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

By EDITH HILDA INGOLD.

EARLY this year, a paper by Partington and Carroll appeared (*Phil. Mag.*, 1925, **49**, 665) dealing with the ratio of the specific heats of hydrocyanic acid. The author's previous measurements of this constant (J., 1922, **121**, 1604) were discussed at some length and criticised on two distinct grounds.

The first of these criticisms is summed up in the remark that "the results obtained by Usherwood, although interesting and useful, are approximate only." * Since results of moderate precision were all that the author attempted to obtain, no exception could be taken to this statement were it not made in association with comments relating to the author's experimental procedure which are without foundation in fact, and are apparently intended to suggest a want of care. Thus, Partington and Carroll state: "The gas used, obtained by the action of dilute sulphuric acid on potassium cyanide,† scarcely fulfils the purity requirements required for the determination of physical constants." It was, however, made clear in the original experimental description (*loc. cit.*, p. 1609), and may again be emphasised, that the "gas used" was not, as this sentence implies, taken *straight from the generating apparatus into the sound-tube*, but was *first liquefied*, dried, fractionated until its boiling point was constant, and frozen, before use. A specimen of hydrocyanic acid, prepared by this method, has recently been sent for the determination of physical constants to another worker, who reports that he has found it satisfactory. Another similar criticism is that the author made no mention of "precautions taken to prevent contamination of the vapour by air, due to leakage into the apparatus." It is true that since the elementary precaution of ensuring that an apparatus is gas-tight is not peculiar to the experiments described, it was omitted from the experimental description. It may now be stated, however, (*a*) that the apparatus *was* tested for leakage before and after every experiment, (*b*) that (excepting in preliminary experiments which were not published) no leakage was found, (*c*) that the arrangement was such that if there had been a leak hydrocyanic acid would have passed into the air, not *vice versa.*

The second main criticism offered by Partington and Carroll is that the results obtained by the author are due not, as was suggested, to the thermal effect accompanying isomeric change, but to the thermal effect accompanying polymerisation, the occurrence of which, in the vapour of hydrocyanic acid, is, according to Partington and Carroll, indicated by the author's measurements of its density.

---

* This conclusion is not, as might perhaps be thought, based on any obvious disagreement between the author's results and those of Partington and Carroll; nor do these authors claim that their measurements are of superior precision, although they may well be, having evidently been conducted with great care and attention to detail. They were carried out at the ordinary temperature and under reduced pressures, whereas the author's observations were made at elevated temperatures.

† It was actually pure sodium cyanide, as appears from the description given (*loc. cit.*, p. 1609).

These measurements showed that, although above about 170°, the density is normal (ideal) to within the limits of experimental error (estimated as 0·2%), on approaching the point of liquefaction substantially higher densities obtain, the value at the lowest temperature investigated being nearly 4% above the theoretical. This type of behaviour is, of course, well known. Vapour densities about 3—6% higher than the theoretical were observed by S. Young (*Proc. Roy. Soc. Dublin*, 1910, **12**, 374) for a great variety of substances, including many, such as fluorobenzene, benzene, hexane, pentane, etc., which could not be suspected of any noteworthy tendency to polymerise. The inert gases exhibit the same characteristic. Partington and Carroll, however, regard such density values as indicating in the case of hydrocyanic acid, not deviations from the gas laws, that is, deviations due to molecular attraction and molecular size (the a and b of van der Waals), but polymerisation. Thus the observed 4% excess over the theoretical density is interpreted as indicating that approximately 8% of the molecules have combined to form $(HCN)_2$. This view of vapour density results appears to the author entirely contrary to accepted principles. If it were valid, the continuity of state would demand that compressed gases and even ordinary liquids (the densities of which at *N.T.P* may be thousands of times their ideal vapour densities) must consist principally of enormously polymerised molecules; indeed there would be no such thing as a non-associated liquid. In contradistinction to this view, the author wishes to maintain that, since hydrocyanic acid behaves, in regard to vapour density, similarly to numerous other substances, including inert gases and paraffin hydrocarbons, which are non-associated *even in the liquid state*, and can therefore safely be assumed to be non-associated as vapour, the densities observed in the case of hydrocyanic acid vapour near the point of liquefaction are to be interpreted, not as proving association, but as effects due to departure from the condition (point-molecules without attraction) imagined in an ideal gas. Partington and Carroll refer to the " association " of water vapour as an established fact, and certainly, since liquid water is markedly associated, its vapour would be expected to afford a particularly favourable case for the detection of association in the gaseous state. Yet Kendall (*J. Amer. Chem. Soc.*, 1920, **42**, 2477; compare Menzies, *ibid.*, 1921, **43**, 851) has proved conclusively that, despite its enhanced density, the degree of association of water vapour, if not zero, is at any rate so small that the most accurate available measurements fail to show it. Numerous other cases in which density results had previously been interpreted as indicating association in the vapour have been shown by Kendall and Menzies to be completely accounted for by deviations from the gas laws.*

THE UNIVERSITY, LEEDS.

[*Received, November 5th,* 1925.]