355. *Mixed Melting Points in Eutropic Series.*

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OUR attention was drawn to this subject by the following cases: (i) the acetylacetonates of the eutropic series aluminium, gallium, and indium melt between 186° and 195°, and but little depression is produced on mixing the compounds in pairs (Morgan and Drew, J., 1921, **119**, 1063); (ii) phenoxthionine and its analogues of the eutropic series sulphur, selenium, tellurium melt between 58° and 88°, and a mixture of all three melts at 55—85° (J., 1928, 512); (iii) the ethylenediethyldisulphine dichlorides of palladium and platinum melt near together (182°, 186°) and show little depression on admixture (Drew and Wyatt, J., 1934, 58); (iv) 3 : 5-dibromo-4-aminobenzophenone and the 3-bromo-5-iodo-compound melt at almost the same temperature and show little depression (Gibby and Waters, J., 1931, 2151).

We thought that, perhaps, in ideal cases, corresponding compounds of a eutropic series of elements would melt at temperatures lying near together, and that a mixture of all would melt within this range or nearly so, provided that there was close isomorphism among the compounds and that the valency angles of the eutropic elements were the same. It was found, however, that the published work on the subject had not apparently extended beyond mixtures of two compounds. There were very marked deviations from the proposed ideal in a number of cases, but not in others. It was therefore decided to investigate the matter further in the expectation that the differences would be minimised by further purification of the compounds concerned. Although we have not succeeded in removing or explaining the deviations, we record some of our results. The m. p.'s were obtained with a calibrated Anschütz thermometer completely immersed.

In Group IV, the tetraphenyl derivatives of C, Si, Ge, Sn, Pb were examined. Pascal (*Bull. Soc. chim.*, 1912, **11**, 321) had already observed some mixed m. p.'s in this series. The highest melting points recorded in the literature are: CPh_4, 285° (corr.); $SiPh_4$, 233° (uncorr.); $GePh_4$,* 232° (uncorr.); $SnPh_4$, 225·7° (corr.); $PbPh_4$, 227·7° (corr.): the fall is therefore not continuous, but it becomes so when our m. p.'s are substituted for the foregoing:

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* Kraus obtained m. p. 235·7°, using a thermocouple; but this value is probably not comparable with the rest. We are much indebted to Prof. G. T. Morgan, O.B.E., F.R.S., for a sample of $GePh_3Br$ from which we prepared the tetraphenyl compound.

	CPh_4.	$SiPh_4$.	$GePh_4$.	$SnPh_4$.	$PbPh_4$.
CPh_4	*285°*	E, 248—257°	E, 245—255°	E, 220—250°	E, 220—250°
$SiPh_4$		*237·5°*	F, 234—236°	[M, 221—221·2°] *	[M, 218·8°]
$GePh_4$			*233·4°*	E, 223—224°	E, 222—223°
$SnPh_4$				*229·2°*	[G, 225·7—226·8°]
$PbPh_4$					*227·8°*

* The m. p.'s given in brackets are Pascal's (*loc. cit.*).

E = equimolecular mixture; M = maximum depression; F = 57% $SiPh_4$; G = 50% $SnPh_4$. The percentages are by weight.

The m. p. of the first member of the series, CPh_4, shows a much greater difference from that of the second member than occurs with other adjacent members of the series.

It will be seen that approximately equimolecular mixtures of adjacent members of the series melt at temperatures intermediate between the separate m. p.'s in the case of CPh_4 + $SiPh_4$ and of $SiPh_4$ + $GePh_4$; but in that of $GePh_4$ + $SnPh_4$ the mixed m. p. is some 6° below that of the lower-melting component, and in that of $SnPh_4$ + $PbPh_4$ there is a similar depression of some 2°. Examining the other possible mixtures, it is seen that the tetraphenyls of C, Si, and Ge are compatible with one another from this point of view, but not with those of Sn or Pb; there is only a slight incompatibility between the tetraphenyls of the last two elements. Thus, in this series there is a change of some function (perhaps a slight change of valency angle) on passing from Ge to Sn, and a lesser similar change on passing from Sn to Pb.

A mixture containing approximately equimolecular proportions of $SiPh_4$, $GePh_4$, $SnPh_4$, and $PbPh_4$ melted at 221—222°; and one containing all five tetraphenyls in equimolecular proportions melted at nearly the same temperature (220—221°).

Since no mixed m. p.'s appear to have been taken with $GePh_4$, the m.-p. curve for $SiPh_4$ + $GePh_4$ was observed by Rheinboldt's micro-method (*J. pr. Chem.*, 1926, **113**, 348). The temperatures at which the mixtures were completely molten could be observed with considerable accuracy, after complete preliminary mixing of the materials by fusion; but the temperatures at which melting just began were very difficult to observe, and the results are only approximate. In all cases the temperatures were observed repeatedly until their constancy indicated that the mixing was complete :

Ph_4Si, %	100·0	80·0	57·5	23·3	0·0
Melting began at	237·5°	235·5°	234·3°	232·7° (?)	233·4°
Melting completed at..................	237·5°	237·1°	236·0°	234·5°	233·4°

In Group V, the triphenyl derivatives of N, P, As, Sb, and Bi were examined. Pascal (*Bull. Soc. chim.*, 1912, **11**, 595; 1923, **33**, 170) obtained the following m. p.'s for these substances: NPh_3, 127·5°; PPh_3, 79·1°; $AsPh_3$, 59·0; $SbPh_3$, 58°; $BiPh_3$, 76°. We attempted to purify the substances further, but succeeded only in recording small alterations in three m. p.'s, *viz.*, $AsPh_3$, 60·5°; $SbPh_3$, 55°; $BiPh_3$, 78·3°. Pascal found a depression of m. p. (63·5°) for NPh_3 + PPh_3 and also for $AsPh_3$ + $SbPh_3$ (37·5°), but an intermediate m. p. (64·2°) for PPh_3 + $AsPh_3$. There were depressions for : NPh_3 + $AsPh_3$, to 45·5°; $AsPh_3$ + $BiPh_3$, to 40°; and PPh_3 + $BiPh_3$, to 42°. We repeated some of Pascal's observations, which were on the whole confirmed :

	M. p. (obs.).	M. p. (Pascal).		M. p. (obs.).	M. p. (Pascal).
PPh_3 (45·4%) + $AsPh_3$	64·5°	64·2°	$AsPh_3$ (70%) + $SbPh_3$	42·1°	37·5°
PPh_3 (47%) + $BiPh_3$	56—57	42	$AsPh_3$ (75%) + $BiPh_3$	44·3	40·0

Our temperatures here are uncorrected and are less accurate than Pascal's, but in some cases our material may have been purer than his.

It will be seen that this series shows large depressions. The outstanding features are that N and Bi are divergent from the other elements, and that only P and As are compatible with one another. It is clear that the relationship between the five elements of this group is not so close as that of the five elements of Group IV, but the purity of some of the materials is still doubtful. Pascal's results for the oxides and sulphides of PPh_3, $AsPh_3$, and $SbPh_3$ (*Bull. Soc. chim.*, 1923, **33**, 170) point for the most part in the same direction.

Pascal's results (*ibid.*, 1912, **11**, 1013) for OPh_2, SPh_2, $SePh_2$, and $TePh_2$ show a less close relationship between the four elements of Group VI than is shown in the phenoxthionine, etc., series; but it is doubtful whether the last two compounds have yet been obtained in a pure state.

In Group VII, reference may be made to the work of Bruni and Gorni (*Atti R. Accad. Lincei*, 1899, **8**, ii, 181; 1900, **9**, ii, 326); of Nagornov (*Z. physikal Chem.*, 1911, **75**, 578); and of Küster (*ibid.*, 1891, **8**, 577).

Austin (*J. Amer. Chem. Soc.*, 1930, **52**, 1049), applying Lindemann's formula to molecules, deduced the following relationship between the absolute m. p. ($T°$), the density at the melting point (D_m), and the molecular weight (M) of organic compounds in homologous series: $M^5 = CD_m^2T^3$, where C is a constant. This formula, however, cannot be applied to the above eutropic series.

We noticed that, for the series of Groups IV and V, the expression $M^{\frac{1}{2}}Tr/D_m^{\frac{1}{2}}$, where r is the calculated radius of the molecule (in Group V, the distance from the centre of the central atom to the periphery of the molecule), approximates to a constant for the particular series. The constancy is sharper for those elements which are the more closely related as deduced from the mixed melting points; but nevertheless it seems probable that the relationship has no fundamental significance.

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