

541.115:546.172.5 533.22

## THERMOCHEMICAL PROPERTIES OF NITROUS OXIDE

BY T. CARLTON-SUTTON, M.A., M.Sc., F.INST.P.,  
H. R. AMBLER, PH.D., F.I.C., AND G. WYN WILLIAMS

*Communicated by Dr Ezer Griffiths, F.R.S., July 7, 1935. Read October 18, 1935*

**ABSTRACT.** Part I: With a view to determining the heat of formation of nitrous oxide by means of a direct decomposition into its elements, the conditions of initiation and of pressure under which this action will propagate itself progressively and explosively through the gas has been examined. Part II: The heat of formation of nitrous oxide has been directly measured, use being made of this explosive thermal decomposition. The figure obtained is  $19.52 \pm 0.1$  Cal./mol. at constant pressure. Part III: A simple method is given for comparing the values for two gases of the product pressure  $\times$  volume, and is applied to the measurement of this product at pressures between 10 and 45 atmospheres in the cases of nitrous oxide and of carbon dioxide.

---

### PART I: THE DECOMPOSITION OF NITROUS OXIDE

BY H. R. AMBLER AND T. CARLTON-SUTTON

IT has long been known that nitrous oxide can be decomposed by heat, and that a burning body will decompose it progressively if the combustion is sufficiently hot. Berthelot<sup>(1)</sup> effected the decomposition of nitrous oxide by compressing it very suddenly to 1/500 of its original volume. A less drastically applied compression, however, had little effect, although it was sufficient to initiate the explosion of a mixture of hydrogen and oxygen<sup>(2)</sup>. Maquenne<sup>(3)</sup> stated that when 0.1 g. of mercury fulminate was detonated in one atmosphere of nitrous oxide, the gas was decomposed with sufficient violence to shatter the vessel in which it was contained. Houseman<sup>(4)</sup> stated that "when under pressure (e.g. in the saturated state) decomposition may be propagated throughout the entire mass of N<sub>2</sub>O with explosive violence; if the compressed gas has a temperature above the critical value (38.8° C.) this method of ignition", i.e. ignition by means of heated iron or platinum wire, "seldom fails to cause explosion"; exact figures and experimental details were lacking however.

Our experience with this gas was not in accord however with the above statements, and a further investigation was undertaken. This has shown that decomposition is not propagated at pressures below 13 atmospheres but can be propagated at pressures above 13 atmospheres.

When small quantities of lead azide were detonated in atmospheres of nitrous oxide at various pressures, it was found that the proportion of nitrous oxide de-

composed increased rapidly with increase of the initial pressure, and that at the higher pressures the explosion was complete and was an intrinsic property of the nitrous oxide itself. For example, while decomposition does not occur at atmospheric pressure, 10 per cent of the nitrous oxide is decomposed at a pressure of 10 atmospheres and more than 99 per cent is decomposed at pressures above 35 atmospheres.

A simpler method of initiation was found in the fusing of an electrically heated platinum wire. The initiation was not due entirely to the energy supplied to the wire and the temperature attained by it, since the fusion of a wire in a low-voltage, low-resistance circuit of low inductance was not sufficient to cause explosion. Explosion was obtained, however, when the production of a spark on the fusing of the wire was ensured by either (i) the introduction of additional inductance and capacity, or (ii) an increase of the voltage above 20. The initial temperature was approximately 20° C. throughout.

As will be seen from table 1, the pressure which determines whether explosion is propagated lies between 12 and 15 atmospheres.

Table 1

| Initial pressure of nitrous oxide (atmos.) | Number of determinations | Nitrous oxide decomposed (per cent) |             |
|--|--------------------------|-------------------------------------|-------------|
|  |                          | Extreme values                      | Mean values |
| 2  |                          |                                     | } < 1       |
| 5  |                          |                                     |             |
| 7  |                          |                                     |             |
| 10   |                          |                                     |             |
| 11   | 3                        | 1.3-7                               | 4           |
| 12   | 3                        | 9-35                                | 23          |
| 13   | 4                        | 0.5-85                              | 41          |
| 14   | 3                        | 66-89                               |             |
| 15   | 1                        |                                     | 88          |
| 30   | 2                        | 91-95                               | 93          |
| 37   | 1                        |                                     | 91          |
| 42   | 6                        | 91-93                               | 92          |
| 48   | 1                        |                                     | 93          |

## PART II: MEASUREMENT OF THE HEAT OF FORMATION OF NITROUS OXIDE BY DIRECT DECOMPOSITION

BY T. CARLTON-SUTTON, H. R. AMBLER AND G. WYN WILLIAMS

### § 1. HISTORICAL

The measurement of the heat of formation of nitrous oxide has become important in recent years on account of its being a datum in the determination of the specific heats of gases at high temperatures. Hitherto the heat of formation has been deduced from measurement of the heat produced when nitrous oxide reacts with

hydrogen or with carbon monoxide. Whichever of these reactions is used, some 80 per cent of the heat measured comes from the oxidation of the combustible gas, the heat of formation of the nitrous oxide contributing the remaining 20 per cent; any error in the thermal measurement will therefore be magnified by about five.

Figures which have been obtained for the heat of formation of nitrous oxide by these combustion methods are given in table 2. The present writers have also used these methods, employing pressures of about 50 atmospheres; the figures which have been obtained and the causes which have made the procedure unsatisfactory at these pressures are discussed in § 4.

Table 2. Determination of heat of formation of nitrous oxide by combustion methods

| Observer                            | Method   | Heat of reaction<br>(Cal./mol.) <sub>cp</sub> | Deduced heat<br>of formation of<br>nitrous oxide.<br>(Cal./mol.) <sub>cp</sub> |
|-------------------------------------|--|---|--|
| Berthelot <sup>(5)</sup>            | Combustion with CO at constant volume                                    | 88.2  | -20.6  |
| Thomsen <sup>(6)</sup>              | Combustion with H <sub>2</sub> at constant pressure                      | 86.3  | -18.01   |
| Thomsen <sup>(6)</sup>              | Combustion with CO at constant pressure                                  | 85.1  | -17.47   |
| Awbery and Griffiths <sup>(7)</sup> | Combustion with CO at constant pressure                                  | 87.1  | -19.5  |
| Fenning and Cotton <sup>(8)</sup>   | Combustion with CO at constant volume; pressure about 5 atm.             | 87.4  | -19.75   |
| Fenning and Cotton <sup>(8)</sup>   | Combustion with H <sub>2</sub> at constant volume; pressure about 5 atm. | 88.0  | -19.74   |

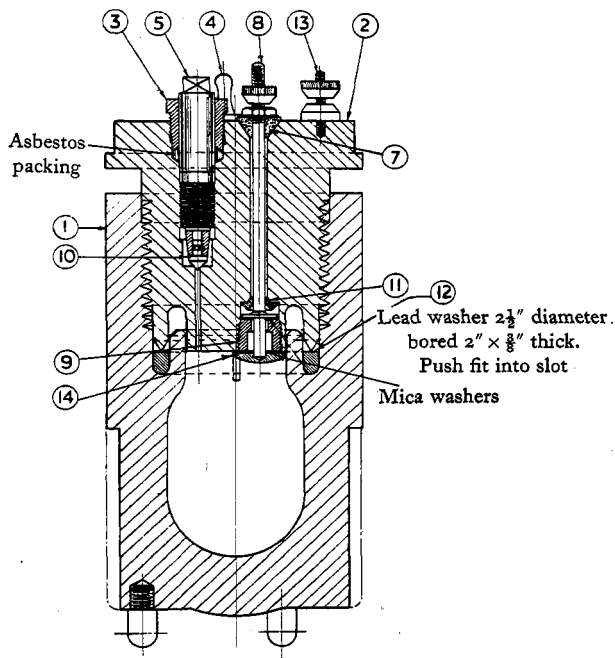
During these investigations, however, it was found that nitrous oxide at a pressure of from 40 to 50 atmospheres can be made to decompose as a mild explosive when initiated by about 0.5 g. of lead azide; on exploring further, it was found that the decomposition can also be produced by fusing a wire in the compressed gas, provided the applied voltage is sufficient to give an arc as the circuit breaks. The latter method has now been applied and will be detailed here.

## § 2. EXPERIMENTAL

*Method.* Nitrous oxide at a pressure of approximately 42 atmospheres was exploded in a calorimetric closed vessel of stainless steel. The heat produced was measured according to a procedure developed in connexion with the calorimetry of propellants and with which measurements are habitually made to one part in a thousand<sup>(9)</sup>. Two mercury-in-glass thermometers<sup>(10)</sup>, calibrated to 0.001° C. and certified to 0.002° C.\*, were used.

\* N.P.L. Ref., Th. 13319.

The closed vessel contained initially nitrous oxide, which was found on analysis to be substantially pure, and finally a mixture which was found to correspond to a decomposition of 90-95 per cent of the original nitrous oxide. The measurement of the heat of formation depended therefore on the precise determination of the quantity and composition of these final products. To determine the mass of nitrous oxide decomposed, three possible methods were available: (i) weighing the nitrous oxide originally taken and determining the amount of nitrous oxide which remained undecomposed; (ii) determining the total free nitrogen produced; and (iii) determining the total free oxygen produced.



Method (i) is limited by the necessarily large mass of the containing vessel, which necessitates the use of a balance capable of taking a load of 10 kg.\* It involves also a difficult and somewhat unsatisfactory determination of nitrous oxide in the final gases. As nitrogen is habitually determined by difference, method (ii) also involves this unsatisfactory determination of nitrous oxide in the final gases. Method (iii) is free from these objections, in that the oxygen may be determined directly. The presence of nitrous oxide, however, seriously affects the accuracy of the standard methods of accurate measurement of oxygen-content hitherto employed. This problem has been investigated at some length therefore in this laboratory, and methods have now been evolved for measuring the oxygen-content of the initial and of final gases to within 0.1 per cent.

\* The mass of nitrous oxide was approximately 15 gm. See table 6.

The heat of formation has been calculated by each of the three methods. The most accurate figure, that given by method (iii), table 6, has been confirmed, table 7, by methods (i) and (ii) within the accuracy obtainable by these latter methods.

*Closed vessel.* The closed vessel, illustrated in the diagram, was made of Stay-brite steel and had a capacity of 128 cm<sup>3</sup>. The main seal 12 was made by means of a steel knife-edge and lead washer. The lead was protected from the action of the hot gases by the presence of two narrow annular passages, 0.015 in. and 0.005 in. wide respectively, through which the hot gases had to pass before reaching the lead; by this means the gases were sufficiently cooled, before coming into contact with the lead, for the lead to be unattacked. Inspection of the seal after each experiment showed that no oxidation of lead had occurred.

*Water equivalent of calorimetric apparatus.* The closed vessel was one of a number used in the calorimetric examination of propellants. When the water equivalent of these was being measured, the possibility of erroneous effects due to reactions between the gases and the steel surfaces was considered, and a diversity of methods were employed for the determination of the water equivalent under varied conditions. These determinations are summarized in table 3, and the effect of the reactions is seen to be inconsiderable.

Table 3. Determination of water equivalent

| Method   | Water*<br>equivalent<br>(g.) | Number<br>of<br>determinations | Mean<br>difference<br>from mean |
|--|------------------------------|--------------------------------|---------------------------------|
| Firing 1 g. benzoic and salicylic acids in 100 atm. of oxygen  | 3769                         | 10                             | 5                               |
| Exploding gaseous mixtures containing 22 atm. CO, 11 atm. N <sub>2</sub> and 67 atm. O <sub>2</sub> and determining the CO <sub>2</sub> produced | 3771                         | 4                              | 4                               |
| Comparing with standard vessel† by firing charges of cordite in an inert atmosphere  | 3774                         | 4                              | 6                               |
| Accepted figure  | 3771                         |                                |                                 |

\* Adjusted to water equivalent = 3 g.

*Nitrous oxide.* Nitrous oxide of very high purity can now be obtained commercially; the gas used for these measurements was stated by the makers, Messrs Coxeter, London, to be 99.995 per cent pure. A sample for analysis was taken from the closed vessel before firing, and tested for oxygen by a sensitive colorimetric method described elsewhere<sup>(11)</sup>. In no case was a figure greater than 0.05 per cent of the nitrous oxide obtained. This procedure served the dual purpose of checking the composition of the nitrous oxide and of showing whether any air had become mixed with it during the process of filling.

*Filling of closed vessel.* At the beginning of an experiment, the closed vessel, containing 1 cm<sup>3</sup> of water‡ and one atmosphere of air, was weighed. It was then

† The water equivalent of this vessel had been determined both electrically and by the combustion of carbon monoxide<sup>(9)</sup>.

‡ In order to absorb the small quantities of higher oxides of nitrogen in the products.

evacuated and filled two or three times with nitrous oxide to about 10 atmospheres and the gas released. It was finally filled to about 45 atmospheres.

*Method of initiation.* Decomposition was initiated by fusing at 50 volts a platinum wire 3 cm. long and 0.012 cm. in diameter. The voltage could be lowered, however, if the production of an arc on fusing was assured by a strongly inductive circuit. The wire was attached by small grooves to two rods of Staybrite steel fixed to the head of the closed vessel. To fire the charge, the circuit was completed and the switch was kept in until, as was shown by an ammeter, the wire fused.

In blank experiments in which the nitrous oxide was replaced by nitrogen or oxygen, the heating effect (4 cal.) was insufficient to be clearly measurable even when it had been magnified by replacing the wire by two similar wires connected in parallel. When a system of smaller thermal capacity was used in the same way, however, rises of 0.004° C. and 0.003° C. were observed, the firing-currents being 8 A. and 6 A. respectively. These rises corresponded to 8 cal. and 6 cal., i.e. to approximately one calorie per ampere. Since this quantity is a small proportion of the total heat, a correction at this rate has been considered adequate.

*Measurement of total gas.* After each calorimetric measurement, the volume of the final gases was measured by connecting the closed vessel with an evacuated bottle and reading the rise in pressure. The bottle was one of a series of measured volume which are used regularly<sup>(12)</sup> for measuring the volumes produced on burning propellants of various compositions. The volumes of the constituent gases were obtained by analysing samples taken separately from the bottle and from the closed vessel\*.

*Analysis of final products. Gases.* Samples from the bottle and from the closed vessel were transferred to a gas-analysis apparatus already described<sup>(13)</sup>. In the later experiments, (4) to (7), i.e. those from which the accepted result is derived, the oxygen-content was determined in two stages. First about 99.5 per cent of the oxygen was removed by absorption with solid phosphorus confined over mercury<sup>(11)</sup>, and next the remainder was determined colorimetrically by means of pyrogallol<sup>(11)</sup>. The accuracy of these methods has already been discussed<sup>(11)</sup>. The measurements were made in duplicate or triplicate; the error in the figures given in table 6 for the oxygen-content does not exceed 0.1 per cent, and it is considered probable that it may be much smaller than this. In the earlier experiments (1), (2) and (3), the nitrous oxide and oxygen were determined by reduction with excess of carbon monoxide<sup>(12)</sup> combined with a density-measurement.

On account of the highly oxidizing nature of the products of explosion, the formation of hydrogen or ammonia from water is precluded. For the same reason nitric oxide is absent. A small proportion of nitrogen dioxide ("peroxide") remains unabsorbed by the water in the closed vessel, and thus occurs in the gases in the bottle. It was determined by bubbling an aliquot part of the gas from the bottle†,

\* The proportion of nitrous oxide remaining in the closed vessel was higher than that in the bottle, because the decomposition did not propagate past the narrow annulus at the bottom of the head, and also because on the release of the pressure some nitrous oxide which had been dissolved in the 1 ml. of water in the vessel was released.

† This was done immediately after the gas-measurement.

e.g. about 2 litres, through weak hydrogen peroxide acidified with sulphuric acid, and determining the nitric acid so formed by the phenoldisulphonic acid method<sup>(14)</sup>. The nitrogen dioxide did not exceed 0.3 per cent on the permanent gas.

In view of the lack of any reliable direct chemical method for the determination of nitrous oxide, a physical method is preferred for the determination of this gas. The large proportional difference between the density of nitrous oxide and that of nitrogen or of oxygen makes the measurement of density a suitable method. The densities were measured by the method of direct weighing<sup>(12)</sup> of the gas, with water vapour and nitrogen dioxide removed, in a glass bulb of approximately 600 cm<sup>3</sup> capacity, a similar bulb containing dry air being used as a counterpoise. The densities were accurate to  $\pm 0.002$  g. per litre, corresponding to  $\pm 0.3$  per cent of nitrous oxide in the gas.

*Non-gaseous residues in the closed vessel.* The closed vessel originally contained 1 cc. of distilled water which absorbed the bulk of the higher oxides of nitrogen. The closed vessel was washed out with distilled water, and an aliquot portion of the washings examined for nitric acid by the Devarda method. In some cases, check tests were made by the phenoldisulphonic acid method. Nitrous acid was shown by Griess tests never to exceed 1.5 mg.

The closed vessel was then opened and washed out with water, and the nitric acid in the washings was determined. Further portions of the washings were tested for iron and for nickel, in order to check whether the walls of the vessel had been attacked by the nitric acid. The iron did not exceed 1 mg. in any case. Nickel was not detected; 0.03 mg. would have been detected.

*Checks on analysis.* It was considered desirable at this stage to estimate in the final products the ratio of the total nitrogen to the total oxygen. Since the vessel originally contained pure nitrous oxide, any deviation from 2 of this value is a measure of the limit of reliability of the analytical procedure and the extent to which minor reactions, for instance with the walls of the vessel, may occur.

As is shown in table 4, no consistent deviation has occurred, and the magnitude of the deviations observed is within the estimated limits of measurement.

Table 4. Balance of elements

| Number of experiment | Quantities of substances present in closed vessel after firing (cm <sup>3</sup> at n.t.p., molecular volumes being taken as 22.40 litres) |                |                  |                               |                 |                              | Ratio of nitrogen to oxygen |                              |
|----------------------|---|----------------|------------------|-------------------------------|-----------------|------------------------------|-----------------------------|------------------------------|
|                      | N <sub>2</sub>  | O <sub>2</sub> | N <sub>2</sub> O | N <sub>2</sub> O <sub>5</sub> | NO <sub>2</sub> | Total N (as N <sub>2</sub> ) |                             | Total O (as O <sub>2</sub> ) |
| 1                    | 6089  | 2958           | 574              | 39.1                          | 18              | 6711                         | 3361                        | 1.997                        |
| 2                    | 6695  | 3228           | 533              | 48.0                          | 19              | 7285                         | 3634                        | 2.004                        |
| 3                    | 7099  | 3417           | 521              | 39.8                          | 4               | 7662                         | 3781                        | 2.026                        |
| 4                    | 7108  | 3459           | 560              | 39.1                          | 14              | 7714                         | 3851                        | 2.003                        |
| 5                    | 7035  | 3424           | 590              | 26.3                          | 12              | 7657                         | 3797                        | 2.016                        |
| 6                    | 6812  | 3341           | 633              | 26.3                          | 22              | 7482                         | 3746                        | 1.997                        |
| 7                    | 6659  | 3273           | 477              | 28.0                          | 4               | 7166                         | 3586                        | 1.998                        |
| Mean                 |   |                |                  |                               |                 |                              |                             | 2.006                        |

Table 5. Effect of formation of nitric acid and nitrogen peroxide on heat and oxygen

| Substance        | Reaction  | Heat produced (cal.) per mg. of substance | Oxygen absorbed per mg. of substance (cm <sup>3</sup> at n.t.p.) |
|------------------|---|---|--|
| HNO <sub>3</sub> | 2N <sub>2</sub> + 5O <sub>2</sub> + 2H <sub>2</sub> O = 4HNO <sub>3</sub> Aq. + 59.6 Cal. | 0.236                                     | 0.45   |
| NO <sub>2</sub>  | N <sub>2</sub> + 2O <sub>2</sub> = 2NO <sub>2</sub> - 3.4 Cal.                            | -0.037                                    | 0.49   |

Table 6. Heat of formation of nitrous oxide

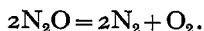
| Number of experiment ...   | (1)                | (2)                | (3)                | (4)                | (5)                | (6)                | (7)                |
|--|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Estimation of reactant nitrous oxide by measurement of resultant oxygen  |                    |                    |                    |                    |                    |                    |                    |
| Initial:   |                    |                    |                    |                    |                    |                    |                    |
| Mass of nitrous oxide (g.)   | 12.9 <sub>6</sub>  | 14.2 <sub>5</sub>  | 15.1 <sub>1</sub>  | 14.8 <sub>8</sub>  | 15.1 <sub>3</sub>  | 14.8 <sub>2</sub>  | 14.1 <sub>1</sub>  |
| % oxygen   | —                  | —                  | —                  | < 0.01             | 0.03               | 0.05               | < 0.01             |
| Whence, free oxygen initially present (cm <sup>3</sup> at n.t.p.)  | —                  | —                  | —                  | < 1                | 2                  | 4                  | < 1                |
| Final:   |                    |                    |                    |                    |                    |                    |                    |
| Volume of gas measuring bottle (cm <sup>3</sup> )  | 8890               | 8890               | 8890               | 8890               | 8890               | 8890               | 8890               |
| Volume of closed vessel (cm <sup>3</sup> )   | 128                | 128                | 128                | 128                | 128                | 128                | 128                |
| Pressure of gas in bottle and closed vessel (cm. of mercury at 20° C.)   | 87.26              | 94.78              | 100.22             | 101.36             | 100.84             | 98.72              | 94.62              |
| Temperature (° C.)   | 19.6               | 19.4               | 20.0               | 21.0               | 21.6               | 22.4               | 20.3               |
| Whence, gas in bottle (cm <sup>3</sup> at n.t.p.)  | 9488               | 10310              | 10883              | 10970              | 10894              | 10635              | 10262              |
| gas in closed vessel (cm <sup>3</sup> at n.t.p. excluding water vapour)  | 134                | 146                | 154                | 156                | 155                | 151                | 146                |
| Percentage composition of gas from bottle  |                    |                    |                    |                    |                    |                    |                    |
| { O <sub>2</sub>   | 30.8               | 30.9               | 31.0               | 31.1               | 31.0               | 31.0               | 31.5               |
| { N <sub>2</sub> O   | 5.8                | 5.0                | 4.6                | 5.0                | 5.3                | 5.8                | 4.4                |
| { N <sub>2</sub>   | 63.4               | 64.1               | 64.4               | 63.9               | 63.7               | 63.2               | 64.1               |
| Percentage composition of gas from closed vessel   |                    |                    |                    |                    |                    |                    |                    |
| { O <sub>2</sub>   | 27.0               | 28.5               | 28.2               | 30.3               | 30.1               | 29.0               | 27.4               |
| { N <sub>2</sub> O   | 18.0               | 12.5               | 13.0               | 7.0                | 8.2                | 10.5               | 17.0               |
| { N <sub>2</sub>   | 55.0               | 59.0               | 58.8               | 62.7               | 61.7               | 60.5               | 55.6               |
| Whence free oxygen in bottle and closed vessel (cm <sup>3</sup> at n.t.p.)   | 2958               | 3228               | 3417               | 3459               | 3424               | 3341               | 3273               |
| Nitric acid in products (g.)   | 0.220              | 0.270              | 0.224              | 0.220              | 0.148              | 0.148              | 0.157              |
| Nitrogen dioxide in products (g.)  | 0.037              | 0.039              | 0.009              | 0.028              | 0.024              | 0.046              | 0.009              |
| Whence, Oxygen produced by decomposition of nitrous oxide (cm <sup>3</sup> at n.t.p.) and, Nitrous oxide decomposed (mol.) | 3075               | 3368               | 3522               | 3572               | 3503               | 3431               | 3438               |
|  | 0.274 <sub>8</sub> | 0.300 <sub>7</sub> | 0.314 <sub>8</sub> | 0.318 <sub>9</sub> | 0.312 <sub>9</sub> | 0.306 <sub>8</sub> | 0.298 <sub>1</sub> |
| Measurement of energy  |                    |                    |                    |                    |                    |                    |                    |
| Temperature rise (° C.)  | 1.465 <sub>5</sub> | 1.595              | 1.679              | 1.707 <sub>5</sub> | 1.672              | 1.637 <sub>5</sub> | 1.593 <sub>1</sub> |
| Water equivalent (g.)  | 3767               | 3771               | 3771               | 3771               | 3767               | 3771               | 3771               |
| Whence, total measured heat (cal. ≡ 4.186 joules)  | 5520               | 6015               | 6332               | 6439               | 6298               | 6175               | 6009               |
| Correction for ignition current (cal.)   | 12                 | 3                  | 2                  | 9                  | 5                  | 3                  | 3                  |
| Correction for nitric acid (cal.)  | 52                 | 64                 | 53                 | 52                 | 35                 | 35                 | 37                 |
| Correction for nitrogen dioxide (cal.)   | -1                 | -1                 | 0                  | -1                 | -1                 | -2                 | 0                  |
| Whence, energy evolved by decomposition of nitrous oxide (cal.)  | 5457               | 5949               | 6277               | 6379               | 6259               | 6139               | 5969               |
| Hence, Heat of formation of nitrous oxide at constant volume (cal./mol.)   | -19.8 <sub>7</sub> | -19.7 <sub>8</sub> | -19.9 <sub>8</sub> | -20.0 <sub>0</sub> | -20.0 <sub>0</sub> | -20.0 <sub>4</sub> | -19.9 <sub>8</sub> |

Mean (from experiments 1 to 7) -19.9<sub>8</sub> cal./mol.  
 (from experiments 4 to 7) -20.0<sub>0</sub> cal./mol.



## § 3. RESULTS

The thermochemistry of the reaction is primarily that of the decomposition of nitrous oxide according to the equation.



It has been found that side reactions are few. These are limited to the formation of higher oxides of nitrogen and their absorption by water; the corrections applied for the energy and volume changes produced by them have been made in accordance with the constants given in table 5.

Table 6 gives the results of seven successive experiments. Of these, numbers (4) to (7) are considered the more reliable because the oxygen figure was obtained by the direct and accurate method developed for the purpose, and because the general technique had become more familiar; the value  $-20.0_0$  cal./mol. at constant volume has therefore been derived from these four experiments\*.

Table 7. Heat of formation, reactant mass of nitrous oxide being estimated by alternative (less accurate) methods

| Number of experiment | Heat of formation (cal./mol.) at constant volume. Mass $\text{N}_2\text{O}$ estimated from |                          |
|----------------------|--|--------------------------|
|                      | Weight and residual $\text{N}_2\text{O}$   | $\text{N}_2$ in products |
| (1)                  | $-20.2_9$  | $-19.9_1$                |
| (2)                  | $-19.8_8$  | $-19.7_4$                |
| (3)                  | $-19.6_1$  | $-19.7_0$                |
| (4)                  | $-20.3_7$  | $-19.9_7$                |
| (5)                  | $-19.7_1$  | $-19.8_4$                |
| (6)                  | $-19.8_9$  | $-20.0_8$                |
| (7)                  | $-19.8_3$  | $-19.9_9$                |
| Mean                 | $-19.9_8$  | $-19.8_9$                |
| Mean of (4) to (7)   | $-19.9_6$  | $-19.9_7$                |

The decomposition of nitrous oxide is accompanied by an increase in volume according to the relation  $2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$ . The value of the product pressure  $\times$  volume for nitrous oxide at 42 atmospheres has been found to be 0.67 times that for a perfect gas, as described in part III of this paper. For nitrogen and oxygen, the deviation from the value for a perfect gas is not sufficient to affect the final result by one unit in the dropped figure, and is consequently neglected here. The difference between the heats of formation at constant volume and approximately 42 atmospheres and at constant pressure is found from this data to be 0.48 cal./mol.

The heat of formation at constant pressure is thus  $-19.5_2$  cal./mol.

\* When the accuracy of these measurements was estimated the determination of oxygen was considered an important limit, and it was not relied upon to closer than 0.1 per cent of the total gas, corresponding to 0.06 cal./mol. in the heat of formation. It is not clear how far the higher accuracy attained in experiments (4) to (7) is fortuitous, and how far it may be taken as evidence of the higher accuracy of the oxygen determination.

## § 4. DETERMINATION OF HEAT OF FORMATION BY COMBUSTION METHODS AT PRESSURES OF ABOUT 50 ATMOSPHERES

In the course of these investigations, the combustion in nitrous oxide of hydrogen and carbon monoxide were examined at pressures of about 50 atm., and one of us published an early value<sup>(15)</sup> obtained for the energy of the former reaction. Values for the heat of formation of nitrous oxide deduced from these two reactions were found however to differ by as much as 1 cal./mol., corresponding to 1 per cent on the measured heats.

A further investigation which was thereupon put in hand showed that thermochemical measurements involving the use of hydrogen in steel vessels at pressures of this order, while likely to give consistent results in any single series of measurements, may be misleading on account of absorption<sup>(16, 17)</sup> (or in some cases emission) of hydrogen at the walls of the vessel. The behaviour of mild gaseous explosions of this kind is thus similar to what occurs when high explosives are detonated in closed vessels<sup>(18)</sup>; in the case of the former, however, no effects which exceed 1 per cent of the measured value have been detected. In the estimation of the heat of formation of nitrous oxide in this way, 1 per cent on the measured heat of reaction corresponds with  $4\frac{1}{2}$  per cent on the heat of formation, and the method becomes an unsatisfactory one.

The mean figure obtained by using carbon monoxide (table 8) was substantially in agreement with the best results obtained by other methods; the variation between individual determinations was, however, considered unsatisfactory.

Table 8. Heat of formation of nitrous oxide by explosion with carbon monoxide in calorimetric closed vessel. Approximate composition:  $N_2O$ , 14 atm.;  $CO$ , 24 atm.;  $N_2$ , 12 atm.

|  |                    |                    |                    |                    |                    |                    |                    |
|--|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Measured heat of reaction<br>$N_2O + CO = N_2 + CO_2$              | 87.2 <sub>2</sub>  | 86.9 <sub>2</sub>  | 86.8 <sub>8</sub>  | 87.2 <sub>3</sub>  | 87.2 <sub>1</sub>  | 87.4 <sub>8</sub>  | 86.7 <sub>4</sub>  |
| Heat of formation of<br>$N_2O$ (cal./mol.) at<br>constant pressure | -19.6 <sub>0</sub> | -19.3 <sub>0</sub> | -19.2 <sub>4</sub> | -19.6 <sub>8</sub> | -19.5 <sub>9</sub> | -19.8 <sub>8</sub> | -19.1 <sub>2</sub> |
|  |                    |                    |                    |                    | Mean               | -19.4 <sub>8</sub> |                    |

When nitrous oxide is not present, for instance if oxygen is exploded with excess carbon monoxide<sup>(9)</sup>, a high order of consistency is obtained, and it would seem that the variability is attributable to some action of the former gas. Nitrous oxide was thus found unsuitable as a substitute for oxygen for thermochemical and calorimetric measurements of the kind for which its use had been proposed.

## PART III: THE DEVIATION OF NITROUS OXIDE FROM THE SIMPLE GAS LAWS

BY T. CARLTON-SUTTON AND G. WYN WILLIAMS

The value of the product pressure  $\times$  volume has been measured for nitrous oxide at pressures of 1 atmosphere and less by Rayleigh<sup>(19)</sup> and by Batuecas<sup>(20)</sup>. Values of this product at pressures between 40 and 50 atmospheres were required in connexion with the measurement of the heat of formation of this gas. The method devised for this purpose measures the value of this product in terms of that of a standard gas, and has the advantages that the measurements involved are simple and the apparatus required is such as may be found in any laboratory.

To obtain a check on the general accuracy of this method, the values for carbon dioxide were measured in terms of those for nitrogen and compared with the classical values of Amagat<sup>(21)</sup>, table 9. In view of the agreement thus obtained the method was considered suitable, and the measurements were extended to pressures lower than those employed by Amagat.

Measurements were also made to obtain data for nitrous oxide in terms of those for nitrogen, and from these the deviation of the former gas from the simple gas laws has been deduced.

For any mixture of dry gases, and subject to the restriction that the constituents must act independently in accordance with their partial pressures, the relation between pressure, volume, temperature and mass is given by

$$\Sigma \frac{m}{M} = v \frac{\Sigma \alpha p}{RT},$$

where  $m$  is the mass,  $M$  the molecular mass and  $p$  the partial pressure of each constituent,  $v$  is the total volume,  $T$  the absolute temperature,  $R$  the gas constant, and  $\alpha$  the deviation of each gas from Boyle's law expressed as the ratio of the products  $p v$  for the perfect and for the actual gas.

A strong closed vessel of volume  $v_1$  containing a dry gas  $X$  at high pressure  $p_1$ , and a large vessel of volume  $v_2$  containing dry air  $A$  at a low pressure  $p_0$  are connected and the pressure changes to  $p_2$  when the contents have mixed isothermally. The total mass remains unchanged and the pressure-volume relations may be obtained by equating the two expressions for this quantity,  $\Sigma m/M$ , which can be derived from the initial and final conditions.

Initially the mass,  $\Sigma m/M$  moles, is

$$\frac{1}{RT} \{x \alpha_1 p_1 v_1 + A \alpha_0 p_0 (g_0 + v_2)\},$$

where the generalized  $x \alpha_{im}$  signifies the deviation of gas  $X$  at pressure  $(p_i - p_m)$  and  $g_n$  signifies the volume of the gauge and connexions at pressure  $p_n$ .

Finally, when the gases have mixed, the total pressure  $p_2$  is composed of a partial pressure  $p_3$  of air and a partial pressure  $(p_2 - p_3)$  of the gas  $X$ , where

$$A \alpha_2 p_3 / A \alpha_0 p_0 = (g_0 + v_2) / (g_2 + v_1 + v_2).$$

$m, M, p$   
 $v, T, R$   
 $\alpha$

$v_1$   
 $p_1, v_2, p_0$   
 $p_2$

$x \alpha_{im}$   
 $g_n$

$p_3$

The mass  $\Sigma m/M$  moles is then

$$\frac{1}{RT} \{x\alpha_{23} (p_2 - p_3) + A\alpha_3 p_3\} (v_1 + v_2 + g_2),$$

which

$$= \frac{1}{RT} \left\{ x\alpha_{23} \left[ (p_2 - p_0) (v_1 + v_2 + g_2) + p_0 v_1 + p_0 (g_2 - g_0) \right. \right. \\ \left. \left. + p_0 (v_2 + g_0) \left( 1 - \frac{A\alpha_0}{A\alpha_3} \right) \right] + A\alpha_0 p_0 (g_0 + v_2) \right\}.$$

Equating these two expressions for  $\Sigma m/M$  we find that

$$p_1 \frac{x\alpha_1}{x\alpha_{23}} = (p_2 - p_0) \frac{v_1 + v_2 + g_2}{v_1} + p_0 + p_0 \frac{g_2 - g_0}{v_1} + p_0 \frac{v_2 + g_0}{v_1} \cdot \frac{A\alpha_3 - A\alpha_0}{A\alpha_3} \dots\dots (1).$$

In a practical case when  $p_2 = 1/3$  atm.,  $p_0 = 1/300$  atm.,  $v_1 = 128$  cm<sup>3</sup>,  $v_2 = 16$  litres, and  $(g_2 - g_0) = 1$  cm<sup>3</sup>, the second term on the right is less than 0.01 per cent of the first term and the remaining terms are still smaller. For such cases, therefore, all terms but the first may be neglected.

If there is no diffusion of air from the large vessel to the strong closed vessel, the final value of  $\Sigma m/M$  may be written

$$\frac{1}{RT} \{x\alpha_{20} (p_2 - p_0) v_1 + x\alpha_0 p_0 v_1 + x\alpha_{20} (p_2 - p_0) (g_2 + v_2) + A\alpha_0 p_0 (g_2 + v_2)\}$$

and equation (1) becomes

$$p_1 \frac{x\alpha_1}{x\alpha_{20}} = (p_2 - p_0) \frac{v_1 + v_2 + g_2}{v_1} + p_0 \frac{x\alpha_0}{x\alpha_{20}} + p_0 \frac{g_2 - g_0}{v_1} \cdot \frac{A\alpha_0}{A\alpha_{20}}.$$

For this expression, also, all terms but the first may be neglected. In practice,  $x\alpha_{20}$  and  $x\alpha_{23}$  are to a high order of accuracy equal, and the two expressions consequently become the same. The final values obtained by this method, therefore, are not affected by the amount of diffusion that takes place.

The simple relation obtained by neglecting the small terms in equation (1) involves two pressures  $p_2$  and  $p_0$  which can be measured on an open mercury manometer, and one pressure  $p_1$  which is too great to be measured conveniently in this way. To compare the values of  $x\alpha_1/x\alpha_{23}$  with the corresponding values for a standard gas, however, no measurement of this pressure  $p_1$  is required, since if the pressure can be reproduced (without measurement) in two experiments, the relation becomes

$$\frac{x\alpha_1}{x\alpha_{23}} \Big/ \frac{x\alpha_1'}{x\alpha_{23}'} = \frac{p_2 - p_0}{p_2' - p_0'} \cdot \frac{v_1 + v_2 + g_2}{v_1 + v_2 + g_2'} \dots\dots (2),$$

where the dashes denote that the quantities refer to the standard gas.

The differences between  $g_2$  and  $g_2'$  have not exceeded  $v_2 \times 10^{-4}$ , and the second factor on the right-hand side has consequently been taken as unity.

With considerable accuracy, therefore,  $x\alpha_1/x\alpha_{23}$ , the ratio of the deviations at pressures  $p_1$  and  $(p_2 - p_3)$  respectively, is directly proportional to the measured rise in pressure in the small vessel. When, as in the present cases, the deviation  $x\alpha_{23}$  at low pressure is known, the deviation  $x\alpha_1$  at any pressure  $p_1$  can be measured in this way.

Table 9

| Volume $v_1$ of small vessel = 128 cm <sup>3</sup> Volume $v_2$ of bottle = 16.46 litres (except in experiments A and K for which $v_2 = 15.35$ litres) |                         |                         |                         |                         |                         |                         |                         |                         |                         |                     |                         |
|---|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|---------------------|-------------------------|
| Experiments in chronological order...   | A                       | B                       | C                       | D                       | E                       | F                       | G                       | H                       | K                       | L                   | M                       |
| Temperature of small vessel... ..   | 19.6                    | 20.0                    | 19.3                    | 20.1                    | 19.4                    | 19.7                    | 19.0                    | 19.1                    | 18.9                    | 19.1                | 19.7                    |
| Pressure-rise, $p_2 - p_0$ (cm.) in bottle in experiments with nitrogen (i) and (v) carbon dioxide (ii) and (iv) nitrous oxide (iii)                    | 12.64<br>14.26<br>14.44 | 14.62<br>17.05<br>17.37 | 20.52<br>26.21<br>26.86 | 17.68<br>21.43<br>22.00 | 26.29<br>37.79<br>40.41 | 25.70<br>36.38<br>38.39 | 23.48<br>32.03<br>33.11 | 20.59<br>26.49<br>27.23 | 29.00<br>41.99<br>45.44 | 5.97<br>—<br>6.37   | 6.99<br>7.44<br>7.55    |
| Pressure $p_2$ (atm.) in small vessel indicated approximately on aneroid gauge derived from the measurements with nitrogen                              | 20<br>19.8              | 25<br>24.6              | 35<br>34.5              | 30<br>29.7              | 45<br>44.0              | 44<br>43.1              | 40<br>39.4              | 35<br>34.5              | 46<br>45.4              | 10<br>10.1          | 11<br>11.8              |
| Values of $\alpha_1/\alpha_2$ for nitrogen (5) carbon dioxide nitrous oxide   | 1.006<br>1.134<br>1.148 | 1.007<br>1.173<br>1.194 | 1.008<br>1.288<br>1.311 | 1.008<br>1.225<br>1.251 | 1.010<br>1.454<br>1.551 | 1.010<br>1.425<br>1.504 | 1.009<br>1.376<br>1.423 | 1.008<br>1.299<br>1.335 | 1.010<br>1.456<br>1.578 | 1.003<br>—<br>1.073 | 1.004<br>1.067<br>1.084 |
| Value of $\alpha_{23}$ for carbon dioxide (5) for nitrous oxide (5,6)   | 1.001<br>1.002          | 1.002<br>1.002          | 1.002<br>1.003          | 1.002<br>1.002          | 1.003<br>1.005          | 1.003<br>1.004          | 1.003<br>1.004          | 1.002<br>1.003          | 1.004<br>1.005          | —<br>1.001          | 1.001<br>1.001          |
| $\alpha$ as deduced at above temperatures and pressures for carbon dioxide for nitrous oxide  | 1.135<br>1.150          | 1.175<br>1.196          | 1.291<br>1.315          | 1.227<br>1.258          | 1.458<br>1.558          | 1.429<br>1.510          | 1.380<br>1.429          | 1.301<br>1.339          | 1.469<br>1.587          | —<br>1.074          | 1.066<br>1.086          |
| $\alpha$ (Amagat) for carbon dioxide  | —                       | —                       | —                       | —                       | 1.450                   | 1.432                   | 1.369                   | —                       | 1.483                   | —                   | —                       |
| Ratio $p_0$ actual/ $p_0$ perfect for carbon dioxide for nitrous oxide  | 0.881<br>0.870          | 0.854<br>0.836          | 0.776<br>0.761          | 0.815<br>0.795          | 0.686<br>0.641          | 0.700<br>0.662          | 0.729<br>0.700          | 0.769<br>0.747          | 0.684<br>0.630          | —<br>0.931          | 0.936<br>0.921          |

It is to be noted that equation (2) does not involve  $p_1$ , the initial pressure in the large vessel. In practice, this pressure has been adjusted so as to be the same for the gas under test as for the standard gas; it has not been necessary to measure it directly since the condensation of the standard gas at pressure  $p_1$  is given by the expression  $\chi \alpha_{23}' (p_2' - p_3') v_2/v_1$ , and from the known properties of this gas the corresponding value of  $p_1$  can be obtained.

To meet these requirements the following apparatus has been used: A strong closed vessel  $v_1$  of capacity 128 cc., designed for use in the calorimetry of propellants; a large bottle  $v_2$  of capacity 16 litres, which had been carefully calibrated for measurement of the volumes of the gaseous products of explosives; a mercury manometer for the measurement of the pressures,  $p_0$  and  $p_2$ , less than one atmosphere; and an aneroid gauge which, while not measuring the pressure, enabled the vessel  $v_1$  to be filled to the same initial pressure in each of a series of experiments.

A complete series consisted of five experiments in which (i) nitrogen, (ii) carbon dioxide, (iii) nitrous oxide, (iv) carbon dioxide and (v) nitrogen were used successively. Agreement between the first and fifth and the second and fourth experiments has been taken as a sign that the indications of the gauge were satisfactory throughout the series. The results are given in table 9.

## REFERENCES

- (1) BERTHELOT. *Ann. Chim. (phys.)* (5), **4**, 145 (1875); *C.R. Acad. Sci.*, Paris, **93**, 613 (1881).
- (2) ——— *Explosives*, p. 191 (1892). *Trans. Hake and Macnab*.
- (3) MAQUENNE. *C.R. Acad. Sci.*, Paris, **121**, 424 (1895).
- (4) HOUSEMAN. *Industrial Gases*, **3**, 87 (1922).
- (5) BERTHELOT. *Thermochemie*, p. 102 (1897).
- (6) THOMSEN. *Thermochemische Untersuchungen*, **2**, 198 (1882).
- (7) AWBERY and GRIFFITHS. *Proc. roy. Soc. A*, **141**, 1 (1932).
- (8) FENNING and COTTON. *Proc. roy. Soc. A*, **141**, 17 (1932).
- (9) SUTTON. In preparation.
- (10) SUTTON. *J. sci. Instrum.* **8**, 98 (1931).
- (11) AMBLER. *Analyst*, **59**, 14, 593 (1934).
- (12) LUNGE and AMBLER. *Technical Gas Analysis*, pp. 32, 179, 276, 277 (1934).
- (13) AMBLER. *Analyst*, **54**, 517 (1929).
- (14) FRANCIS and PARSONS. *Analyst*, **50**, 262 (1925).
- (15) SUTTON. *Phil. Mag.* **14**, 275 (1932).
- (16) INGLIS and ANDREWS. *J. Iron Steel Inst.* **128**, 383 (1933).
- (17) COX. *Trans. Amer. Inst. chem. Engrs.* **29**, 43 (1933).
- (18) SUTTON and AMBLER. *Trans. Faraday Soc.* **22**, 406 (1926).
- (19) RAYLEIGH. *Philos. Trans. A*, **196**, 205 (1901); **198**, 417 (1902); **204**, 351 (1905). *Proc. roy. Soc. A*, **74**, 446 (1905).
- (20) BATUECAS. *J. Chim. phys.* **22**, 101 (1925); **28**, 572 (1931). *An. Soc. esp. Fis. Quim.* **29**, 538 (1931).
- (21) AMAGAT. *Ann. Chim. (Phys.)*, **29**, 110 (1893).