.5736	$35 \cdot 1 \\ 31 \cdot 5 \\ 29 \cdot 3$	4·82 4·82 4·78 Mea	650·9 650·7 649·5 an 650·4	224·2 243·5	$1.2451 \\ 1.2269$	25·3 23·3	10·6 10·5 Mea	636-0 632-3 an 635-4

Phase Equilibria.—The preparation of the systems followed common practice except with a few mixtures in which the supercooling was so marked that it was necessary either to cool the mixtures in an ice-box or to scratch the glass to induce solidification. The apparatus and procedure employed for the thaw-melt determinations (Bowden, "The Phase Rule and Phase Reactions", Macmillan and Co., 1938, p. 209) were modified only in so far as the observation of the thaw-point was made by reflected light and that of the melt-point by transmitted light from an electric lamp which was shielded with a white, translucent screen. In Table V, c represents the molar percentage of the second component.

					I ABL	Еν.					
	Thaw	Melt		Thaw	Melt		Thaw	Melt		Thaw	Melt
с.	point.	point.	с.	point.	point.	с.	point.	point.	с.	point.	point.
NPh	3 and As	Ph3.	NPh <sub>3</sub>	and St	Ph <sub>3</sub> .	NPh	and B	iPh₃.	CHP	n <sub>3</sub> and N	IPh <sub>3</sub> .
0.00	127·5°	$127.5^{\circ}$	0.00	127·5°	127·5°	0.00	127·5°	127·5°	0.00	92·0°	92·0°
8.53	92.0	$124 \cdot 2$	1.38	83.8	127.3	0.96	$92 \cdot 4$	$127 \cdot 1$	1.53	77.7	91.3
14.86	73.5	120.8	4.29	45.5	126.4	3.62	$65 \cdot 4$	126.3	5.23	76.8	89.9
23.56	58.0	114.9	7.19	43.0	124.5	5.72	62.5	125.6	10.23	76.7	86.7
32.56	50.0	108.4	$14 \cdot 24$	<b>43</b> ·1	119.7	19.26	62.6	118.5	12.39	76.6	83.7
<b>44</b> ·64	<b>49</b> ·8	<b>98</b> ·7	23.76	<b>44</b> ·8	115.6	36.02	62.5	102.3	20.44	76.6	81·4
54.44	<b>49</b> ·8	88.5	28.26	43.8	111.8	$45 \cdot 42$	62.5	<b>88·3</b>	31.64	76.6	94.3
6 <b>4</b> •09	<b>49</b> ·8	<b>74</b> ·0	40.39	43.1	98.5	58.30	62.5	75.4	42.07	76.7	101.7
75.67	50.0	55.0	53.55	43.2	$82 \cdot 4$	67.23	62.5	66·8	50.06	76.9	106.7
83.47	<b>49</b> ·8	$54 \cdot 2$	60.31	43.2	72.3	$84 \cdot 20$	62.5	71.5	62.00	$78 \cdot 2$	113.9
89.77	50.0	56.9	72.47	<b>43</b> ·3	49.4	89.17	64.0	75.1	68.98	85.2	115.8
93.29	$52 \cdot 4$	58.5	82.33	<b>43</b> ·1	45.7	95.27	70.0	77.3	79.65	97.0	120.8
100.00	60.8	60.8	88.55	<b>4</b> 3·3	50.0	100.00	<b>78·3</b>	<b>78·3</b>	89.48	111.7	$123 \cdot 9$
			94.63	$43 \cdot 2$	51.7				100.00	127.5	127.5
			99.08	46.2	$54 \cdot 6$						
			100.00	55.0	55.0						
PPh <sub>3</sub>	and Sb	Ph <sub>3</sub> .	SbPh	and B	iPh <sub>s</sub> .	CHPh	and A	sPh3.	CHPh	and S	bPh <sub>3</sub> .
0.00	80.5	80.5	0.00	55.0	55.0	0.00	92.0	92.0	0.00	92.0	92.0
7.21	67.6	76.7	11.44	$55 \cdot 8$	58.2	7.75	68·3	88.3	9·46	65.7	89.1
14.88	60.9	72.3	21.83	$57 \cdot 2$	60·4	14.56	57.8	85.1	15.86	$54 \cdot 2$	85.7
$24 \cdot 89$	53.7	66·3	36.07	60.8	$63 \cdot 1$	25.00	50.5	<b>79·3</b>	24.00	38.1	<b>80·0</b>
33.67	<b>48</b> ·1	60.1	40.73	$62 \cdot 4$	$64 \cdot 3$	34.49	45.6	$73 \cdot 1$	31.03	36.7	75.0
42.46	43.9	$54 \cdot 9$	44.63	$62 \cdot 4$	65.3	44.59	43.1	67.5	40.43	36.8	67.6
52.86	<b>4</b> 0·6	48.5	47.38	$62 \cdot 4$	65.8	53.65	42.0	57.8	<b>49</b> ·80	36.8	57.4
62.76	39.1	<b>41</b> ·8	54.63	63.7	67.2	66.33	<b>41.6</b>	<b>4</b> 9·9	$62 \cdot 20$	36.7	42.2
75.01	39.7	<b>44</b> ·8	73.93	<b>68</b> .0	70.9	75.23	$43 \cdot 2$	$53 \cdot 2$	74.22	36.7	42.7
85.81	43.7	<b>49</b> • <b>4</b>	88.19	72.8	74.3	87.24	47.4	$57 \cdot 2$	83.26	38.7	48.2
100.00	55.0	55.0	100.00	78.3	78.3	100.00	60.8	60.8	$93 \cdot 26$	46.8	53.0
									100.00	55.0	55.0

	TABLE V (continued).										
	Thaw	Melt		Thaw	Melt		Thaw	Melt		Thaw	Melt
с.	point.	point.	с.	point.	point.	с.	point.	point.	С.	point.	point.
CHPh	and P	Ph <sub>3</sub> .	CHPh	and B	iPh3.	SnPh	$n_4$ and N	Ph <sub>3</sub> .	SnPl	$n_4$ and F	Ph <sub>3</sub> .
0.00	92.0	92.0	0.00	92.0	92.0	0.00	$225 \cdot 9$	225.9	0.00	$225 \cdot 9$	$225 \cdot 9$
4.56	77.2	90.0	5.89	67.6	88.8	1.87	$122 \cdot 2$	$225 \cdot 8$	6.06	77.0	224.6
9.55	$74 \cdot 1$	87.2	12.00	57.4	86.0	15.11	$122 \cdot 1$	$223 \cdot 8$	<b>41·39</b>	76.8	210.1
20.90	73.6	80.7	27.50	55.4	77.8	<b>34</b> ·48	$122 \cdot 1$	217.5	56.31	76.8	196.4
$28 \cdot 30$	73.7	77.4	36.43	55.4	70.4	54.29	$122 \cdot 1$	204.0	70-30	76.8	182.7
35.34	73.7	75.2	45.50	$55 \cdot 4$	62.0	<b>69</b> .04	$122 \cdot 1$	187.3	82.87	76.8	160.3
38.44	73.7	75.0	50.45	$55 \cdot 4$	57.4	<b>74</b> ·79	$122 \cdot 1$	179.8	90.50	76.8	142.0
44.65	73.7	74·6	57.86	$55 \cdot 4$	58.6	82.34	$122 \cdot 1$	167.2	$93 \cdot 85$	76.7	123.8
48.28	73.7	75.2	70.21	55.5	65.0	88.15	$122 \cdot 1$	150.7	96.99	76.7	100.8
51.20	73.7	75.4	<b>84</b> .00	59.5	71.3	93.67	$122 \cdot 1$	$123 \cdot 2$	97.92	76.8	<b>79</b> ·9
58.28	73.7	75.8	90.52	63·8	73.4	95.22	$122 \cdot 1$	$123 \cdot 9$	99.35	<b>76</b> ·8	<b>80·3</b>
69.97	73.6	76.4	100.00	78.3	78.3	<b>97</b> .00	$122 \cdot 1$	125.5	100.00	80.5	80.5
79.02	73.7	77.5				99.62	$122 \cdot 1$	$127 \cdot 1$			
89.46	75.4	79.1				100.00	127.5	127.5			
92.99	77.0	79.7									
100.00	80.5	80.5									

	Thaw	Melt		Thaw	Melt		Thaw	Melt	
с.	point.	point.	с.	point.	point.	с.	point.	point.	
$SnPh_4$ and $AsPh_3$ .			SnPh	$a_4$ and Sb	Ph <sub>3</sub> .	SnPl	SnPh <sub>4</sub> and BiPh <sub>3</sub> .		
0.00	$225 \cdot 9$	$225 \cdot 9$	0.00	$225 \cdot 9$	$225 \cdot 9$	0.00	225.9	$225 \cdot 9$	
1.28	59.4	$225 \cdot 8$	1.01	$53 \cdot 1$	$225 \cdot 8$	1.46	61.8	225.7	
32.37	58.2	217.0	29.64	51.9	216.5	24.77	61.9	216.7	
58.11	58.2	197.7	57.68	51.9	196.5	53.70	61.7	196.2	
80.30	58.4	168.2	$82 \cdot 28$	52.0	164.4	80.65	62.0	165.7	
89.22	58.3	147.5	91.45	$52 \cdot 0$	140.3	88.32	61.8	146.0	
92.46	58.3	$142 \cdot 1$	96.55	51.9	110.4	96.65	61.8	105.5	
96.67	58.5	97.7	97.12	52.0	104.0	97.19	61.9	83.8	
97.25	58.3	84·7	98.75	52.0	54.4	<b>98</b> .77	61.9	73.3	
98.58	58.3	60.3	99.60	$52 \cdot 0$	$54 \cdot 8$	99.31	61.9	75.8	
99.45	58.4	60.7	100.00	55.0	55.0	100.00	<b>78·3</b>	78.3	
100.00	60.8	60.8							

Polycomponent Systems.—Thaw-melt measurements on systems containing equimolar amounts of the components gave the following results.

System.	Thaw point.	Melt point.
$NPh_3 + PPh_3 + AsPh_3$	57·4°	80·2°
$NPh_{3} + AsPh_{3} + BiPh_{3}$	41.5	<b>74</b> ·9
$NPh_3 + PPh_3 + AsPh_3 + SbPh_3$	39.9	69.0
$NPh_{s} + AsPh_{s} + SbPh_{s} + BiPh_{s}$	38.4	65.0
$NPh_3 + PPh_3 + AsPh_3 + SbPh_3 + BiPh_3 \dots$	38.3	68.0

TATEM LABORATORIES, UNIVERSITY COLLEGE, CARDIFF.

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