

CCII.—*The Specific Heats of Hydrogen Cyanide. A Reply.*

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A RECENT statement [(Mrs.) Ingold, this vol., p. 26] that there is no "obvious disagreement between the author's results and those of Partington and Carroll" for the ratio of the specific heats of hydrogen cyanide seems to call for correction. Whereas the value found by the last two experimenters at 20° was 1.282 (422 mm.), that of Mrs. Ingold at the lowest temperature used, 65°, was 1.310 (1 atm.), and the curve in Fig. 2 in Mrs. Ingold's former paper (J., 1922, 121, 1610) would indicate that at 20° the value should be of the order of 1.315, which is 2.3% higher than the value found by Partington and Carroll (*Phil. Mag.*, 1925, 49, 665). It is not considered that such agreement is satisfactory.

Mrs. Ingold has discussed in a very general manner the statement that "although the vapour is associated, the association is small" (Partington and Carroll, *ibid.*, p. 680). Since the critical data were not known at the time, the latter authors contented themselves with an approximate calculation, but the statement that this was "unjustified" is not confirmed by an examination of the paper. Some caution is necessary in approximate calculations, but this must not be mistaken for doubt as to the approximate validity of the results found. In reality, as Mrs. Ingold points out, the calculation of the critical constants has been very satisfactorily confirmed by the experiments of Bredig and Teichmann (*Z. Elektrochem.*, 1925, **31**, 449), which appeared later, and these authors have repeated our calculations of c_p/c_v from our own and Mrs. Ingold's experiments and have shown that they are very close to those obtained with the actual experimental data for the critical constants. The regular nature of the curve in Fig. 2 in Mrs. Ingold's first paper would therefore seem to be disturbed in the manner previously pointed out by Partington and Carroll.

It would seem possible to test the assumption of a small association of hydrogen cyanide vapour by a calculation of the density on the assumption that deviations from the gas laws alone, without association, are operative, and then comparing the results with the experimental values. The method used is one which, it is stated (Ingold, this vol., p. 26), 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." The densities have been calculated from the ideal value by division by

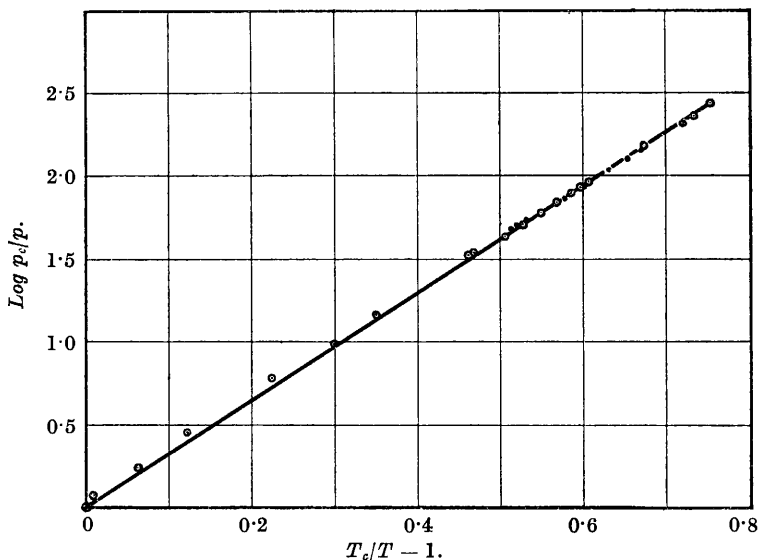
$$\lambda = 1 + \frac{9}{128}\pi\tau(1-6\tau^2)$$

in accordance with Berthelot's equation, which may be expected to apply with some accuracy at atmospheric pressure. In this expression, π and τ have been calculated from the critical data of Bredig and Teichmann ($p_c = 53.2$ atm.; $T_c = 456.6^\circ$). The results in Table I indicate that, below 100° , the calculated densities are distinctly lower than those found by Mrs. Ingold. At 65° , the observed density, which lies on the smooth curve, is 2% higher than that corrected for deviations from the gas laws, although the experimental error is stated to be only 0.2%. (The two observed values at 132° and 175° lie well below the smooth curve.) This seems to indicate that, if the density measurements are as accurate as they are claimed to be, there must be some such small association of hydrogen cyanide vapour as was assumed by Partington and

Carroll, and that the opposite conclusion, arrived at by Mrs. Ingold on very general grounds, and without specific reference to hydrogen cyanide, is improbable.

In a cursory reference to Bredig and Teichmann's paper, Mrs. Ingold has not emphasised the fact that these authors show, by no fewer than five different sets of experimental data, that hydrogen cyanide is associated in the liquid state and that they express agreement with our calculations for the gas.

FIG. 1.



It is also of interest to plot the values of $\log p/p_c$ against those of $(T_c/T - 1)$, in the manner used by van der Waals. Bredig and Teichmann refer to this in their paper, but do not reproduce the

TABLE I.

$t^\circ \text{C.}$	$T^\circ \text{abs.}$	$\tau.$	$\lambda.$	$\Delta \text{ obs.}$ (air=1).	$\Delta \text{ obs.}$ (O=16).	$\Delta \text{ calc.}$
65	338.1	1.3505	0.9822	0.968	14.06	13.77
96	369.1	1.2371	0.9866	0.951	13.79	13.70
97.5	370.6	1.2321	0.9868	0.952	13.80	13.70
132	405.1	1.1271	0.9901	0.936	13.57	13.66
140	413.1	1.1053	0.9907	0.938	13.60	13.65
175	448.1	1.0190	0.9930	0.932	13.51	13.61
177	450.1	1.0145	0.9931	0.934	13.54	13.61

curve. This curve has been constructed from the data of Bredig and Teichmann (*loc. cit.*) and of Perry and Porter (*J. Amer. Chem. Soc.*, 1926, 48, 299), the former being denoted by circles and the latter by dots on the curve. It will be seen from Fig. 1 that practi-

cally all the points lie on a straight line passing through the origin. The gradient of this line is 3.26. According to van der Waals the normal value is 3.0, whilst from the curve for water given by Nernst ("Theoretische Chemie," 8—10 Aufl., p. 248) the value 3.3 is found. It may be remarked that, in reality, the gradient depends somewhat on the molecular weight and that, although it is reasonable to compare water and hydrogen cyanide as associated substances, carbon disulphide, for which the gradient is lower than 3, should probably be chosen as a normal substance for comparison. There would seem to be very little, if any, doubt that hydrogen cyanide is associated in the liquid state.

Summary.

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, and that when the qualitative arguments put forward on general grounds are applied quantitatively to the specific case of hydrogen cyanide they lead to conclusions exactly opposite to those arrived at by Mrs. Ingold. Attention is also drawn to the fact that all the experimental evidence, of various kinds, points to association in the liquid state.

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