

## 116. *The Surface Tension and Density of Nitric Oxide.*

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NITRIC oxide presents one of the few cases where, unless association occurs, it is certain that there is a deviation from one or other of the rules postulating sheaths of eight electrons or bonds consisting of even numbers of shared electrons. It was hoped that a determination of the parachor of this substance would afford material for comparison with chlorine dioxide (compare Cheesman, J., 1930, 35). Although Johnson and Giauque (*J. Amer. Chem. Soc.*, 1929, 51, 3104) considered the liquid to be non-associated, yet the parachor and the Ramsay-Shields function deduced from the present results indicate considerable abnormality.

### EXPERIMENTAL.

The gas was prepared by dropping sodium nitrite solution into acidified ferrous sulphate solution, and was passed over solid caustic soda, condensed in liquid air, and three times fractionated. It was then stored in a bulb immersed in liquid air.

Since nitric oxide is very sensitive to traces of air, taps were replaced by mercury ventils of the type developed by Stock (*Z. Elektrochem.*, 1917, 23, 33). Densities were measured in a small pycnometer, similar to that used in the work on chlorine dioxide Cheesman, *loc. cit.*), measured amounts of nitric oxide being introduced by the method described by Purcell and Cheesman (this vol., p. 826). Corrections were applied for the contraction of the pycnometer at low temperatures and for the amount of material in the gas phase, which, owing to the large vapour pressure of nitric oxide, becomes appreciable even a few degrees above the m. p.

Surface-tension measurements were carried out by means of the two-capillary method of Sugden (J., 1921, 119, 1483) and call for no special comment.

The measurements were conducted in a bath of liquid ethylene contained in an unsilvered Dewar vessel. The bath was cooled by passing liquid air through a copper tube immersed in the liquid, and temperatures were measured with a three-junction copper-constantan thermocouple and millivoltmeter. The m. p. of nitric oxide ( $-163.4^{\circ}$ ) was taken as a fixed point in calibrating the instrument.

The probable error in the density measurements is about 0.2% : the pycnometer, having been made for use with chlorine dioxide, was somewhat small, and in measuring the nitric oxide in the large

bulb of the measuring apparatus a pressure of only 43 mm. was required, which did not allow the full accuracy of the method to be developed. However, the readings were repeated five times and the deviation from the mean was satisfactorily small. The normal density of nitric oxide was taken as 1.3402 g./litre (Gray, J., 1905, 87, 1601).

Between  $-147^{\circ}$  and  $-162.5^{\circ}$ , 11 measurements of density and 17 of surface tension were made, and the following values are interpolated from these.

Temp. ....	$-163.0^{\circ}$	$-159.5^{\circ}$	$-156.0^{\circ}$	$-153.6^{\circ}$
Density (g./c.c.) .....	1.332	1.306	1.277	1.227
$\gamma$ (dynes/cm.) .....	27.79	25.95	24.12	22.11

The only value available for comparison is that of Adwentowski (*Bull. Acad. Krakow*, 1909, 742), *viz.*, 1.269 for the density at the b. p. This is higher than the present value, but a very slight error in temperature would account for the difference.

The very rapid variation of these properties may be compared with the steep gradient of the vapour-pressure curve (Johnson and Giauque, *loc. cit.*). The gradient of the Ramsay-Shields function is greater than the normal for non-associated liquids. This is peculiar, since association manifests itself by a low gradient. Extrapolation to zero gives  $T = -88^{\circ}$ , from which a critical temperature of  $-82^{\circ}$  may be inferred: observed values lie nearer  $-96^{\circ}$ .

The parachor,  $P = M^{1/4}/(D-d)$ , where  $M = 30$ , is not constant, but rises with temperature:

Temp. ....	$-163.0^{\circ}$	$-159.5^{\circ}$	$-156.0^{\circ}$	$-153.6^{\circ}$
$P$ .....	51.75	51.88	52.13	52.84

The parachor calculated from the sum of the atomic constants is 32.5. Near the m. p. the value tends to approach constancy, and the rapid rise may be due to depolymerisation to an unsaturated form, but it is hardly justifiable to speculate on this from parachor data alone.

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