106. *The System Nitric Oxide–Nitrogen Peroxide. Part I.*

By Ronald Herbert Purcell and Geoffrey Herbert Cheesman.

The compound commonly termed nitrogen trioxide or nitrous anhydride was first reported in 1816 (Dulong, *Ann. Chim. Phys.*, **3**, 240); many experimenters have described its properties, but the divergencies between their reports are very large. Early work showed that the trioxide can be formed from and decomposes into nitric oxide and peroxide. Unfortunately, it was not fully realised that, as a result of this dissociation, the material is exceedingly susceptible to any exposure to air or oxygen, and consequently many of the published observations refer to material with a much greater oxygen content than was imagined.

A very complete bibliography will be found in Mellor's "Comprehensive Treatise," Vol. VIII, p. 454, and as many of the earlier papers are of little importance it is unnecessary to review them in detail. Attention is, however, drawn to the work of Baume and Robert (*Compt. rend.*, 1919, **169**, 968), who studied the vapour pressures of these mixtures. We were unable to repeat their success in employing ordinary stopcocks for manipulating the materials, and the measurements have been made in an apparatus in which taps and ground joints are completely eliminated. Nitric oxide does not affect hydrocarbons or mercury in the absence of oxygen, but if traces of air gain admittance, tap grease is rapidly attacked.

The present investigation has been along the lines of the phase rule, and this paper embodies the data which have been obtained for the gas–liquid and gas–solid equilibria of the system at pressures of 1 to 100 cm. of mercury. Over the range of correspondence they admirably confirm Baume and Robert's figures, but we differ from the conclusions they draw by extrapolation of their curves.

EXPERIMENTAL.

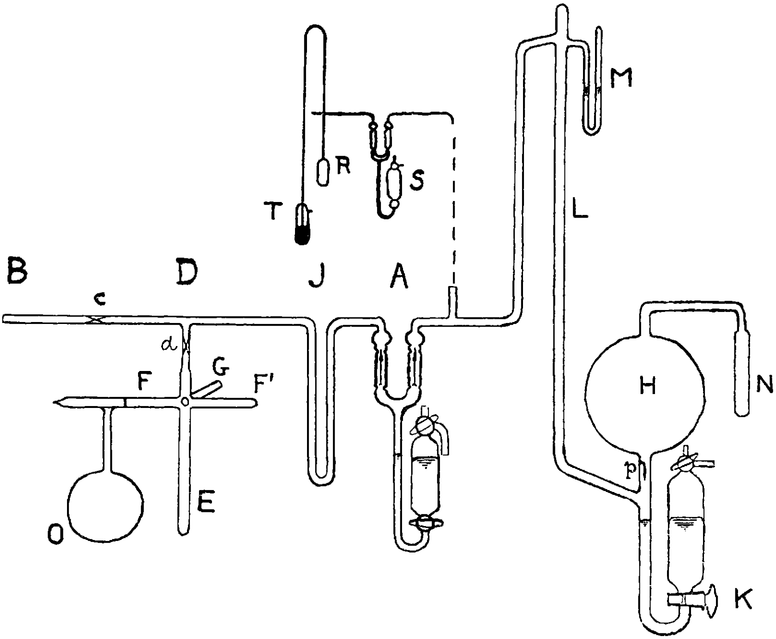
Nitric oxide was prepared by dropping sodium nitrite solution into a concentrated solution of ferrous sulphate containing considerable hydrochloric acid. No rubber joints were used in the apparatus. The gas was evolved in a regular stream, and passed through sulphuric acid and then up a column filled with pellets of caustic soda. It was then condensed in a bulb immersed in liquid air. A tap served to isolate this bulb from the generator, and when sufficient material was collected, the tap was closed and the bulb evacuated with a Hyvac oil pump. The lead containing the tap, and finally the pump lead, were sealed off.

The condensed nitric oxide was fractionated three times, the final product being distilled into a bulb shown diagrammatically at *R* in Fig. 1. This storage bulb was fitted with a mercury ventil *S* for removal of material, and a rough manometer *T* which acted as a safety device should the pressure rise unduly.

The nitric oxide was a pale indigo-blue liquid which froze to a solid, clear and colourless like ice in thin layers, but dirty bluishwhite in bulk owing to the formation of many small cracks through the mass. About 10 c.c. of liquid were usually made at one run, and preserved by keeping a 2-litre Dewar vessel of liquid air round the bulb *R*.

Oxygen was prepared by heating pure potassium permanganate in an evacuated apparatus, passing it through a condensing tube immersed in liquid air to remove traces of carbon dioxide and water, and into a series of bulbs of determined volumes. When sufficient oxygen had been evolved, as indicated by a mercury manometer, the permanganate was allowed to cool, and the bulbs sealed off one by one, the temperature and pressure being read at the removal of each bulb. The volumes of these bulbs, including the stem as far as the sealing capillary and the septum through which they were emptied, were determined by weighing them empty and filled with water; the effect on the volume of sealing off at the capillary amounts only to a few hundredths of a c.c. and is negligible.

Fig. 1.



Mixtures of nitric oxide and oxygen were prepared in the apparatus shown in Fig. 1, which was permanently connected to the storage bulb by the ventil *S*. The ventil *A* served to isolate the measuring apparatus, which was kept evacuated, and the lead *B* was taken to the mercury-vapour pump with provision for sealing at *C*. The branch *D* led through a capillary to the condensing tube *E*; an appropriate bulb of oxygen *O* was sealed on at *F*, with a piece of glass rod for breaking the septum accommodated in *F′*. An additional branch *G* was provided with a septum for the subsequent transfer of the material to the apparatus in which it was studied.

The apparatus was baked out under *X*-ray vacuum, and finally sealed at *C*. The ventil *A* was then closed, and *S* opened; the liquid air was removed from around the storage bulb *R*, and nitric oxide allowed to evaporate and pass into the bulb *H* till sufficient pressure was indicated on the manometer *T*. Adjustment of the cooling on the storage bulb enabled the pressure to be held steady while mercury was admitted through tap *K* to cut off communication between *H* and the vertical tube *L*. The nitric oxide was then frozen in *R*, more mercury being let in through *K* to keep *H* isolated.

The difference between the levels of mercury in *L* and in the tube below *H* served to measure the pressure in *H*. At the temperature of liquid air, nitric oxide has a vapour pressure of several mm., but by providing a means for evaporating the liquid air round *R* under a Hyvac pump, this residual pressure could be made very small. The progress of this could be followed on the small manometer *M*. (This procedure was instituted in early experiments before ventil *A* was put in. In later experiments, the pumps were cut off at *A* before the nitric oxide was passed into *H*, and reconnected after the bulk of the surplus had been frozen back in *R*; *C* was then sealed.) When *M* indicated that the line was completely evacuated, the volume of gas in *H* was adjusted by admitting or withdrawing mercury through *K* till the meniscus just touched a glass point *p* fixed axially in the tube, and the difference between this level and that in *L* was measured with a cathetometer. The temperature of *H* was read at the same time. The volume enclosed in this manner was 1169·0 c.c.

In order to transfer the sample to *E*, ventil *A* was opened, and liquid air applied at *N*; mercury was then withdrawn through *K* to re-establish connexion between *H* and *L*. The nitric oxide was then distilled into *E*, a bath of alcohol at – 100° round *J* arresting any mercury vapour. The condensation was completed by applying a pump to the liquid air on *E*, manometer *M* again indicating the course of the operation; *A* was then closed and capillary *d* sealed. The rod in *F′* was then shaken through the septum to admit the oxygen to the nitric oxide, and the two were allowed to react.

This method of preparing mixtures of known composition has been described in some detail, as it formed the essential feature, not only of the present series of measurements, but also in other physical measurements on such mixtures, the results of which will be communicated later.

For the measurements of vapour pressures in equilibrium with liquids of known composition, the samples were transferred to glass-spring manometers of the type described by Smits (J., 1924, **125**, 2555). The gaseous contents of the apparatus after being mixed were apparently largely dissociated; when they were condensed into the bulb attached to the manometer (whose capacity was made as small as possible) and re-evaporated, excessive pressures were initially set up by volatilisation of nitric oxide before the remainder had melted : when the blue solid did melt, the surplus

Fig. 2*a*.

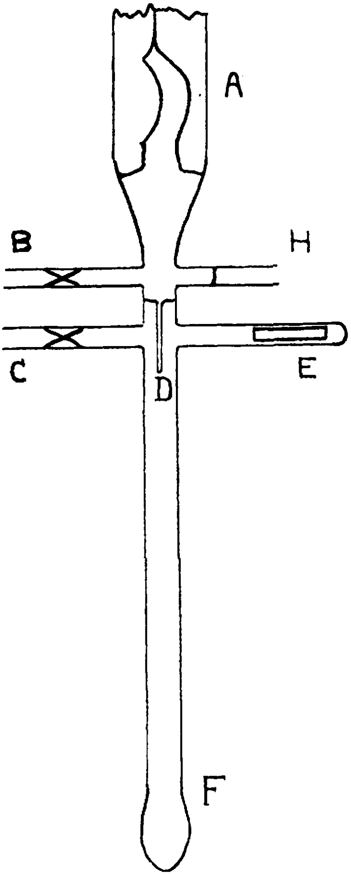
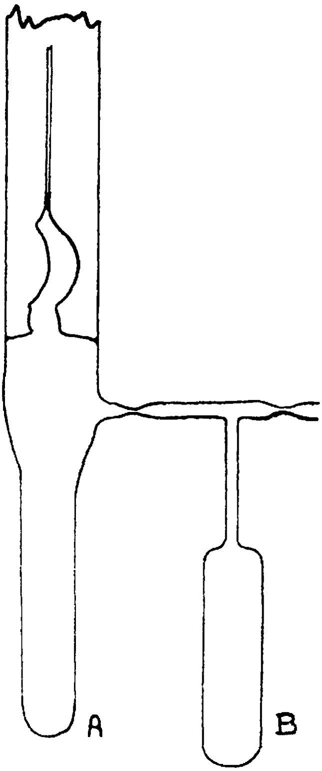


Fig. 2*b*.



nitric oxide dissolved and the pressure fell again. These fluctuations proved to be very violent, and many springs were broken in this manner. Hence, particularly with mixtures containing higher proportions of nitric oxide, it was found necessary to bring the material into a small volume before connexion was made to the manometer, and a special form of apparatus shown in Fig. 2*a* was employed.

The actual spring, *A*, was of the usual form, the only feature being that it was made rather small to reduce the volume of the apparatus. The tube *C* was connected to the septum of the bulb of nitric oxide–peroxide mixture (*G* of Fig. 1) and to the pumps, and the whole evacuated and sealed off. The septum was broken, and the material condensed into *F* and sealed at *C*. The whole was then allowed to come to equilibrium at room temperature, while the top section was evacuated through *B*; *F* was now chilled again, and capillary *D* knocked off with a piece of rod in *E*. When *F* became warmer, the pressure fluctuations were not too severe to follow on the manometer. Septum *H* was provided for removing the sample after the completion of the measurements.

The measurements of vapour pressure were carried out in an alcohol–ether bath contained in a large Dewar vessel of about $2\frac{1}{2}$ litres capacity. For the measurements below $-100°$, a smaller bath of liquid ethylene was used, which was cooled by passing liquid air through a copper tube immersed in the liquid. Temperatures were measured on a millivoltmeter, a copper-constantan thermocouple with three pairs of junctions being used. The constant-temperature junctions were kept in ice; the instrument was calibrated throughout the working range against known fixed points. Pressures below 80 cm. were measured on a closed U-manometer with one evacuated limb, which was fitted on a glass mirror scale; higher pressures up to 2 atmos. were measured with the cathetometer on an open U-manometer. For still higher pressures, a long, open manometer was erected against a paper scale pasted on the wall. This scale was calibrated with a metre rule previously verified against the cathetometer.

In these vapour-pressure measurements, the volume of the gas phase was in each case about 20 c.c., and the composition of the liquid phase, with samples of 1—2 g. employed, would be sensibly the same as the gross composition of the sample. At relatively high pressures, however, a correction may be applied, as has been done for series V (see Table II). This is inappreciable below 1 atm.

The measurements relating to the gas–liquid and gas–solid equilibria with known gas phases were carried out by enclosing gaseous nitric oxide–peroxide mixtures of known composition at a convenient pressure in a bulb fitted with a spring manometer and determining the P–T curve. As long as the contents were entirely gaseous, the pressure fell slowly in accordance with the ordinary thermal contraction, but as soon as liquid or solid separated, the pressure fell more rapidly. The P–T curve obtained thus consisted of two branches; at their intersection the P and T values represent the conditions at which liquid (or solid) just comes into equilibrium with gas of the composition introduced into the spring.

Five springs of the form shown in Fig. 2*b* were joined to a common line, four having extra bulbs B attached as shown. The line was connected to the pumps and through a 1400 c.c. bulb to a bulb of nitric oxide–peroxide mixture prepared in the usual way. The springs and bulbs were baked under high vacuum and sealed from the pump. The septum was then broken with a piece of iron enclosed in a glass tube, operated by a solenoid; the gas streamed into the springs, the large 1400-c.c. bulb preventing too violent a surge which would endanger the springs, and also enabling larger samples to be expanded. In preparing the mixture, the volumes were so chosen that all the material was gaseous in the bulb before expanding, and the total pressure after expansion was about 5 cm.

The pressure in the mantles was adjusted to 2·5 cm. before the septum was broken, so there was an excess pressure of the same amount inside the springs after the expansion. This is a safe overload for this type of gauge. Time was allowed for pressure to become equalised throughout the apparatus, and then each spring was sealed off with its auxiliary bulb. Finally, the contents of each bulb and spring were frozen out in the lower portion of the latter (A in Fig. 2*b*), the process being completed with liquid air which had been cooled by evaporation under the pump; the auxiliary bulb was then sealed off. Thus, on being warmed, each of the five springs contained a portion of the known gaseous mixture at a different pressure. A series of P–T observations was conducted with each of these springs, the same bath, thermocouple, and manometers being used as for the vapour-pressure observations.

The data for the P–T discontinuities of these sets of springs are given in Table I. It is seen that each set gives a series of five

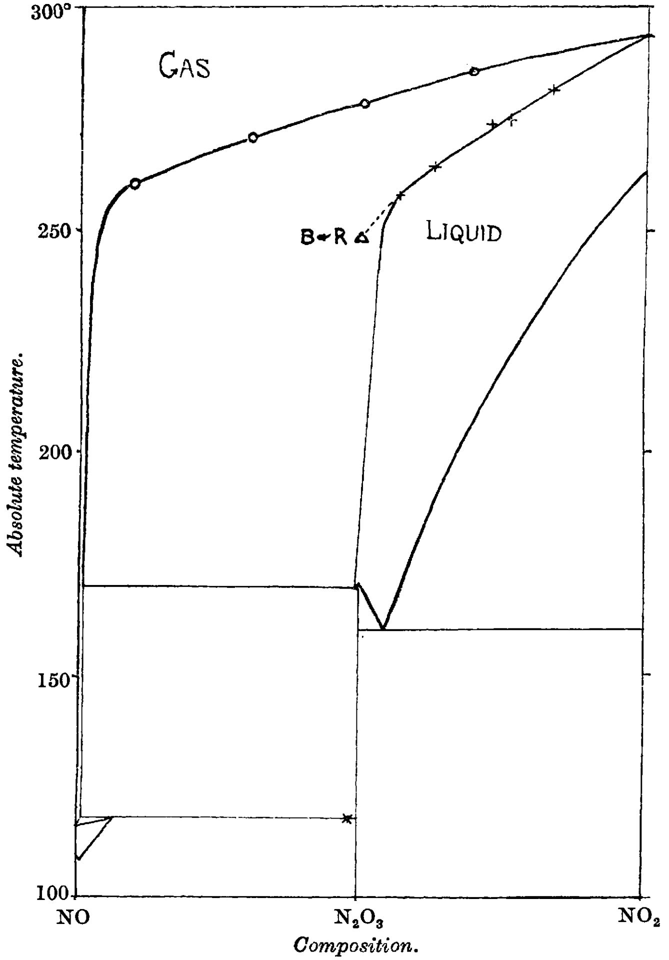
TABLE I.

	Series I.		Series II.		Series III.		Series IV.	
Spring	NO_2, 50·2%.		NO_2, 30·2%.		NO_2, 69·8%.		NO_2, 8·9%.	
No.	P.	T.	P.	T.	P.	T.	P.	T.
1	67·5	3·5°	79·4	− 1·2°	41·25	1·0°	162·2	− 1·5°
2	43·1	− 4·4	51·0	− 9·7	26·6	− 7·5	105·5	−12·5
3	22·5	−17·0	27·8	−19·3	15·9	−16·4	60·0	−16·5
4	11·2	−28·5	14·6	−30·3	7·2	−27·0	24·9	−32·4
5	4·96	−40·1	6·3	−42·5	2·95	−37·5	7·15	−47·5

points for a given gas composition, and the data for the P–X and T–X diagrams of the system are interpolated from these data. The peroxide content is expressed as mols. %, and P is given in cm. of mercury in this and the succeeding table.

FIG. 3.

The system NO–NO_2: *temperature–composition section for* $p = 76$ *cm.*



In Table II are given the smoothed values of the vapour pressures of liquids of known composition. In series V the composition of the liquid phase corrected for the nitric oxide in the gas phase is given in column *b*. The values are not extrapolated beyond the regions observed.

TABLE II.

	Series I.	Series II.	Series III.	Series IV.	Series V.		Series VI.
Temp., Abs.	NO_2, 72·8%.	NO_2, 85·6%.	NO_2, 76·0%.	NO_2, 56·6%.	*a.*	*b.*	NO_2, 62·8%.
280°		69·9					
270	65·0	40·2	59·9	129·1	352	51·6	98·0
260	38·9	27·8	35·2	83·5	294	50·9	63·0
250	22·6	14·2	20·7	51·1	252	50·5	36·6
240	12·1	9·5	11·9	29·2	218	50·2	20·7
230	5·7	5·8	6·0	14·4	194	49·9	10·5
220	3·5			6·2	181	49·9	4·6
210				2·3	175	49·9	2·1
200					170	49·9	

The data of Table II lie satisfactorily on the curve through Baume and Robert's points; but in the light of series V their extrapolation to composition N_2O_3 (shown dotted, Fig. 3) is not justifiable, since 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. The curve must therefore fall off very sharply as shown by the full curve. Measurements in this region involve pressures higher than are desirable in plain blown glass apparatus, and the technique has been considerably varied for this portion of the investigation which forms the subject of a later paper.

The fact that the gas phase contains only a very small proportion of nitrogen peroxide renders any boiling-point determination by dynamic methods entirely useless on account of the rapid change of composition undergone by the liquid. Similarly, any attempt to purify a liquid of composition near to N_2O_3 by fractionation will in effect separate it into the two components.

The authors wish to express their thanks to Professor H. B. Baker, F.R.S., in whose laboratory this work was carried out, for his kindly interest. They also desire to thank the Government Grants Committee of the Royal Society for providing funds for the purchase of a pump. One of them (G. H. C.) expresses his gratitude to the Trustees of the Beit Fellowships for Scientific Research for a Fellowship during the tenure of which the above work has been carried out.

ROYAL COLLEGE OF SCIENCE,
SOUTH KENSINGTON.

[*Received, January* 13*th*, 1932.]