# *Some Physical Properties of Nitryl Fluoride.*

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This paper adds to the rather few data available on the physical properties of nitryl fluoride, its density, surface tension, and viscosity within the range −120° to −65°. An experimental value for the critical temperature, in agreement with that derived from densities and surface tensions, is given. The properties of nitryl chloride, the only other nitryl halide known, are tabulated for comparison.

THE density, freezing point, boiling point, and vapour pressure of liquid nitryl fluoride were determined by Ruff, Menzel, and Neumann (*Z. anorg. Chem.*, 1932, **208**, 293)—previous work was on material of doubtful authenticity—but, as yet, data for the surface tension, viscosity and critical temperature have not been available. Measurements of these, together with a redetermination of the density, are now provided.

The densities of nitryl fluoride in Table 1 are the results of two experiments. They cover a range of temperature from −103·8° to −64·6°, are expressed by the relationship $d_{\mathrm{L}} = 2{\cdot}046 - 0{\cdot}00276T$ g. cm.$^{-3}$, and have a root mean square deviation from the calculated values of ±0·002 g. cm.$^{-3}$. This gives densities which agree well with those derived from the equation of Ruff *et al.* (*idem, loc. cit.*), *viz.*, $d_{\mathrm{L}} = 2{\cdot}143 - 0{\cdot}00323T$ g. cm.$^{-3}$.

TABLE 1.

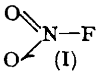
| Temp. (° K) | $d_{\mathrm{L}}$ (g. cm.$^{-3}$) Obs. | Calc. | $\Delta d_{\mathrm{L}}$ | Temp. (° K) | $d_{\mathrm{L}}$ (g. cm.$^{-3}$) Obs. | Calc. | $\Delta d_{\mathrm{L}}$ |
|---|---|---|---|---|---|---|---|
| | | | *Expt.* 1. | | | | |
| 169·2 | 1·577 | 1·579 | −0·002 | 200·2 | 1·493 | 1·493 | 0·000 |
| 183·7 | 1·539 | 1·539 | 0·000 | 203·2 | 1·483 | 1·485 | −0·002 |
| 186·2 | 1·532 | 1·532 | 0·000 | 206·4 | 1·476 | 1·476 | 0·000 |
| 194·2 | 1·511 | 1·510 | +0·001 | 208·4 | 1·472 | 1·471 | +0·001 |
| 198·7 | 1·501 | 1·498 | +0·003 | | | | |
| | | | *Expt.* 2 | | | | |
| 171·7 | 1·574 | 1·572 | +0·002 | 196·9 | 1·503 | 1·503 | 0·000 |
| 173·2 | 1·567 | 1·568 | −0·001 | 200·9 | 1·489 | 1·491 | −0·002 |
| 194·2 | 1·508 | 1·510 | −0·002 | 203·4 | 1·481 | 1·484 | −0·003 |

The coefficient of cubical expansion of the liquid, calculated from the densities for the temperature range, is 0·00118 cm.$^3$ cm.$^{-3}$ deg.$^{-1}$.

Measurements of surface tension at three temperatures by differential capillary rise made in a modified arrangement of Mills and Robinson's closed system (*J.*, 1927, 1823) gave the following results :

| Temp. (°c) | $-114{\cdot}3$ | $-104{\cdot}5$ | $-94{\cdot}3$ |
|---|---|---|---|
| Surface tension (dynes cm.$^{-1}$) | 29·5 | 27·6 | 25·7 |

The parachor of nitryl fluoride calculated from the density and surface tension is 94·3; that expected for structure (I) is 99·8 (Sugden, " The Parachor and Valency," Routledge, London, 1930, p. 181).



(I)

The slope of the Katayama plot of $\gamma/(D - d)^{2/3}$ against $T$, where $\gamma$ is the surface tension (dynes cm.$^{-1}$), $D$ is the density of the liquid, and $d$ that of the vapour (g. cm.$^{-3}$) at the appropriate temperature, indicates a critical temperature ($T_C$) of 76·3°.

In spite of several explosions, a direct observation was obtained of the liquid passing through its critical temperature; this lies between 75° and 76°. The result agrees well with the calculated value and, when used, gives a boiling point : critical temperature ratio, $T_B : T_C$, of 0·57.

The viscosity of nitryl fluoride was measured in a modified Ostwald viscometer (cf. Maass and Boomer, *J. Amer. Chem. Soc.*, 1922, **44**, 1709; Steacie and Johnson, *ibid.*, 1925, **47**, 754) which was calibrated with benzene at 25° at which temperature it has about the same surface tension as the liquid under investigation.

Table 2 sets out the physical properties of the two known nitryl halides.

TABLE 2.

| | Nitryl fluoride | Nitryl chloride |
|---|---|---|
| Melting point | $-166°$ | $-145°$ |
| Boiling point | $-72{\cdot}5°$ | $-15{\cdot}9°$ |
| Density of liquid at 65° above m. p. (g. cm.$^{-3}$) | 1·571 | 1·500 |
| Surface tension at $-104{\cdot}5°$ (dynes cm.$^{-1}$) | 27·6 | — |
| Viscosity (*a*) at 65° above m. p. (P) | 0·00572 | — |
| (*b*) at b. p. (P) | 0·00460 | 0·00616 |
| Critical temperature | 76·3° | — |
| Vapour pressure at 65° above m. p. (mm.) | 113·8 | 16·1 |

## EXPERIMENTAL

All apparatus was of Pyrex glass which, when adequately dried, suffered little attack from nitryl fluoride at the relatively low temperatures used. It was cleaned with chromic acid–nitric acid, followed by copious amounts of water and then alcohol, and dried by repeated change of dry air and heating in a vacuum. Prepared by fluorinating sodium nitrite (Aynsley, Hetherington, and Robinson, *J.*, 1954, 1119), the nitryl fluoride was fractionated several times in a vacuum to rid it especially of volatile impurities and finally put in glass bulbs fitted with " break-seal " joints and stored at a low temperature. It was further fractionated *in vacuo* immediately before use and kept in the measuring apparatus for the shortest possible time.

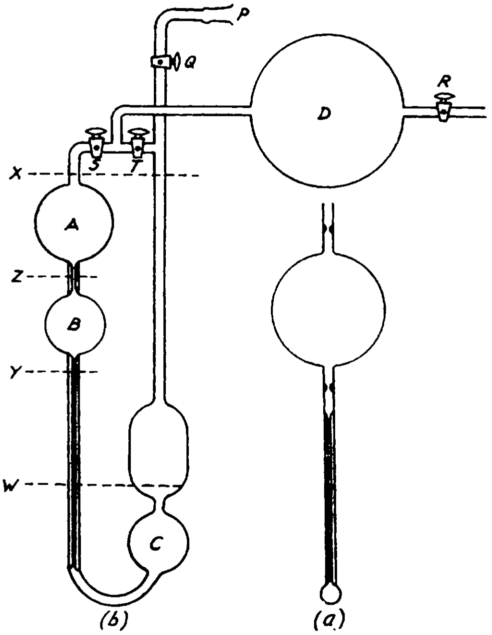
*Liquid Density.*—The apparatus (*a*, see Fig.) consisted of a small bulb with a calibrated capillary stem. To the stem was joined, by a short length of quill-tubing, a bulb of 200 c.c. capacity which, in turn, was attached to a vacuum train carrying tubes for final fractionation and the break-seal tube of nitryl fluoride. This arrangement enabled the internal surfaces to be thoroughly dried, the liquid to be further fractionated, and an adjusted volume of the purified compound to be transferred to the apparatus and sealed off therein under vacuum. Thus charged, the apparatus was immediately weighed, the capacity of the larger bulb preventing the fluoride from developing a dangerous pressure. Without loss of time, the liquid was completely collected into the small bulb and stem, and frozen there until the larger bulb had been sealed off.

While still cold, the density bulb was supported vertically in a bath of *n*-pentane already cooled to the working temperature with liquid nitrogen in a 1·5 l. clear Dewar vessel, well lagged except for an observation slit, furnished with a magnetic stirrer and a calibrated copper–Constantan thermocouple. The height of the meniscus at a series of temperatures was observed with a cathetometer. Volumes are considered accurate to $\pm 1 \times 10^{-4}$ c.c. and temperatures to $\pm 0{\cdot}2°$. The weighing of the nitryl fluoride was at once completed by freezing the liquid, breaking open the stem, removing the contents, and weighing the pieces along with the large bulb.

*Surface Tension.*—The apparatus, a slightly modified version of Mills and Robinson's (*loc.*

*cit.*), held two capillary tubes carefully selected for uniformity of bore. The mean radius of each was ascertained by accurately measuring the length of a mercury thread in overlapping positions. After scrupulous cleaning and rigorous drying on a vacuum train carrying traps and a break-seal vessel of nitryl fluoride, the latter was opened, and some liquid quickly fractionated into a trap and there frozen. In order to minimise the time of contact with the capillary tubes, the liquid was not distilled, but quickly poured into the well-cooled apparatus where it immediately froze. With all speed, the apparatus was detached and mounted in the *n*-pentane bath at near the working temperature. Here the nitryl fluoride melted and, as soon as it reached bath temperature, was caused to flow up the tubes by tilting the apparatus. The difference in the heights of the fallen menisci was measured with a cathetometer and the operations of wetting and measuring were repeated at two other temperatures. An accuracy of ±0·2 dyne cm.$^{-1}$ is claimed.

*Critical Temperature.*—The procedure and precautions described above being followed, nitryl fluoride was condensed into a heavy-walled (3 mm.) Pyrex tube, 5 cm. long and with specially thickened draw-offs (cf. Parker and Robinson, *J.*, 1927, 2977). When about one-third full, the liquid was frozen and the tube was drawn off to leave a heavy seal. The critical-temperature tube was kept in a well-stirred water-bath which was slowly heated until the meniscus disappeared, and then cooled until it reappeared again. There was some decomposition and some attack on the tubes, several of which exploded at, or near, the critical temperature. An accuracy of ±0·5° is claimed.



*Viscosity.*—The modified Ostwald viscometer (*b*, see Fig.) had a bulb *C* of about the same size as the measuring bulb *B*, to simplify the process of charging with the correct volume of nitryl fluoride. The taps, lubricated with a fluorocarbon grease immune to the fluoride, and the 100 c.c. bulb *D*, enabled the apparatus to be filled and the liquid manipulated. The procedure was to attach, by the socket *P*, the clean dry viscometer to the train delivering nitryl fluoride and, after further drying with *S* and *T* open, to condense liquid in a vacuum until it reached *W*. After *Q* had been closed, the apparatus was detached from the train, the liquid was frozen, and dry air admitted, *via R*, to a pressure of one atmosphere. The viscometer was submerged to level *X* in the *n*-pentane bath; and, as soon as it melted, the fluoride was rapidly raised above level *Z* by an appropriate heating and cooling of *D* and turning of taps *S* and *T*. Then *S* and *T* were opened to equalise the pressure, and the fall of the liquid between *Z* and *Y* was timed. The measurement was repeated at several temperatures, after which the nitryl fluoride was distilled, and finally swept by a current of nitrogen out of *P* to be absorbed, either in saturated potassium hydroxide solution (Expt. 1) or concentrated sulphuric acid (Expt. 2). In this way its weight was ascertained.

The viscometer had been previously calibrated with benzene at 25°, whence the time of fall of any particular weight, or volume, could be found. The volume of the nitryl fluoride was deduced from the density at the temperature of operation. The viscosity was calculated from the expression $\eta = \eta' dt/(d't')$, where $\eta$, $d$, and $t$ are absolute viscosity, density, and time of fall, respectively, of nitryl fluoride, and $\eta'$, $d'$, and $t'$, the corresponding quantities for benzene at 25°. No attempt was made to correct for the vapour of nitryl fluoride because, at the temperatures used and under one atmosphere pressure of air, the amount is believed to be negligible. The results in Table 3 show a root mean square deviation from the calculated values of ±0·06 mP.

TABLE 3.

| | $\eta$(mP) | | | | | $\eta$(mP) | | | |
|---|---|---|---|---|---|---|---|---|---|
| Temp. | Obs. | Calc. | $\Delta\eta$ | 100 $(\Delta\eta)^2$ | Temp. | Obs. | Calc. | $\Delta\eta$ | 100$(\Delta\eta)^2$ |
| | | | | *Expt.* 1. | | | | | |
| −113·6° | 6·79 | 6·64 | +0·15 | 2·2 | −98·2° | 5·55 | 5·57 | −0·02 | 0·0 |
| −112·0 | 6·58 | 6·50 | +0·08 | 0·6 | −94·5 | 5·39 | 5·38 | +0·01 | 0·0 |
| −111·5 | 6·53 | 6·46 | +0·07 | 0·5 | −90·8 | 5·21 | 5·21 | 0·00 | 0·0 |
| −104·5 | 5·91 | 5·94 | −0·03 | 0·1 | −87·5 | 5·01 | 5·08 | −0·07 | 0·5 |
| −102·4 | 5·75 | 5·81 | −0·06 | 0·4 | | | | | |
| | | | | *Expt.* 2. | | | | | |
| −118·5 | 7·07 | 7·12 | −0·05 | 0·2 | −96·2 | 5·47 | 5·46 | +0·01 | 0·0 |
| −116·0 | 6·87 | 6·86 | +0·01 | 0·0 | −94·0 | 5·42 | 5·35 | +0·07 | 0·5 |
| −113·2 | 6·59 | 6·60 | −0·01 | 0·0 | −88·3 | 5·16 | 5·11 | +0·05 | 0·2 |
| −107·0 | 6·21 | 6·11 | +0·10 | 1·0 | −84·2 | 5·02 | 4·95 | +0·07 | 0·5 |
| −102·5 | 5·89 | 5·81 | +0·08 | 0·6 | | | | | |

By solving the equation of the absolute viscosity–temperature curve, $\eta_t = \eta_0/(1 + At + Bt^2)$ using values from the smoothed curve, it was found that $A = -0{\cdot}000759$, $B = -0{\cdot}0000384$ and $\eta_0 = 0{\cdot}00392$. This gave an absolute viscosity at the boiling point of nitryl fluoride (−72·5°) of 0·00460 P.

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