934. *Dinitrogen Trioxide. Part III.* The Vapour Pressure of Mixtures of Nitrogen Dioxide and Nitric Oxide.*

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The vapour pressure of mixtures of nitrogen dioxide and nitric oxide has been measured at various temperatures. Our results can be expressed by $\log_{10}$ (pressure in mm.) $= 8{\cdot}95 - f(x)/T$, where $f(x)$ is a function dependent only on the composition of the mixture. The apparent boiling point of dinitrogen trioxide is at least 40° below the accepted value. Low-temperature vapour-pressure data indicate that Giauque and Kemp's equation for nitrogen dioxide can be extrapolated to about $-50°$.

THE only recent work on the vapour pressure of mixtures of nitric oxide and nitrogen dioxide at pressures below one atmosphere is that of Whittaker and his co-workers.[1] Unfortunately, their results do not extend beyond the region near nitrogen dioxide, where they are in reasonable agreement with those of Baume and Robert.[2] The data of Baume and Robert [2] and of Purcell and Cheesman [3] cover the whole range of composition from nitrogen dioxide to dinitrogen trioxide. However, Baume and Robert's results [2] do not extend below $-20°$, and in this region agreement with Purcell and Cheesman's results [3]

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* Part II, Beattie, Bell, and Vosper, preceding paper.

[1] Whittaker, Sprague, Skolnik, and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 4794.

[2] Baume and Robert, *Compt. rend.*, 1919, **169**, 968.

[3] Purcell and Cheesman, *J.*, 1932, 826.

is poor. Further, in the latter paper only " smoothed " results are given, which lie very erratically on a graph of $\log_{10}$ (pressure) against the reciprocal of the absolute temperature. Results at higher pressures and temperatures are primarily of technical importance.[4,5]

We have measured the vapour pressures of mixtures of nitrogen dioxide and nitric oxide at various temperatures, covering the range from pure nitrogen dioxide to a composition close to that of dinitrogen trioxide. As nitrogen dioxide and nitric oxide have considerably different physical properties and are volatile, for a given total composition the composition of the liquid (and of the gas in equilibrium with it) changes with temperature. Therefore the experimental results take the form of a vapour pressure, a temperature, and a composition. (The composition of the liquid was known, as the weights of nitric oxide and nitrogen dioxide in the gas phase were determined.) The three variables need not be simply related. We found that plotting $\log_{10}$ (pressure) against the reciprocal of the absolute temperature for a given total composition gave approximately linear relationships. The slopes of these lines were then used to correct the individual pressure readings to a given temperature. The interpolation on a single point was always less than 5°. The composition of the liquid was also corrected to the same temperature. In this way we were able to plot a graph of composition against vapour pressure at several temperatures (Fig. 1). The scatter of our points on the graph reflects the experimental errors in view of the method of correction used. From this Figure it is possible to read off the values of the pressure at any given composition, for various temperatures. Hence graphs of $\log_{10}$ (pressure) against the reciprocal of the absolute temperature could be drawn for these compositions. These graphs were again linear within our experimental error. The values of m and C in the expression

$$\log_{10} p_{\text{mm}} = -m/T + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

are given in Table 1, inspection of which shows that, the last two figures in the column headed C being excluded, there is no obvious trend in C values with composition. However, there is a clear trend in the values of m, which decreases with increasing nitric oxide content. Further, a plot of m against x (composition in terms of NO_x as the formula for the liquid) shows that values of C which deviate markedly from the mean value have anomalous m values. A low C value corresponds to a low m value. Inspection of the results of Whittaker *et al.*[1] arranged in a similar manner (Table 2) shows a corresponding random scatter of C values about the mean value of 9·026, but with a clear trend in m values. Again, the only m value falling out of a fairly regular sequence has a high C value (9·116). The results of earlier investigations [2,3] also indicate a decrease in the slope m with increasing concentration of nitric oxide. It appeared possible that all these results could be expressed satisfactorily by using a single value for C, resulting in the general equation

TABLE 1.

C	8·808	8·722	8·642	8·562	8·869	8·971	8·985	8·960	8·957
m	1742	1716	1691	1666	1732	1730	1723	1707	1687
x	1·991	1·985	1·982	1·974	1·936	1·876	1·846	1·816	1·785
C	8·885	8·693	8·831	8·965	8·916	8·708	8·348	7·694	
m	1651	1552	1581	1555	1523	1445	1349	1173	
x	1·747	1·656	1·644	1·560	1·545	1·525	1·517	1·502	

TABLE 2.

C	9·012	8·970	9·011	9·116	8·985	9·035
m	1782	1751	1745	1760	1704	1702
x	1·956	1·917	1·878	1·846	1·799	1·763

$$\log_{10} p_{\text{mm.}} = A - \mathrm{f}(x)/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[4] Epstein and Cirkova, *Zhur. priklad. Khim.*, 1939, **12**, 14.

[5] Selleck, Reamer, and Sage, *Ind. Eng. Chem.*, 1953, **45**, 814.

where f(x) represents a function dependent only on composition of the mixture and A is a constant. We obtained a reasonable representation of our experimental results by using the equation

$$\log_{10} p_{\text{mm.}} = 8{\cdot}95 - \mathrm{f}(x)/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

with f(x) defined by the points of Fig. 2. Using this relation we were able to draw the curves shown in Fig. 1. These curves fit our experimental data to within the experimental accuracy and agree quite well with the results of the other workers, excluding those of Purcell and Cheesman.[3]

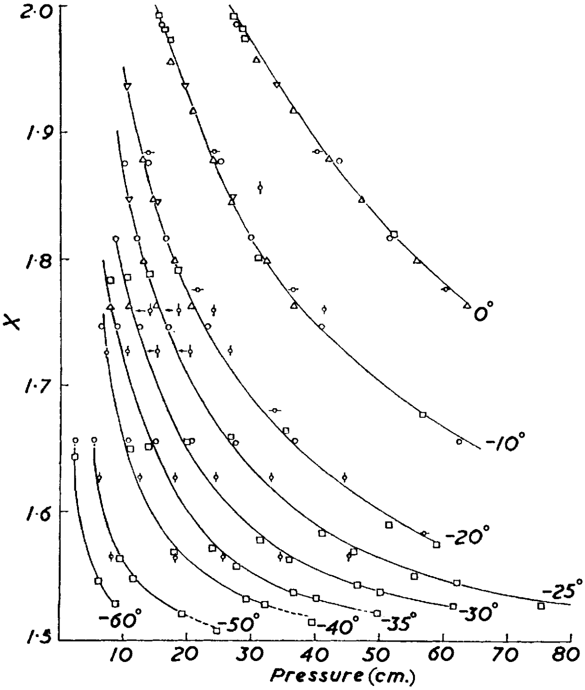


FIG. 1. *The vapour pressure of liquid mixtures of nitric oxide and nitrogen dioxide at various temperatures.*

△ Whittaker *et al.*;[1] ▽, ○, and □, this work runs 1, 2, and 3; ⦶ Purcell and Cheesman;[3] -○- Baume and Robert;[2] —— equation (3).

FIG. 2. f(x) *in eqn.* (3) *as a function of x* (*the composition of the liquid in terms of the formula* NO_x).

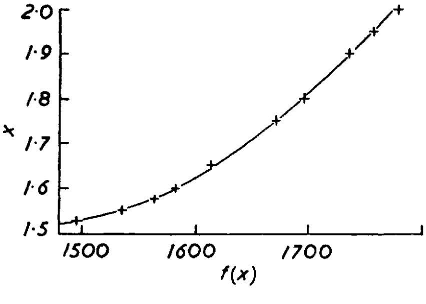
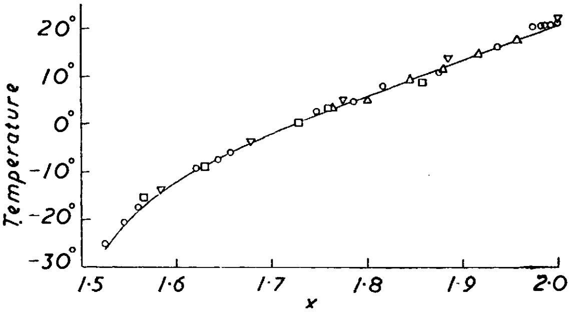


FIG. 3. *The boiling point–composition curve for mixtures of nitrogen dioxide and nitric oxide.*



○ This work; △ Whittaker *et al.*;[1] □ Purcell and Cheesman;[3] ▽ Baume and Robert;[2] —— equation (3).

By use of equation (3), and putting $p = 760$ mm., it is possible to obtain a boiling point–composition curve (Fig. 3). Our experimental points were obtained by graphical interpretation using the figures given in Table 1. The agreement between the two methods appears to be satisfactory. It is clear from Fig. 3 that extrapolation to $x = 1{\cdot}5$ (the composition corresponding to dinitrogen trioxide) is not justified. Similarly, Fig. 2 shows that f(x) cannot be obtained at $x = 1{\cdot}5$ by simple extrapolation. N.B.S. Circular 500 [6] gives the boiling point of dinitrogen trioxide (the temperature at which the vapour pressure of a mixture of this composition reaches 760 mm.) as +2°. Baume and Robert [2] by an extrapolation obtained the value −27°. Purcell and Cheesman,[3] who consider an extrapolation to be unjustified, state " a mixture containing only a trace of nitric oxide in excess of composition N_2O_3 never exerts a pressure below 2 atm. till all the trioxide is frozen solid, and liquid nitric oxide begins to separate." It appears that the apparent boiling point of dinitrogen trioxide is below −40°, and in this composition region the pressure will be very sensitive to slight changes in composition.

It is not possible to give a theoretical discussion of this system at present, although a few deductions may be made from these observations. The species which may be present in the gas and the liquid are NO, N_2O_2, N_2O_3, NO_2, and N_2O_4, plus other unknown species. Preliminary magnetic measurements [7] suggest that dinitrogen trioxide in the liquid state is diamagnetic in the range −10° to −95°. This is in agreement with Soné, who found [8] dinitrogen trioxide to be diamagnetic. This suggests that dissociation is not extensive, unless the nitric oxide is dimeric. Pure liquid nitric oxide [9] is 2·7% dissociated (into the monomer) at −163°, and 5% dissociated at −153°. This may indicate that it would be largely dissociated in solution at temperatures above −95°. If this reasoning is correct, a liquid mixture of nitrogen dioxide and nitric oxide may consist largely of dinitrogen trioxide and dinitrogen tetroxide. If we assume that nitric oxide has a low *physical* solubility in such mixtures, the abrupt change of vapour pressure with composition in the region of the dinitrogen trioxide composition is to be expected. The linear relationship between $\log_{10}$ (pressure) and the reciprocal of the absolute temperature is probably fortuitous and without theoretical significance. However, the decrease in the slope of such plots as the nitric oxide content of the solution increases may be due to solution near the dinitrogen trioxide composition being physical in nature, while in the nitrogen dioxide-rich regions it will be predominantly a chemical reaction plus a physical sorption.

Our experimental data on the vapour pressure of pure nitrogen dioxide indicate that Giauque and Kemp's equation [10] can be extrapolated to about −50°, in agreement with Dixon's work.[11]

EXPERIMENTAL

The preparation of the reactants [12] and the method of mixing [13] have already been described. Vapour pressures were measured by using a glass spiral gauge as a null-point instrument, mercury manometers (1·6 cm. internal diameter, precision-bore tubing), and a Precision Tool and Instrument Co. Ltd. cathetometer which had been previously calibrated against a standard bar. All results are expressed in mm. of mercury at 0°.

Run 3 was carried out in an all-glass apparatus, no taps or joints being used. In Runs 1 and 2 greaseless taps with fluorocarbon diaphragms were used.

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[6] Rossini, Wagman, Evans, Levine, and Jaffe, Nat. Bur. Stand., Circular 500, 1952.
[7] Beattie and Mabbs, unpublished work.
[8] Soné, *Sci. Reports Res. Inst., Tôhoku Univ.*, 1922, **11**, 139.
[9] Smith and Johnston, *J. Amer. Chem. Soc.*, 1952, **74**, 4696.
[10] Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.
[11] Dixon, *J. Chem. Phys.*, 1940, **8**, 157.
[12] Beattie and Bell, *J.*, 1957, 1681.
[13] Beattie, Bell, and Vosper, preceding paper.