## **205.** The Composition of the Compounds of Picryl Chloride and of s-Trinitrobenzene with Benzene.

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A COMPOUND between picryl chloride and benzene was first described by Mertens (*Ber.*, 1878, **11**, 844), who, from a determination of the loss in weight that occurred when a specimen was exposed to the air, deduced an equimolecular composition,  $C_6H_6, C_6H_2(NO_2)_3Cl$ . Hepp (*Annalen*, 1882, **215**, 376) prepared an analogous compound of benzene with s-trinitrobenzene and assigned to it the composition  $C_6H_6, C_6H_3(NO_2)_3$ , also as the result of an analysis.

These two compounds very readily lose benzene on exposure to

the air, and although both Mertens and Hepp note this fact, neither of them appears to have taken any special precautions to prevent loss of benzene when preparing their specimens for analysis. Lack of such precautions makes their analytical results suspect, and we have therefore determined solid-liquid equilibria in the two-component systems benzene-picryl chloride and benzene-s-trinitrobenzene.

Pure specimens of the components were weighed into bulb-tubes, which were sealed and heated in a variable thermostat until the temperatures  $T^{\circ}$  were found at which the last trace of solid phase



just disappeared. The data obtained are given in the tables and are plotted in the figure. Compositions of liquid phases given in the tables are expressed as mols.% of the nitro-compound.

Benzene-Picryl Chloride.									
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5.55 $2.5^{\circ}$	${10.6 \atop 20.8^{\circ}}$	${15.9\atop 27.6^{\circ}}$	$23.8 \\ 34.0^{\circ}$	$28.0 \\ 36.4^{\circ}$	$rac{34\cdot 3}{39\cdot 0^\circ}$	$37.9 \\ 38.2^{\circ}$	$41.6 \\ 40.2^{\circ}$	47·7 44·2°
	52.7 $48.6^{\circ}$	$56 \cdot 2 \\ 51 \cdot 8^{\circ}$	$\begin{array}{c} 61{\cdot}8 \\ 56{\cdot}7^{\circ} \end{array}$	$\begin{array}{c} 65\cdot 3 \\ 58\cdot 5^{\circ} \end{array}$	70.7 $64.0^{\circ}$	$76 \cdot 3 \\ 68 \cdot 2^{\circ}$	$82.3 \\ 71.5$	90.0 $75.6^{\circ}$	$^{100}_{81\cdot0^\circ}$
Benzene-s- $Trinitrobenzene$ .									
$ \begin{array}{c} \text{Mols. } \% \\ T \\ \dots \end{array} $	$0.0 \\ 5.4^{\circ}$	4∙44 40∙4°	$9.99556.7^{\circ}$	$15.7 \\ 62.3$	$\begin{array}{ccc} 7 & 22 \\ 8^{\circ} & 67 \end{array}$		8·6 9·4°	${34 \cdot 7} \over 71 \cdot 2^{\circ}$	40∙9 70•9°
$_{T}^{Mols. \% \ldots}$	$44.2 \\ 71.5^{\circ}$	$47.4 \\ 74.6^{\circ}$	50·7 77·9°	$51.2 \\ 79.3$	2 60 8° 86	$   \frac{\cdot 2}{\cdot 7^{\circ}} = 10 $	:0·3 :6·6°	$100 \\ 121.0^{\circ}$	

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The curves indicate that in each system there is a compound with a congruent m. p. and containing 33.3 mols.% of nitro-compound, the formulæ of the *compounds* stable in contact with liquid being  $2C_6H_6, C_6H_2(NO_2)_3Cl, m. p. 39^{\circ}$  [Found : loss in a vacuum desiccator over sulphuric acid, 41.3, 42.0.  $2C_6H_6, C_6H_2(NO_2)_3Cl$  requires  $2C_6H_6, 38.7\%$ ], and  $2C_6H_6, C_6H_3(NO_2)_3$ , m. p. 71° [Found : loss on heating in a steam-oven, 43.0, 43.5.  $2C_6H_6, C_6H_3(NO_2)_3$  requires  $2C_6H_6, 42.3\%$ ]. Specimens for analysis were obtained by crystallisation at the ordinary temperature from benzene, some of the solid being removed on a spatula and rapidly dried between filter paper. The specimens were immediately enclosed in a glassstoppered bottle for weighing.

Since the equimolecular compounds would require losses of only 24.0 and 26.8% respectively, the 2:1 ratio of benzene to nitrocompound is established.

The possibility of the existence of 1:1 molecular compounds is being investigated.

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