

CCCLXXIV.—*The Specific Heats of Hydrocyanic Acid.*  
*A Reply.*

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MY original contribution on this subject (J., 1922, **121**, 1604) having been criticised by Partington and Carroll (*Phil. Mag.*, 1925, **49**, 665) on the ground that, in their opinion, my vapour density measurements indicated marked association in the gaseous state, it became necessary to point out (this vol., p. 26) that the argument on which Partington and Carroll based their contention was not in accordance with accepted physico-chemical principles. In reply, Partington (this vol., p. 1559) abandons the former method of calculation (or at least does not refer to it) and adopts a new one, my vapour density measurements being now compared with numbers calculated from Bredig and Teichmann's critical data (*Z. Elektrochem.*, 1925, **31**, 499).

That considerable uncertainty surrounds all such calculations \*

\* This is also true of the numerical comparisons contained in the first paragraph of Partington's paper, which involve both temperature and pressure extrapolations in the case of a vapour not far removed from liquefaction.

is illustrated by Menzies's elaborate investigation of the case of water vapour (*J. Amer. Chem. Soc.*, 1921, **43**, 851) for which comparatively extensive experimental data are available, and in the case of hydrocyanic acid the uncertainty is particularly great for reasons which have already more than once been pointed out (Partington and Carroll, *loc. cit.*; Ingold, *loc. cit.*). But even taking the calculated numbers as they stand, the excess of the observed over the calculated density, assumed to represent the association, varies almost equally on either side of zero (up to  $\pm 0.7\%$ ) if the value for  $65^\circ$  be excluded from the series. Whether this isolated discrepancy (the difference is nearly  $2\%$ ) is due to experimental or theoretical inaccuracies, as may well be the case, or whether it represents evidence of association, as Partington claims (contrary to analogy), matters not in the slightest, since Partington and Carroll's criticism would remain valid only if association were proved to occur throughout the whole temperature range over which the specific-heat ratio was measured.

In the "Summary" at the end of the paper Partington's conclusions are set forth as follows: "It is shown that the reasons advanced against the assumption of Partington and Carroll that hydrogen cyanide vapour is associated to a small \* extent at room temperature are inconclusive." This statement is misleading in several particulars. First, Partington and Carroll's "assumption" of association was *not confined to room temperature*, but included higher temperatures: otherwise there would have been no point in their discussing my experiments, which were conducted between  $65^\circ$  and  $210^\circ$ , the upper part of the range being the more important. Secondly, the vapour density of hydrocyanic acid has not yet been determined at room temperature; and, naturally, I did not "advance reasons against" any assumption which Partington and Carroll might have made relating to a temperature for which no data exist. The implied restriction of Partington and Carroll's "assumption of association" to a temperature for which it cannot at present be tested, and which, in any case, is outside my experimental range, represents a welcome modification of the position previously adopted. It remains to be added, in connexion with the stress laid by Partington on the probable association of hydrocyanic acid in the liquid state, that I had already drawn an analogy between this substance and water, which is strongly associated in the liquid state and yet has been shown by Menzies (*loc. cit.*) to yield an unassociated vapour.

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\* Actually, associations to the extent of  $13\%$  were contemplated.