STUDIES IN THE DINITROGEN TRIOXIDE SYSTEM.

by

STEPHEN WILLIAM BELL

A Thesis submitted to the University of Sheffield for the Degree of Doctor of Philosophy.

DECEMBER 1958.

STUDIES IN THE DINITROGEN TRIOXIDE SYSTEM.

GwBell

SUMMARY.

The chemistry of dinitrogen trioxide is reviewed.

By use of an all glass apparatus the equilibrium between nitrogen dioxide, dinitrogen tetroxide, nitric oxide and dinitrogen trioxide has been studied in the gas phase by two methods at 5°, 15°, 25°, 35° and 45°C. The equilibrium constant at each temperature has been determined over a wide concentration range, enabling thermodynamic constants to be obtained by extrapolation to zero pressure. Values of ΔS and ΔH are given. The significance of the results is discussed.

The melting and freezing points of mixtures of dinitrogen trioxide with dinitrogen tetroxide have been measured at concentrations 70% to 100% N_2O_3 giving temperatures in the region of -100°C. The freezing point of pure N_2O_3 was obtained by extrapolation. Criticisms of the work are made and suggestions for improvements put forward.

Some reactions of the dinitrogen trioxide system have been investigated.

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Dr. I.R.Beattie and Dr.J.Lewis for their constructive criticism and encouragement during the course of this work.

Thanks are also due to The University of Sheffield for the award of a Robert Styring Postgraduate Scholarship.

"Cette combinaison d'oxygène et de gas nitreux, qui n'avait pas été distinguée, au moins que je sache, et que je désignerai provisoirement par le nom d'acide pernitreux, ne peut être obtenue isolée: aussitôt qu'on sature la potasse avec un acide, il se degage du gaz nitreux, et il se produit de l'acide nitreux ordinaire qui rest en dissolution dans l'eau. En réduisant le gaz nitreux en se éléméns, on trouve que la proportion de 100 d'oxygène à 400 de gaz nitreux, revient à celle de: Azote, 100

Oxigene, 150".

L.J.Gay-Lussac,

Ann.Chim.Phys (2), 1, 400 (1816).

CONTENTS.

CHAPTER 1.

INTRODUCTION.

Dinitrogen trioxide is an interesting and important substance, the properties of which are to a remarkable extent unknown, in spite of the great length of time (over 140 years) it has been known to exist. With the passing of the lead chamber process for the manufacture of sulphuric acid, much of the industrial importance of N_2O_3 disappeared, but it retains its important place in all processes which involve the reactions and equilibria of oxides and acids of nitrogen. Apart from this industrial relevance it is of considerable academic interest.

Most important of the unknown properties of N_2O_3 are the conditions of its stability. Without a complete knowledge of these all other chemical and physical measurements are largely meaningless since we do not know what molecular species we are measuring.

Some attempts have been made to define the stability limits of N_2O_3. The earliest of these sought to show the existence of N_2O_3 in the gaseous phase. Other workers attempted to evaluate constants for it, but achieved little numerical agreement. Its freezing point was likewise uncertain.

The work recorded here attempts to define these stability limits more closely.

CHAPTER II.

FORMATION AND PREPARATION OF DINITROGEN TRIOXIDE.

The earliest dinitrogen trioxide to be observed was probably formed in the lead chambers during the manufacture of sulphuric acid, about the 15th century. It may also possibly have been observed in the investigations on nitric oxide which date from about the 17th century.

The existence of a nitrogen oxide with the stoichiometric formula corresponding to N_2O_3 was first announced by L.J.Gay-Lussac (1) in 1816. Later in that year P.L.Dulong (2) reported that partial oxidation of nitric oxide, the collection of the products of this reaction, and their analysis. From their writings also it seems certain that the colouration brought about by N_2O_3 under various conditions had been observed for a considerable time. Gay-Lussac called it "acide pernitreux".

Dinitrogen trioxide may be formed as the result of reactions differing greatly in type. In addition to the simple combination of nitric oxide and nitrogen dioxide it may be formed after reduction, oxidation, hydrolytic, or metathetical reactions.

1. Reduction of Nitric Acid.

(i) By Arsenious Oxide.

Many earlier workers prepared N_2O_3 by the action of strong nitric acid on dry, powdered, vitreous arsenious oxide reported to be

$$As_2O_3 + 2HNO_3 \rightarrow N_2O_3 + 2HAsO_3$$

Lunge found the concentration of nitric acid to be critical, weaker acid giving a product enriched in nitric oxide, stronger acid producing nitrogen dioxide enrichment (3). Nitric acid of density 1.30 g/cc was recommended by Stenhouse and Groves (4). Other workers to use this method include Nylander (5), Luck (6), Hasenbach (7), Ramsay and Cundall (8) Geuther (9), and Ramsay (10,11). Mercuric ion (12) and concentrated sulphuric acid (101,102) have been used as catalysts for this reaction.

(ii) By Copper.

Rather impure N_2O_3 can be obtained from the reduction of nitric acid with copper. This may be represented approximately by

$$6HNO_3 + 2Cu \rightarrow 2Cu(NO_3)_2 + 3H_2O + N_2O_3$$

To obtain N_2O_3 free from the water which is also produced in the reaction would be extremely difficult.

(iii) By Starch.

Lunge (3) and Peligot (13,14) prepared N_2O_3 by the action of nitric acid of density 1.33 g/cc on starch paste. Geuther and Michaelis (15) showed that carbon dioxide was also produced.

(iv) By Sodium Nitrite.

Hofmann and Zedtwitz (16) prepared N_2O_3 by the action of 68 per cent nitric acid on sodium nitrite at 0°C.

$$2NaNO_2 + 2HNO_3 \longrightarrow NO.NO_2 + 2NaNO_3 + H_2O$$

2. Reduction of Dinitrogen Tetroxide.

(i) By Selenium.

Barnes (21) showed that N_2O_4 could be reduced by finely divided selenium at 0°C.

$$2N_2O_4 + Se \longrightarrow SeO_2 + 2N_2O_3$$

(ii) By Phosphorus Trioxide.

Thorpe and Tutton (22) showed that phosphorus trioxide could be oxidised to phosphorus pentoxide by N_2O_4, with the consequent production of N_2O_3. The course of the reaction is uncertain.

(iii) By Zinc.

Addison & Lewis (49,50,51) have shown that N_2O_4 may be reduced by zinc as follows:

$$Zn + 2N_2O_4 \longrightarrow Zn^{++} + 2(NO_3)^- + 2NO$$

$$N_2O_4 + 2NO \longrightarrow 2N_2O_3$$

It is interesting to note the further course of the reaction

$$Zn(NO_3)_2 + 2N_2O_4 \longrightarrow 2NO^+ + [Zn(NO_3)_4]^=$$

3. Oxidation of Nitrogen.

Mixtures of nitrogen and oxygen at temperatures in the region of the boiling point of liquid air can be made to combine by the action of an electric spark or arc to give dinitrogen trioxide and other oxides of nitrogen (23 to 36).

4. Partial Oxidation of Nitric Oxide.

Although theoretically possible , few attempts have been made to form a gaseous mixture of dinitrogen trioxide composition, by mixing the theoretical quantities of nitric oxide and oxygen. However, a great deal of work has been done on the mechanism of the oxidation of nitric oxide.

$$2NO + O_2 \longrightarrow 2NO_2$$

$$NO + NO_2 \rightleftharpoons N_2O_3$$

The first reaction, important industrially in the manufacture of nitric acid is interesting also in that it is kinetically a third order reaction of which the velocity constant decreases with increasing temperature (37,38).

At low temperatures the end product is not N_2O_4 as might be expected but is N_2O_3, or other oxides of nitrogen which readily decompose near the boiling point of liquid oxygen to give N_2O_3 (24,35,39,40).

The kinetic aspects of the reaction have been discussed (41 - 45) and reviewed by Glasstone, Laidler and Eyring (46), and Gray and Yoffe (47).

5. Catalytic Oxidation of Hydrogen Cyanide.

A current of air carrying 6 per cent of hydrogen cyanide, when passed over a platinum catalyst at 700°C gives 70.7 per cent N_2O_3, 24.2 per cent NO_2 and 5.1 per cent nitrogen (20).

6. Hydrolysis of Nitrosyl Bisulphate.

$$H_2O + 2NO^+ + 2HSO_4^- \longrightarrow N_2O_3 + 2H_2SO_4$$

This reaction naturally gives very impure N_2O_3, but is interesting since it affords one of the earliest productions of the material: i.e. from "chamber crystals" and water (17,18,19).

All the foregoing formations and preparations give impure N_2O_3 to a greater or lesser degree, with the exception of the partial oxidation of nitric oxide, about which little is known. The remaining two methods are thought to give a quality of product superior to the above.

7. Metathesis.

It has been reported (48) that silver nitrite reacts with nitrosyl chloride thus:

$$AgNO_2 + NOCl \longrightarrow AgCl + N_2O_3$$

Since both of the reactants can be obtained in a reasonably high state of purity, if nitrosyl chloride be placed with an excess of silver nitrite, the quantitative production of silver chloride will be accompanied by the evolution of a very pure N_2O_3 gas mixture.

8. Nitric Oxide - Nitrogen Dioxide Mixture.

This method for the preparation of dinitrogen trioxide has been most extensively employed and is the one exclusively used in the work subsequently to be described. The two starting materials can readily be prepared in a pure state and may be mixed so as to emphasize the influence of either of the constituents on the behavious of the system.

A possible disadvantage of this method is in the case where a mixture of composition precisely that of N_2O_3 is required. Because of the difficulty of adding accurate predetermined quantities of the materials, method 7. above would perhaps be preferred in this case.

Rate of Formation of Dinitrogen Trioxide.

This has been investigated in nitrous acid solution at 0°C (95) and in nitrous acid/acetate buffer solutions at 25°C (96).

CHAPTER III.

THE GAS PHASE EQUILIBRIUM.

Qualitative Considerations.

Towards the end of the last century it was not certain whether dinitrogen trioxide existed as such in the vapour phase. No one denied that it was present in the liquid phase at low temperatures since the marked colour change on cooling could not other wise be explained.

Ramsay and Cundall (8,57) found good agreement between their measured vapour density for a mixture of nitric oxide and nitrogen dioxide and that calculated for a simple mixture of the two gases. They concluded from this that dinitrogen trioxide was absent from the vapour phase. This conclusion was also reached by Dixon and Peterkin (58,59) and Luck (60). Raschig (61,62,63) and Lunge (3,19, 64-69) however came to the opposite conclusion mainly from consideration of chemical evidence. Discussion was long, heated and bitter, and was not resolved until further proof of the existence of dinitrogen trioxide in the vapour phase became available (70 -78).

Quantitative Work.

Jones(81) was the first to seek a quantitative expression for the dissociation of dinitrogen trioxide. The method he used was measurement of vapour density. The material was extensively dried with phosphoric oxide by Baker (79,80), and this work further sought the phenomena found by Baker (l.c.). Since Baker's work had suggested the formation of the N_4O_6 molecule, Jones was largely preoccupied with the possible behaviour of this molecule and did not consider the reaction hereinafter studied. It may be said here however, that Jones failed to substantiate the postulated presence of N_4O_6 molecules and obtained no vapour density values above 35 (N_2O_3= 38 theoretically), his results agreeing roughly with those expected from this work. It should also be noted here that in a system involving molecules of N_4O_6, N_2O_3, N_2O_4, NO_2, and NO all in equilibrium it is theoretically impossible for the system to be solved if no measurements other than initial concentrations and pressures be taken. (See Chapter VIII, page **42**).

Work of Wourtzel.

Wourtzel (53) measured the pressures of mixtures containing oxygen with an excess of nitric oxide.

With the help of his own equilibrium constants for the reaction

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad (82)$$

he was able to calculate a constant for the equilibrium.

$$NO + NO_2 \rightleftharpoons N_2O_3$$

Two experiments only were performed. In each of these the concentration of dinitrogen trioxide was rather low (partial pressure of N_2O_3 being approximately 5mm of mercury in each case) and his experimental error rather high (approximately 10 per cent in certain pressure readings). Readings were taken at one temperature only (25°C) in each case.

He found

$$K = \frac{p_{N_2O_3}}{p_{NO} \cdot p_{NO_2}} = \frac{1}{1100} \ \& \ \frac{1}{1190} \ mm.^{-1}$$

where K is the equilibrium constant of the reaction at finite concentration of reactants,

and p indicates the partial pressure in mm of mercury of the molecular species indicated.

Converting this to the system used in this work gives

$$K = \frac{p_{NO} \cdot p_{NO_2}}{p_{N_2O_3}} = \frac{1100}{760} \ \& \ \frac{1190}{760}$$

$$= 1.45 \text{ and } 1.57 \text{ atm.}$$

Work of Abel and Proisl.

Abel and Proisl (53) carried out rather more experiments and recorded their work in "Zeitschrift fur Elektrochemie" where they promised that a fuller account of the work would appear later in "Zeitschrift fur physikalische Chemie". This did not appear.

Using an all-glass apparatus they mixed measured quantities of nitric oxide and nitrogen dioxide by breaking a glass partition. A hollow quartz helical diaphragm, Bodenstein's Quartzmanometer, viewed by microscope was used as a null point indicator in conjunction with conventional mercury manometers.

The equilibrium constants quoted were calculated using Bodenstein's data (38) for the nitrogen dioxide-dinitrogen tetroxide equilibrium.

It is difficult to assess and compare their work with that of later workers since complete experimental details and the method for the calculation of the results are not given. Values are quoted for one experimental mixing where the N_2O_4 concentration was only 2.36×10^{-3} moles per litre. The equilibrium constants from this are calculated at 8.13°C and 34.8°C only. They are:

	K_p (atmospheres)	K^o_p (atmospheres)
8.13°C	0.56	0.54
34.8°C	2.58	2.39

K^o_p shows the value obtained by arbitrary extrapolation to zero N_2O_4 concentration. These values have been corrected to conform with the convention observed in this work. Interpolation of these figures gives a value for the thermodynamic equilibrium constant at 25°C of 1.43 atmospheres.

Another observation which can be made on the above figures is that the deviations from ideality go in the opposite direction from those found by Verhoek and Daniels and the writer. Compare figure 1. (from the above figures) with figure 25, and figure 27.

The authors state that measurements were made on other experimental mixtures and at other temperatures. However, the figures for these are not given and the following criticisms may be made.

Because of the low N_2O_4 concentration the N_2O_3 concentration will be of the same low order of magnitude; this, coupled with a calculation procedure (see chapter VIII) which amplifies errors in concentration of the reactants and particularly in the N_2O_3 concentration, will give rise to gross errors in the equilibrium constant. The extent of the error cannot be estimated without further data.

Abel & Proisl also attempted, without success, to choose between two possible routes for the reaction,

$$NO + NO_2 \rightleftharpoons N_2O_3$$

and

$$2NO + N_2O_4 \rightleftharpoons 2N_2O_3.$$

This is considered impossible by the method under discussion and is dealt with in more detail in chapter VIII.

Work of Verhoek and Daniels (54).

Like Abel and Proisl, these American workers recognised that earlier work had been rendered inaccurate by the use of materials which were not completely inert towards the gases involved. The all-glass apparatus which they used solved this problem. Again like Abel and Proisl they mixed measured quantities of nitric oxide and nitrogen dioxide by breaking a glass partition.

To measure pressure, they used a "click gauge". This again is a null point indicating instrument which is placed between the corrosive gas and the manometer system. The null point is shown by the "make" or "break" of electrical contact at the points AA (figure 3). This device may not be as accurate as the glass helix type.

In their working out of the theoretical equations for the equilibrium an error may be found: compare the final equation for p_{NO} (54) with equation 6 page 44 chapter VIII. If this error has persisted to the final equilibrium constant, the effect would be most serious; however, it is thought that this is not so since the specimen calculation (54, page 1258) shows the omission rectified.

Verhoek and Daniels intended to plot their equilibrium constants as a function of the concentration of dinitrogen trioxide assuming no dissociation ($C^o_{N_2O_3}$). But they write

$$C^o_{N_2O_3} = \frac{(p_{NO_2} + p_{NO} + 2p_{N_2O_3})}{2RT}$$

It is submitted that,

$$C^o_{N_2O_3} = \frac{(2px + 2pN_2O_3)}{2RT}$$

where p_x is the equilibrium partial pressure of nitric oxide or nitrogen dioxide, whichever is the smaller, more correctly represents the zero dissociation concentration of dinitrogen trioxide. This could make the graphical representation of their results quite meaningless.

Their work was carried out at three temperatures, 25°C, 35°C and 45°C. Eleven results were obtained at 25°C, seven results at 35°C and six at 45°C. The experimental error they assess as about ±10 per cent. The graphs of their results are shown, traced from their figures, in figure **2** . The radius of each circle represents an error of 10 per cent.

They say,

"The straight line relation between $C^{o}_{N_2O_3}$ and $K_{N_2O_3}$ seems definitely to indicate that the reaction is actually

$$NO + NO_2 \rightleftharpoons N_2O_3$$

No other reaction gives a smooth straight line. If the equilibrium constant is calculated from

$$2NO + 2NO_2 \rightleftharpoons N_4O_6$$

the 'constant' varies greatly with pressure, even though fairly regularly. If the reaction is considered to be

$$N_2O_4 + 2NO \rightleftharpoons 2N_2O_3$$

the equilibrium 'constant' shows wide and irregular variations. If the calculations are made from

$$N_2O_4 + 2NO \rightleftharpoons N_4O_6$$

the 'constant' is very irregular".

It is submitted that:

(1) Any plot involving $C^o_{N_2O_3}$ as calculated above is unreal.

(2) All the above reaction considerations are but special cases of the general scheme:

$$\begin{tikzcd}
NO + NO_2 \arrow[r, shift left, "K_2"] \arrow[d, shift left, "K_1"] & N_2O_3 \arrow[l, shift left] \arrow[d, shift left, "K_4"] \\
\tfrac{1}{2}N_2O_4 \arrow[u, shift left] & \tfrac{1}{2}N_4O_6 \arrow[u, shift left]
\end{tikzcd}$$

Equilibrium considerations usually cannot tell us anything of the course of the reactions, but only the equilibrium constants above, and then only if adequate practical measurements can be made. Verhoek and Daniels plots of "constants" from alternative reactions merely show the multiplication of the already considerable errors. The mathematical aspects of this general reaction scheme are dealt with in chapter **VIII** page **42**.

Rate of Attainment of Equilibrium in the Vapour Phase.

Leifer (56) in his work upon the exchange of N^{15} between nitric oxide and nitrogen dioxide, found an extremely rapid reaction. For

$$N^{14}O + N^{15}O_2 \rightleftharpoons N^{15}O + N^{14}O_2$$

the rate constant was found to be greater than 10^6 cc moles $^{-1}$ sec $^{-1}$ at a temperature of - 35°C and a total pressure of 2.5 cm of mercury.

Excellent support for the accuracy of his work was provided by investigations of other reactions involving nitrogen oxides, whilst more recently Begun and Melton (91), in similar work, show good agreement.

Equilibrium in the Presence of Water.

This is itself an extensive subject and little discussion can be allowed here. However, recently Klemenc (152) has used the equilibrium values of Abel and Proisl in defining the system

$$HNO_3/HNO_2/NO_2/N_2O_4/N_2O_3/NO/H_2O$$

CHAPTER IV.

PROPERTIES OF THE LIQUID AND SOLID.

1. General.

Just as much of the early work on the existence of gaseous dinitrogen trioxide was rendered uncertain and in some cases misleading by the use of impure materials and less exact physical methods, so the early work on the liquid and solid material was clouded, although the existence of N_2O_3 was not really doubted. No agreement amongst the early workers existed even on the colour of N_2O_3. Various shades of dark blue and green were reported for the liquid, whilst the colour of the solid has been given as both pale blue and pale green. No modern summary of the colour changes has yet appeared. The following is a summary of the colour observations made during the described work.

Throughout most of the region of stability of the liquid, its colour is an intense royal blue, only becoming tinged with green when the temperature rises to where the formation of nitrogen dioxide becomes appreciable (i.e. towards 0°C). When the liquid freezes (about -100°C: see chapter IX page 102) the intense colour disappears and there remains only a very pale blue tinge.

2. Effect of Phosphorus Pentoxide.

Some rather curious results have been obtained by physico-chemical measurements on "extra dry" dinitrogen trioxide. Baker (79,80) suggested that on prolonged drying N_2O_3 underwent association with the formation of the N_4O_6 molecules. His evidence was based on the fact that when liquid dinitrogen trioxide was stored in a sealed tube with phosphorus pentoxide for a period of months or years, the vapour density then varied between 38.1 and 62.2. The molecular weight of this material (by depression of freezing point of dry benzene) gave values of 83,83,and 95. Its boiling point was found to be 43°C at a pressure of 757mm.

Baker also found a similar effect with P_2O_5 drying of dinitrogen tetroxide. Three years drying gave a product having a boiling point of 69°C.

Other workers (81,156,157) have attempted to repeat Baker's work without success, and it has been suggested that the following take place,

$$P_2O_5 + 2N_2O_3 \longrightarrow P_2O_5.2NO + N_2O_4$$

$$P_2O_5 + N_2O_4 \longrightarrow P_2O_5.2NO + O_2$$

3. Equilibrium.

No experimental work has been performed to evaluate the position of equilibrium at low temperatures in the liquid or solid phases, no doubt because of the extreme technical difficulties. However some idea of it may be gained from extrapolation of existing data and in particular that evaluated in this work.

For $K = \dfrac{p_{NO} \times p_{NO_2}}{p_{N_2O_3}} = 10^{-2}$, the temperature would probably be about - 48°C. It is considered then that for most purposes a mixture of composition N_2O_3 in the liquid phase and athigh pressures would exist largely as N_2O_3 molecules at temperatures below -50°C. This figure has been calculated from data presented in this work and discussed more fully in a later chapter. In calculating the temperature at which the N_2O_3 species greatly predominates it has been assumed that the equilibrium in the gas phase and also in solution is ideal. Considerable deviations from ideality will exist however (see chapter VIII) and the extrapolation may contain a large error.

At lower temperatures still, in the solid state, there is surer evidence that the dissociation products of N_2O_3 are still of detectable concentration. Leifer (56) showed that when solid N_2O_3 containing a high isotopic content of N^{15}, at -118°C, was put into contact with nitric oxide for "several minutes", N^{15} was detected in the resulting NO. This led Leifer to suggest that N_2O_3 was unstable even at -118°C and could exist only in equilibrium with its components.

The work of Leifer supports qualitatively the conclusions of Purcell and Cheeseman (89) who found that on freezing mixtures of N_2O_3 composition (slightly NO rich) there always tended to remain a pressure of at least two atmospheres of nitric oxide until all the N_2O_3 was solid.

Other low temperature equilibria have been reported in this system. Francesconi and Sciacca (40) conclude from their work that, at -100°C, N_2O_3 undergoes the reaction

$$N_2O_3 \;{+\!\!\!\!\longrightarrow}\; 2NO \;{+\!\!\!\!\longrightarrow}\; 2N_2O_4$$

At still lower temperatures, at - 150°C, they claim the reduction of N_2O_4, thus

$$N_2O_4 + 2NO \longrightarrow 2N_2O_3$$

Their work was used by Ingold and Ingold (90) as evidence leading to the structures of dinitrogen trioxide and tetroxide.

4. Phase Studies.

Three groups of workers have sought to elucidate the position of the condensation point for various gas compositions. They are Guye and Drouginine (111), Baume and Robert (108) and Purcell and Cheeseman (89).

Baume and Robert measured the vapour pressures of a series of compositions at several temperatures in the region of 0°C ± 24°C. Baume and Robert extrapolated their curves to 100 per cent N_2O_3 composition, and found that the "boiling point" of pure N_2O_3 was about - 27°C. Purcell and Cheeseman carried out a similar series of experiments over a rather wide range of temperatures and obtained similar results. Both the latter groups of workers realised the importance of using pure materials and unreactive apparatus.

More recently, a group of American workers (109) have studied the vapour pressures of dinitrogen tetroxide-nitric oxide mixtures over a short range of compositions and temperatures, and have expressed their results in mathematical form. Vapour pressure/ temperature curves are shown in figure 5.

The solidus curve has been investigated by four groups of workers; namely, von Wittorff (103,104), Baume and Robert (108), Whittaker et al (109), and this writer.

Von Wittorff measured the freezing points of several compositions lying between 100 per cent NO_2 and 100 per cent N_2O_3. By a rather difficult interpolation he concluded that the system showed a eutectic at 88 per cent N_2O_3 by weight at a temperature of -112°C. Helbig (26), in a single determination also found a eutectic temperature of - 112°C.

The curve drawn from the work of Baume and Robert does not lie very close to that drawn by von Wittorff, but agrees closely in the matter of eutectic composition and temperature. In all Baume and Robert took freezing point measurements of a total of 18 different compositions. Although it might be thought that their results would be inaccurate because they used an isopentane thermometer of high heat capacity, in fact they are well supported at higher temperatures by the work of Whittaker et al. and the writer.

The position of the solidus curve after von Wittorff and Baume and Robert was most in doubt in the region between the eutectic and "pure N_2O_3". In particular the freezing point of pure N_2O_3 is given variously as -97°C (Baume and Robert) and -103°C (von Wittorff). The shape of the curve at this point is also dubious; the humped configuration shown in Gmelin (110) being apparently without scientific foundation.

5. Crystal Structure of Solid Dinitrogen Trioxide.

By the use of single crystal X-ray photographs, Lipscomb and Reed (92) attempted to solve the crystal structure of N_2O_3. At - 115°C they found that the unit cell was tetragonal with

$a = 16.4$ Å

$c = 8.86$ Å and contained 32 molecules of N_2O_3. Complete hkl data showed that the space group was D_4^{10} - I4,2.

On cooling the crystal to - 125°C a marked transition was observed, where the single crystal reflections split into a powder pattern. A complete elucidation of the molecular structure could not be made and a disordered crystal was postulated.

CHAPTER V.

CHEMICAL PROPERTIES.

The chemistry of dinitrogen trioxide is largely that of its dissociation products, nitric oxide and nitrogen dioxide, since even at room temperature this decomposition is extensive. The properties of these substances must therefore be constantly borne in mind whilst the chemistry of their parent is being considered. The chemistry of the system is further extended by the wide series of reactions undergone by nitric oxide and nitrogen dioxide. Both may themselves associate and dissociate, both may be reduced and oxidised, and both show free radical properties. A wide and complex series of reactions occurs between each compound and other compounds both inorganic and organic.

Many reported reactions involving dinitrogen trioxide may be considered doubtful since it is not yet known how pure N_2O_3 may be made. Earlier workers may have been in error because of the presence of water in their material. Until the limits for the existence of pure N_2O_3 are fully worked out most reactions ascribed to this molecular species cannot be regarded as completely certain. However, reactions of the equilibrium system are certainly of some interest.

It has long be observed that whilst dinitrogen tetroxide reacts with alkali to give a mixture of nitrite and nitrate, dinitrogen trioxide gives only nitrite in similar conditions. The product of reaction is again the same with metal oxides, Boh (114) using this method for the production of anhydrous nitrites suggests

$$CuO + N_2O_3 \longrightarrow Cu(NO_2)_2$$

It has been reported (112) that in the case of mercury the reaction product with N_2O_3 is a mixture of nitrite and nitrate.

With phosphorus trichloride, Noyes (113) has reported the production of nitrous oxide.

More interesting from the point of view of the structure of N_2O_3 was the report of a complex $BF_3.N_2O_3$ by Backman and Hokama (115). Another such interesting complex is $N_2O_3.3SO_3$ which has been shown to be $(NO)^+_2(S_3O_{10})^=$ (162,163).

Work has been carried out on the behaviour of N_2O_3 in certain organic solvents.

In chloroform it has been found that (116) N_2O_3 dissolved at -20°C apparently without reaction to give a blue solution. At 0°C, on shaking this solution with water, the blue colour distributes itself between the two liquids.

In carbon tetrachloride (117) N_2O_3 dissolves at -40°C apparently without reaction to give a blue solution. The same workers report that the addition of stannic chloride to this solution gives rise to the disappearance of the colour and the formation of an addition compound.

Reports can also be found of the solution of N_2O_3 in benzene and toluene again without record of any reaction (79,80,105).

Dinitrogen Trioxide as an Intermediate.

It has been postulated (118) that N_2O_3 is an intermediate in the reactions of Aromatic Nitration and N-nitrosation (including deamination and diazotisation). It has also been suggested that it is involved in the formation of nitrito- and nitro- cobalt III complexes (119), and also in the reactions of nitric acid in the presence of urea.

(i) Aromatic Nitration.

It has been shown that nitrous acid acts as an anticatalyst in aromatic nitration, in the manner described briefly below.

In the presence of excess nitric acid, nitrous acid exists essentially in the form of N_2O_4. This N_2O_4 is ionised nearly completely in the pure nitric acid solvent, but only as a weak electrolyte in organic solvents containing nitric acid.

$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

Whence the nitrate ions now deprotonate the important nitric acidium ion,

$$NO_2.OH_2^+ + NO_3^- \rightleftharpoons NO_2\cdot OH + HNO_3$$

With higher concentrations of nitrous acid in the presence of some water a stronger form of anticatalysis sets in

$$2N_2O_4 + H_2O \rightleftharpoons N_2O_3 + 2HNO_3$$
$$NO + NO_2 \rightleftharpoons N_2O_3 \rightleftharpoons NO^+ + NO_2^-$$

The nitrite ion, being the stronger base, is much more effective in deprotonating than is the nitrate ion, and thus, even more depresses the rate of reaction.

(ii) Deamination and Formation of Nitrosamines of Aliphatic amines.

It has been shown that, for the deamination of primary aliphatic amines and the formation of nitrosamines from secondary aliphatic amines, for moderate conditions of acidity

$$\text{The rate} \propto [\text{free amine}][\text{undissociated nitrous acid}]^2$$

Hammett (120) suggested that two molecules of nitrous acid interact first to give a two nitrogen atom nitrosating agent, which could only be N_2O_3.

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

The attack of the N_2O_3 on the amine would be the rate determining step.

(iii) Aromatic Diazotisation.

Here again it can be shown that the nitrosating agent is N_2O_3, by methods similar to the above. Also, on many occasions, the N_2O_3 is visible as a blue colour in the aqueous nitrous acid.

Certain exceptions to types (i), (ii) and (iii) above have been found (119,96,121).

(iv) Formation of Nitro- Cobalt Complexes.

Pearson et al (119) investigated the reaction,

$$[Co(NH_3)_5Cl]^{++} + NO_2^- \longrightarrow [Co(NH_3)_5NO_2]^{++} + Cl^-$$

and found the following mechanism.

$$[Co(NH_3)_5Cl]^{++} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{+++} + Cl^-$$

$$[Co(NH_3)_5H_2O]^{+++} + H_2O \rightleftharpoons [Co(NH_3)_5OH]^{++} + H_3O^+$$

$$[Co(NH_3)_5OH]^{++} + N_2O_3 \longrightarrow [Co(NH_3)_5ONO]^{++} + HNO_2$$

$$[Co(NH_3)_5ONO]^{++} \longrightarrow [Co(NH_3)_5NO_2]$$

(v) Behaviour of N_2O_3 in Pure Sulphuric Acid.

Gillespie et al (135,136) suggested the following ionisation of N_2O_3 in sulphuric acid (a behaviour similar to that in (i) above).

$$N_2O_3 \rightleftharpoons NO^+ + NO_2^-$$

i.e. $N_2O_3 + 3\ H_2SO_4 \rightleftharpoons 2NO^+ + H_3O^+ + 3HSO_4^-$

(vi) Reactions of Nitric Acid in the Presence of Urea.

It is known that in the presence urea, nitric acid is prevented from undergoing its normal oxidation reactions. For example in these conditions nitric acid will not oxidise organic substances, but only nitrate them. The mechanism of this is thought (158) to involve the reaction of N_2O_3 with the urea, thus

$$N_2O_3 + CO(NH_2)_2 \longrightarrow CO_2 + 2N_2 + 2H_2O$$

Addition to Olefinic Bonds.

Levy and Scaife (148) have shown that N_2O_3 adds to simple olefins to form nitro- nitroso adducts in which the nitro group attaches to the carbon atom with the greatest number of hydrogen atoms.

Reaction with Selenic Acid.

Pure selenic acid reacts with excess of N_2O_3 (160,161) to form nitrosonium hydrogen selenate $NO^+ - HSeO_4^-$, a white crystalline solid with a melting point of 80°C.

Rate of Reaction of N_2O_3 with Aqueous Alkali.

The presence of nitric oxide in an N_2O_4 gas mixture causes a very much enhanced rate of absorption in aqueous alkali, and virtually excludes the formation of nitrate ion. Instead

$$N_2O_3 + H_2O \longrightarrow 2\ HONO$$

$$2HONO + 2OH^- \longrightarrow 2H_2O + 2NO_2^- \qquad (167,168)$$

Reaction of N_2O_3 with Alcohols (169,170).

If the temperature of the reaction is kept low to retard oxidation we find that no nitric acid is formed but only the nitrous ester. The reaction may be represented:-

$$ROH + N_2O_3 \longrightarrow RONO + HONO$$

$$ROH + HONO \longrightarrow RONO + H_2O$$

CHAPTER VI.

PHYSICAL PROPERTIES.

(i) Ultra Violet and Visible Spectroscopy.

Certain absorption bands in the UV spectrum of a gaseous mixture of nitric oxide and nitrogen dioxide can be attributed to N_2O_3 (122-125). Their maxima lie at

3843 Å
3682
3539
3509
3417
3386
3305
3279
2200 to 2400 band

Ramsay (126,127) found that liquid N_2O_3 at - 50°C possessed an absorption band from 544 to 590mμ.

Solutions of N_2O_3 in toluene (with concentrations varying from 0.32 to 0.67 mole/litre toluene) showed transmission maxima at 475mμ.

(ii) Infra-Red Spectroscopy.

D'Or and Tarte (107) give the following table of new bands which appear on the addition of nitric oxide to a gaseous NO_2-N_2O_4 system.

cm^{-1}	
3413	
3257	
3125	
2915	
2681	
2597	
2164	
2053	
(1876	NO)
1830	X
1700	
1615	X
1309	X
990	
770	X
430	X

The bands marked X are very much more intense than the others and are thought to represent the fundamental frequencies.

(iii) Magnetic Susceptibility.

N_2O_3 has been found to be diamagnetic.

Specific susceptibilities (χ) have been investigated by two workers whose results are summarised in the following table.

$\chi_{N_2O_3}$	Conditions	Worker
-0.303×10^{-6}	liquid at -16°C and 770 mm	Pascal (128,129)
-0.21×10^{-6}	liquid at 18°C under pressure	Soné (130)

(iv) Electrical Conductivity.

Wieland (131) placed platinum electrodes beneath the surface of liquid N_2O_3. With a potential difference across them of 20,000 volts he found that the electrodes could be brought as near as 0.1mm without any indication of conductivity.

(v) Solubility.

Some account of the behaviour of N_2O_3 in organic solvents has already been given (see chapter **V** page **30**).

Many workers have observed that N_2O_3 is insoluble in liquid oxygen, liquid nitrogen and liquid air. Von Wittorff (103,104) found that solid N_2O_3 was insoluble in liquid nitric oxide. Ramsay (126,127) found that N_2O_3 was miscible with liquid nitrous oxide and formed a deep blue solution.

(vi) Raman Spectroscopy.

Raman shift observations (135) on solutions of N_2O_3 in pure sulphuric acid have led to a suggestion involving the ionisation of N_2O_3,

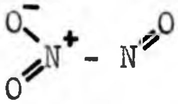
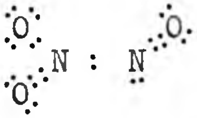
$$N_2O_3 \rightleftharpoons NO^+ + NO_2^-$$

in that medium.

CHAPTER VII.

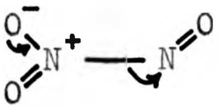
THE STRUCTURE OF DINITROGEN TRIOXIDE.

In attempting to deduce the structure of N_2O_3, two possible configurations must be considered

I  i.e. 

II $O=N-O-N=O$ i.e. $\ddot{O}::N:\ddot{O}:N::\ddot{O}$

Ingold and Ingold (90) have construed the results of Levy and Scaife (148) to favour structure I. They consider that the attack of olefinic bonds by N_2O_3 occurs in two stages, first nitronium, then "monomeric hyponitrite ion" adding. The necessary polarisation is shown below



The ready dissociation of N_2O_3 tends to favour structure I since it is known that such N - N bonds tend to be rather weak (90,149,150) although structure II is in no way precluded.

Structure I is also favoured by the work of Francesconi and Sciacca (40) who find the oxidation of N_2O_3 at -100°C and the reduction of the resulting N_2O_4 by NO at -150°C.

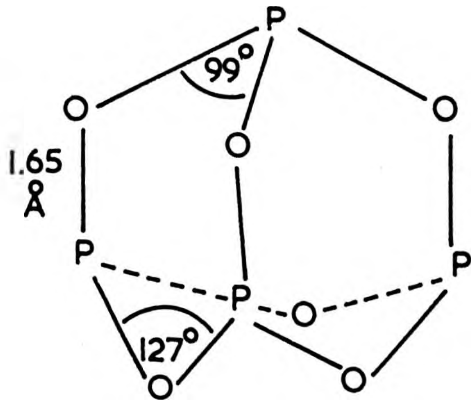
Structure I is not favoured by the work of Leifer (56) who finds that there exists a very rapid exchange between

$$N^{14}O + N^{15}O_2 \rightleftharpoons N^{15}O + N^{14}O_2$$

indicating the equivalence of each nitrogen atom. These results are supported by those of Begun and Melton (91).

Infra-Red Spectroscopy of the gaseous equilibrium mixture (107) supports structure I in a very convincing manner, although at lower temperatures, X-ray crystallography of the solid was inconclusive.

Little can be deduced from a comparison with the equivalent oxide of phosphorus. Phosphorus trioxide, so called, exists in the solid, solution and vapour states as its dimer P_4O_6 which possesses the structure (151)



The extraordinary stability of this dimer leads one to think that the dimer N_4O_6 may indeed be stable, particularly in the solid state, although little evidence for this is available. The change of colour from dark blue to very pale blue as the liquid solidifies, seems to indicate something of this nature. However, a similar colour change is observable with nitrosyl chloride which changes from very dark red to pale yellow on solidification, and yet the existence of a dimer of this has not been suggested.

In certain circumstances N_2O_3 can be considered to behave in an ionic form $NO^+ NO_2^-$, but in media of low dielectric constant the contribution of this form has been found to be insignificant. No figures for the specific conductivity of the liquid are available.

CHAPTER VIII.

MEASUREMENT OF THE EQUILIBRIUM CONSTANT.

(i) Theoretical Considerations.

We wish to express quantitatively the equilibrium relations which exist in a system consisting of molecules of NO, NO_2, N_2O_4, N_2O_3 and possibly also N_4O_6.

(A) Let us assume we have a mixture containing the equilibria:

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad (\alpha)$$

having equilibrium constant

$$K_1 = \frac{p^2_{NO_2}}{p_{N_2O_4}} \qquad (1)$$

at constant Temperature T,

where p_{NO_2}, $p_{N_2O_4}$ indicate the partial pressures at equilibrium of the molecular species indicated:

and $$N_2O_3 \rightleftharpoons NO_2 + NO \qquad (\beta)$$

having equilibrium constant

$$K_1 = \frac{p_{NO_2} \cdot p_{NO}}{p_{N_2O_3}} \qquad (2)$$

at constant Temperature T

where p_{NO_2} , p_{NO}, $p_{N_2O_3}$ indicate equilibrium partial pressures as before.

We are required to find the value of K_2. In addition to equation (1) above, we have,

$$\overset{o}{p}_{NO} = p_{NO} + p_{N_2O_3} \qquad (3)$$

where $\overset{o}{p}_{NO}$ is the partial pressure the nitric oxide would have in the absence of any N_2O_3 formation,

and $p_{N_2O_3}$ is the equilibrium partial pressure of the N_2O_3 species.

Also

$$2\overset{o}{p}_{N_2O_4} = 2p_{N_2O_4} + p_{NO_2} + p_{N_2O_3} \qquad (4)$$

where $\overset{o}{p}_{N_2O_4}$ is the partial pressure of N_2O_4 in the system, assuming the absence of dissociation and reaction.

Also

$$P = p_{N_2O_4} + p_{NO_2} + p_{NO} + p_{N_2O_3} \qquad (5)$$

where P is the total pressure of the system at equilibrium.

From (5)

$$2p_{NO} = 2P-2p_{N_2O_4}- 2p_{NO_2}-2p_{N_2O_3}$$

Substituting for $2p_{N_2O_4}$ via (4)

$$2p_{NO} = 2P - 2p^{o}_{N_2O_4} + p_{NO_2} + p_{N_2O_3} - 2p_{NO_2} - 2p_{N_2O_3}$$

$$= 2P - 2p^{o}_{N_2O_4} - p_{NO_2} - p_{N_2O_3}$$

Substituting for $p_{N_2O_3}$ via (3)

$$2p_{NO} = 2P - 2p^{o}_{N_2O_4} - p_{NO_2} - p^{o}_{NO} + p_{NO}$$

$$p_{NO} = 2P - 2p^{o}_{N_2O_4} - p_{NO_2} - p^{o}_{NO} \qquad (6)$$

[Contra Verhoek & Daniels (54)]

From (5) via (3) and (1)

$$P = \frac{p^{2}_{NO_2}}{K_1} + p_{NO_2} + p_{NO} + p^{o}_{NO} - p_{NO}$$

$$\therefore \quad P = \frac{p^{2}_{NO_2}}{K_1} + p_{NO_2} + p^{o}_{NO}$$

$$\therefore \quad p^{2}_{NO_2} + K_1 p_{NO_2} + K_1(p^{o}_{NO} - P) = 0 \qquad (7)$$

whence

$$p_{NO_2} = \frac{-K_1 \pm \sqrt{K_1^{2} - 4K_1(p^{o}_{NO} - P)}}{2}$$

Since $P > p^{o}_{NO}$ always, and for real roots and pressures

$$p_{NO_2} = \frac{1}{2}\left[-K_1 + \sqrt{K_1^2 + 4K_1\ (P - p^{o}_{NO})}\right] \qquad (8)$$

From (3), (6) and (8), K may be calculated via (2)

(B) If the reaction

$$2N_2O_3 \rightleftharpoons N_2O_4 + 2NO \qquad (\gamma)$$

is a valid equilibrium in addition to (α) and (β)

we have

$$K_3 = \frac{p_{N_2O_4} \cdot p_{NO}}{p_{N_2O_3}} \qquad (9)$$

But from (1)

$$p_{N_2O_4} = \frac{p_{NO_2}}{K_1}$$

$$K_3 = \frac{1}{K_1} \cdot \frac{p_{NO_2} \cdot p_{NO}}{p_{N_2O_3}} \qquad (10)$$

$$= \frac{K_2}{K_1}$$

If reaction (γ) is valid and (β) is not, equations

(1), (3), (4) and (5) are still correct and so therefore are (6) and (8). K_3 can therefore be calculated from the same equilibrium partial pressures. It should be noted that the calculation of either equilibrium constant, K_2 or K_3, and the variation of these values with the concentration of reactants or products, provides no evidence regarding the probability or otherwise of reactions (β) and (γ). This point has not always been fully realised in the past (54),(81).

(C) If we have, in addition to reactions (α), (β) and/or (γ) the formation of N_4O_6 molecules such that

$$N_4O_6 \rightleftharpoons 2N_2O_3 \qquad (\delta)$$

we shall have a new set of primary equations which are simultaneous at equilibrium.

$$K_1 = \frac{p_{NO_2}}{p_{N_2O_4}} \qquad (1)$$

$$K_4 = \frac{p_{N_2O_3}}{p_{N_4O_6}} \qquad (11)$$

$$p^{o}_{NO} = p_{NO} + p_{N_2O_3} + 2p_{N_4O_6} \qquad (12)$$

$$2p^{o}_{N_2O_4} = 2p_{N_2O_4} + p_{NO_2} + p_{N_2O_3} + p_{N_4O_6} \qquad (13)$$

$$P = p_{N_2O_4} + p_{NO_2} + p_{NO} + p_{N_2O_3} + p_{N_4O_6} \qquad (14)$$

From (14)

$$2p_{NO} = 2P - 2p_{N_2O_4} - 2p_{NO_2} - 2p_{N_2O_3} - 2p_{N_4O_6}$$

Substituting for $2p_{N_2O_4}$ via (13)

$$2p_{NO} = 2P - 2p^{o}_{N_2O_4} + p_{NO_2} + p_{N_2O_3} + 2p_{N_4O_6} - 2p_{NO_2} - 2p_{N_2O_3} - 2p_{N_4O_6}$$

$$= 2P - 2p^{o}_{N_2O_4} - p_{NO_2} - p_{N_2O_3}$$

Substituting for $p_{N_2O_3}$ via (12)

$$2p_{NO} = 2P - 2p^{o}_{N_2O_4} - p_{NO_2} - p^{o}_{NO} + p_{NO} + 2p_{N_4O_6}$$

$$p_{NO} = 2P - 2p^{o}_{N_2O_4} - p_{NO_2} - p^{o}_{NO} + 2p_{N_4O_6} \qquad (15)$$

From (14) via (1)

$$P = \frac{p^{2}_{NO_2}}{K_1} + p_{NO_2} + p_{NO} + p_{N_2O_3} + p_{N_4O_6}$$

Substituting for $p_{N_2O_3}$ via (12)

$$P = \frac{p^2_{NO_2}}{K_1} + p_{NO_2} + p^o_{NO} - 2p_{N_4O_6} + p_{N_4O_6}$$

$$= \frac{p^2_{NO_2}}{K_1} + p_{NO_2} + p^o_{NO} - p_{N_4O_6}$$

$$\therefore \quad p^2_{NO_2} + K_1 p_{NO_2} + K_1(p^o_{NO} - p_{N_4O_6} - P) = 0$$

whence for real roots and since $P + p_{N_4O_6} > p^o_{NO}$

$$p_{NO_2} = \tfrac{1}{2}\left[-K_1 + \sqrt{K_1^2 - 4K_1(P + p_{N_4O_6} - p^o_{NO})}\right] \qquad (16)$$

whence

$$p_{N_2O_3} = \tfrac{1}{4}\left[-K_4 + \sqrt{K_4^2 + 8K_4(p^o_{NO} - p_{NO})}\right] \qquad (17)$$

These equations cannot by themselves be solved for K_2 and K_4. Section A may be regarded as the special case of section C, i.e. when $p_{N_4O_6} = 0$

(D) If we have the reaction

$$N_4O_6 \rightleftharpoons N_2O_4 + 2NO \qquad (\varepsilon)$$

in addition to (α), (β), (γ) and (δ), the system is again insoluble for the desired constants.

The presence of N_4O_6 molecules in the absence of N_2O_3 is considered chemically improbable.

It has been shown that if N_2O_3 undergoes an association reaction to form N_4O_6 molecules and is in equilibrium with them, it is impossible to calculate the required equilibrium constants. If, however, the value for any calculated constant shows a large progressive drift with concentration of any reactant or product this may be evidence of the possible formation of N_4O_6. The probable direction of drift can be ascertained from the above equations. This is discussed more fully in relation to experimental results in chapter VIII (4) page 83.

The dissociation of nitrogen dioxide

$$2NO_2 \rightleftharpoons 2NO + O_2$$

has been extensively investigated (38,83 - 88). It may be said that the dissociation is negligible below 150°C. For this reason it has been omitted from the above theoretical discussion.

2. Experimental Details.

(i) Requirements and Apparatus Design Considerations.

It is necessary to design an apparatus which will prepare the reacting gases in a highly pure state, convey these gases to the reaction vessel in accurately known quantities, and measure the final equilibrium pressure under conditions of constant temperature in a range between 5°C and 45°C.

We wish to prepare nitric oxide and nitrogen dioxide, both in a high state of purity. Since nitric oxide readily reacts with oxygen it must be made in a vacuum system, and as nitrogen dioxide is normally produced in the presence of oxygen, good vacuum is again required to remove all traces of oxygen. The apparatus used to handle the nitrogen dioxide must also be completely inert.

An important question upon which the design of the apparatus hung was, under what conditions is it possible to use greased stopcocks? The use of stopcocks or mercury cut-offs would simplify the operation of the apparatus, by obviating the necessity of using all glass seals and breakable diaphragms which must be rebuilt into the glassware after each experimental run.

It was known that any normal hydrocarbon grease would be unstable towards nitrogen dioxide and of doubtful stability towards nitric oxide. The only other possibly suitable grease available at the start of this work was

Dow-Corning High Vacuum Silicone. This grease is difficult to remove from glassware which cannot be immersed in a suitable solvent, and shows a tendency to cement stopcock keys immovably in position, and so it was not looked upon very favourably.

Soon, however, samples of fluorinated hydrocarbon greases were received from Messrs. I.C.I. Ltd. (General Chemicals Division, Widnes) and were tested in various ways to ascertain their suitability. Their Florube W grease was eventually found suitable for most purposes except prolonged contact with concentrated sulphuric acid when charring tended to occur.

The grease was found to be quite soluble in N_2O_4, and to absorb large quantities of $NO2/N_2O_4$ when in contact with that vapour in a closed vessel. On evacuation however the gases could be recovered unchanged.

The grease was found to melt and run at 45°C. This prevented the use of a reaction vessel having taps to facilitate filling, mixing etc. Johnstone (132) later reported observations materially the same as these.

Another grease that was also tested was a poly-chlorotrifluorethylene high temperature grade grease manufactured by Halocarbon Products Corporation, of New Jersey, to whom we are indebted for a small sample.

This behaved in precisely the same way as the I.C.I. sample except that it showed no tendency to run at 45°C. On the other hand taps greased with it could not be moved at temperatures below about 25°C.

In handling the gases therefore, care was taken so as to allow the smallest possible contact between gas and grease before the gases reached the reaction cell, and no trace of grease whatsoever near the cell. All joints and taps were always only partially greased (see figure **6**) so as to present only a thin circle to the gas.

Stopcocks which came into contact with the corrosive gases only on the exhaust side were greased with "Apiezon L" grease.

(ii) The Vacuum System.

This is shown diagrammatically in figure **7**.

The primary vacuum was obtained by a two-stage rotary oil pump [Edwards type 2S20] of speed 20 litres per minute. A ground joint float was arranged between the backing pump and the Dunoyer type mercury vapour pump to prevent accidental movement of the pump oil into the apparatus. The mercury vapour pump was a compact two-stage unit - one jet stage, one diffusion stage - well lagged and gas fired.

In order to deter mercury vapour from being driven from the pump to the liquid air trap and backing pump, short loops were placed in the lead tubes as shown. These acted as air condensers. The loops in the lead-in tube to the McLeod Gauge were introduced to trap stopcock grease.

Liquid oxygen or liquid nitrogen was used round the trap according to availability. The trap itself was regularly removed and cleaned.

This pumping system was capable of creating a vacuum of 10^{-6} mm of mercury as recorded on the McLeod Gauge positioned as in the diagram. Under favourable conditions even lower pressures were occasionally obtained.

(iii) Generation of Nitric Oxide.

The method adopted was similar to that of Johnston and Giauque (133) and was carried out in the apparatus shown in figure 8. All taps shown in this figure were greased with Florube W. Immediately after construction, the apparatus was flushed out with a stream of dry nitrogen, evacuated and heated with a luminous flame whenever possible.

$$2KNO_2 + 2KI + 2H_2SO_4 \rightarrow 2K_2SO_4 + 2H_2O + 2NO + I_2$$

The reaction was carried out in the 1 litre flask A.

Into this whilst under vacuum was drawn a saturated solution containing potassium nitrite and potassium iodide in stoichiometric proportion. The solution had been made up with de-aerated water using 'Analar' quality potassium iodide and 'pure recrystallised' potassium nitrite, recrystallised once more. The final potassium nitrite crystals were colourless.

The nitric oxide was generated by the dropwise addition of de-aerated 50 per cent (vol/vol) sulphuric acid prepared from 'Analar' concentrated sulphuric acid. The gas from the almost explosive reaction was bubbled slowly through 90 per cent 'Analar' sulphuric acid contained in the demountable 'bubbler' trap B. Much of the main impurity of the nitric oxide produced was iodine which remained largely in the vessel A although some found its way into sulphuric acid solution. The acid also preliminarily dried the nitric oxide.

The gas next passed to a demountable trap surrounded by a bath of crushed solid carbon dioxide and acetone. Here it was cooled for about half an hour to remove iodine, water and N_2O_3 (if any). The gas was next passed through a long spiral containing pellets of potassium hydroxide to remove any remaining acidic matter

(N_2O_3, NO_2 or H_2SO_4) and from thence through another spiral containing granular phosphorus pentoxide.

The first batch of nitric oxide was used to flush out the generation system and was rejected. The gas collected from later batches in a liquid air trap formed as fine white needle shaped crystals.

Provision was also made to allow further purification by bubbling the gas through liquid nitric oxide. However it was not thought necessary to use this method since the nitric oxide produced visibly seemed purer than any hitherto reported. The fine white needles on melting gave a clear colourless liquid, the bulk of which when collected at the bottom of the vessel was very faintly tinged with blue. Whilst Johnston and Giauque (133) reported that their product was dark blue in colour, it has more recently been stated (134) that pure liquid nitric oxide possessed a "pale straw green colour".

Before being used, the fractions distilling first and last from the bulk reported above were rejected.

(iv) Generation of Nitrogen Dioxide.

Nitrogen dioxide was made in the apparatus shown in figure 9 'Analar' lead nitrate was oven dried for several days at 250°C before loading into tube A which was then sealed on to the apparatus. The glassware was 'flamed out' before preparations were started. The lead nitrate was heated electrically, in vacuo initially, and the gases evolved passed through the column of P_2O_5 to dry them.

$$2Pb(NO_3)_2 \longrightarrow 4NO_2 + O_2 + 2PbO$$

The product was collected in the trap C refrigerated with solid carbon dioxide acetone mixture, whilst the oxygen was allowed to bubble away via manometer E. Liquid oxygen was on occasion used successfully as the refrigerant for trap C. Liquid nitrogen is not to be recommended for this duty since liquid oxygen would also collect, which might give rise to hazardous internal pressures on boiling. An interesting phenomenon was observed when liquid oxygen was used as refrigerant in conjunction with very low internal pressures maintained by constant pumping. On this occasion it was found that much blue N_2O_3 was formed in the trap presumably from the high temperature dissociation of the nitrogen dioxide.

$$2\ NO_2 \rightleftharpoons 2NO + O_2$$

which would be favoured also by the low pressure. Since collisions between nitric oxide and oxygen molecules would be less frequent also at the low pressure, a proportion of the nitric oxide could react

$$NO + NO_2 \rightleftharpoons N_2O_3$$

when it was frozen out before being further oxidised. This particular run was abandoned and the method discontinued.

After the collection of an adequate quantity of N_2O_4 in trap C the heated section of the apparatus was allowed to cool and all excess oxygen pumped away. The N_2O_4 was purified twice by redistillation between traps C and D, each time rejecting the portions distilling first and last, and pumping hard on the solid material to remove all traces of oxygen. Finally ampoules (see figure 10) of accurately known weight were filled by distillation and sealed off by a blowpipe flame.

It was the intention to obtain small, accurately known quantities of N_2O_4 in easily handled form which could be liberated easily within a sealed all glass apparatus. The ampoule design shown was satisfactory. Great care was taken to use the minimum of grease on the B10 joints so that the whole of the ground surface was not covered. Another point which was taken into consideration to facilitate the removal of all grease before the final weighing was to provide a bend in the ampoule tube so that if any grease were 'washed' into the tube from the joint it would remain at the bend. Removal of all grease was effected by wiping with benzene soaked rag or filter paper on exposed surfaces and by copious benzene washing of internal surfaces. Halocarbon greases are moderately soluble in benzene.

(v) Weighing Technique.

The following details refer to the accurate weighings of ampoules and N_2O_4 used in the equilibrium experiments.

The balance used was an undamped semi-micro type mounted on cushioned feet on a slate bench. Weighing was by the method of swings using scale divisions of one hundredth of a milligram observed optically. The beam error was found to be 1/200 mg per g. and was therefore ignored.

Stainless steel weights were used which were calibrated against a standard nickel-chromium one gram weight with N.P.L. Class A certificate.

Each ampoule tube was thoroughly cleaned and rinsed many times (the final rinsings with double distilled water) before oven drying. After cleaning, the tube was stored in a desiccator over silica gel until required to be weighed. During weighing it was handled only with chamois fingers or with tongs. This procedure also applied to the filled and divided ampoules.

On weighing, once the correct weights had been added to the pan the balance was left totally enclosed for half an hour to allow air currents and other variables to settle down. After this time the balance was allowed to swing and the weight determined. Temperature, barometric pressure and relative humidity readings were taken with every weighing.

The following expression was used to calculate the mass of N_2O_4 in the ampoule:

Mass of N_2O_4

$$M_{N_2O_4} = M_o - M_o' + M_a + \frac{d_a}{d_{wts}}\left(M_{N_2O_4} - M_a\right)$$

where M_o is the observed apparent mass of the ampoule containing only air, when weighed in air and before the application of any buoyancy correction.

where M_a is the mass of air which would occupy the volume of the N_2O_4 at the time of weighing the N_2O_4.

where M_o' is the observed apparent mass of the ampoule containing N_2O_4.

where d_a is the density of the air at the time of weighing
M_o'.

and d_{wts} is the density of the weights used.

The difference in the buoyancy corrections for the mass of glass due to different conditions of temperature, pressure and humidity was calculated and found to be negligible.

(vi) <u>The Equilibrium Cell.</u>

This, and the manometer system is shown in figures 11 and 12.

The main volume of the cell was a spherical bulb of about one litre capacity. Joined to this by two tubes was a cylindrical cell 10 cm long possessing optically flat windows of 5 cm diameter. The upper part of the cylindrical cell was connected to the inside of the hollow spiral diaphragm (q.v.) Beneath the cylinder was a closed tube (C) used for freezing out the contents of the cell. Fixed to the opposite side of the spherical bulb was a tube (A) of calibrated internal dimensions. The volume of the cell system to a definite height up this tube was known. This was measured by weighing the system containing air and again containing air free water at a known temperature. Buoyancy corrections were applied and calibrated weights were used.

Tube A was also used to contain the N_2O_4 ampoules together with their steel in glass breaker. After the introduction of the ampoule tube A was joined to the rest of the apparatus with the introduction of a constriction to facilitate sealing whilst under vacuum.

The volume of the reaction vessel at equilibrium was found in the following way. It has already been mentioned that the volume of the vessel has been calibrated to any height in tube A. The distorted top of tube A after the run was cut off at a point on the calibrated tube and its volume measured by water from a burette. These figures give the total volume of the vessel from which must be subtracted the volume of the breaker and the volume of the glass from the ampoule.

(vii) The Measurement of Pressure.

This is carried out in two parts; the adjustment of the null point diaphragm approximately to zero and the measurement of the pressure equivalent to this position.

(a) Spiral Gauge.

The hollow glass spiral null point indicator (shown in figure 11) consisted of about 15 turns of fine thin walled capillary tubing sealed at its upper extremity and crowned with a mirror 5mm x 3mm. The whole was held centrally by a fine glass guide rod fitting loosely in a narrow tube possessing a by-pass hole for the rapid equalisation of pressure. For the construction of this gauge I am greatly indebted to Mr.S.G.York of the University of Bristol who has described the construction (137,138). The instrument was fully capable of withstanding a pressure difference of one atmosphere.

(b) Manometers.

The manometers were each of one metre length Chance's "Veridea" glass tubing. Both limbs were fed by a common reservoir of mercury, the pressure above which could be raised or lowered. The pressure above one limb was maintained at a high vacuum whilst the other limb was connected with the outer jacket of the spiral gauge. With the gauge at is zero position therefore, the pressure in the system was given by the difference in the two levels. Since the reservoir was common to both limbs the instrument was self compensating for changes in atmospheric pressure. The high quality glass tubing was chosen for its low distortion of the meniscus image when viewed through a microscope and also for its uniform bore giving identical meniscus depressions for each tube at all heights. Great care was taken in cleaning the mercury and manometer tubes before use so that meniscus errors would be absent. About half way through the series of experimental runs the surfaces were observed to be slightly contaminated; they were removed, cleaned throughly and replaced with fresh clean mercury.

(c) Illumination of Recording Mirror.

To attain the greatest accuracy in reading the spiral gauge the longest possible optical beam was arranged. The distance from the mirror to the screen was finally about three metres. Because of this, a particularly powerful and well defined light source was needed to produce a clear and visible image from such a small mirror at so large a distance.

The optical diagram is shown in figure **13**.

A 6 volt, 24 watt projection lamp was used to illuminate a slit, the light being focussed by lens A, a two-lens anastigmat of 7.5cm focal length. The image of the slit was directed towards the recording mirror with an 8" f2.9 aircraft camera lens (B) and brought to focus on the screen (a sheet of millimetre graph paper). The position of this image could be recorded to the nearest half millimetre.

The positions of lamp, lenses and slit could be moved in any direction so as to obtain the brightest clearest image, then held rigidly in that position. These mechanical devices are shown in figure 14

(d) Illumination of Menisci.

Each mercury meniscus was illuminated by a small diffuse slit of light obtained as shown in figure 15. A narrow slit was used so that reflections from the mercury surface would not interfere with the precise viewing of its position.

(e) Manometer Measuring Device.

It was originally intended to use a cathetometer for measuring the distance between the mercury levels, so that the operator could stand about 1 metre from them and not influence them with his body heat. A cathetometer was obtained from Messrs. Pye Ltd., Cambridge. It was found to be at fault in the following respects:

(i) On raising or lowering the telescope by the micrometer screw the axis of viewing did not remain horizontal but tilted in an irregular manner.

(ii) The vernier scale was in no way connected to the micrometer screw. Since the vernier could be read only to one tenth of a millimetre, the accuracy of the instrument was so limited.

It proved possible, however, to modify the instrument usefully. The telescope provided was designed for use at a distance of not less than one metre where the aforementioned tilting gave serious error. When the telescope was replaced by a microscope unit focussing at about 3 cm from the meniscus the tilting error could not be detected.

On moving the vernier from A (figure 17) to an added block of steel B where it could be moved through the micrometer screw, it was found that, with the aid of a lens, its zero line could be set against any line on the central shaft of the instrument with an accuracy better than one hundredth of a millimetre. The micrometer screw could be read easily to a thousandth of a millimetre.

The instrument, with modifications, is shown in figures 16 and 17.

(f) Accuracy.

The accuracy with which reaction vessel pressures could be read was limited by the spiral gauge system. Calibration showed that one millimetre division on the screen of this system was equivalent to 0.004cm of mercury. Since the screen could be read to $\frac{1}{2}$ mm, each pressure reading was therefore accurate to 0.002 cm of mercury.

(g) Thermostat Equipment.

To maintain the contents of the reaction vessel at constant temperature the whole was immersed in a bath of water the temperature of which was controlled. Only the upper portion of the spiral gauge was above the surface of the water.

The apparatus is shown in figure 18 .

The bath consisted of a galvanised steel water tank 12" x 12" x 18" which was clamped to the bench. Through the sides were fitted four brass sleeves of 5 cm diameter. These were threaded centrally and held in position by threaded rings tightened securely on rubber washers sealed with "Bostik" to make the system watertight. Filling and emptying of the tank was carried out by way of the pipe and valve at P. The outside of the tank was lagged.

A 750 watt immersion heater was provided for the rapid warming of the contents of the tank, whilst for the maintenance of low temperatures refrigeration coils were fitted. The refrigerator unit, was housed beneath the thermostat unit. Heating for the fine temperature control was provided by a Robertson lamp (250 watts nominal) and regulated by a mercury-toluene regulator and "Sunvic" control. The voltage to the lamp could be varied by a 0 to 240 volt

8 amp variable transformer and also by an additional variable resistance placed between the control unit and the lamp. A 15 watt pilot light was also fitted.

The heat imput to the bath could therefore be varied between very wide limits so that accurate temperature stabilisation could be obtained. To regulate at temperatures of $5^{o}C$ and $15^{o}C$ the refrigerator was run continuously and the heat input regulated.

Although four brass tubes were provided in the tank wall only one opposite pair was used; the remaining pair were sealed on the inside. The open tubes were joined to the cylindrical portion of the reaction vessel by rubber tubes securely fixed and made watertight. The rubber tubes were made from sheet rubber cut to size and joined to form a cylinder by vulcanising. The bore of the rubber tubes was prevented from collapsing due to the water pressure by inserting short lengths of 4 cm internal glass tubing.

Brass filter holders fitting tightly over the outer ends of the tubes formed a space which was kept dry and free from condensation by small quantities of silica gel.

The water in the bath was vigorously stirred.

Temperature variations in other parts of the apparatus were minimised by the following precautions.

(i) The manometer system between the spiral gauge and the mercury column was lagged to prevent gauge and mercury level fluctuations.

(ii) The mercury reservoir for the manometers was lagged for a similar reason.

(iii) A fan was provided to direct the air from local sources of heat away from the pressure measuring system.

(iv) The laboratory fume cupboard was switched on to provide a flow of air of more uniform temperature and to eliminate pockets of hot air.

(h) Experimental Procedure.

After the production of a satisfactory supply of N_2O_4 ampoules, and rechecking each portion of the vacuum system for the absence of leaks a 'run' was commenced. For the sake of clarity and brevity the procedure will be enumerated.

(i) Place ampoule in reaction cell together with breaker

(ii) Complete glass circuit with constriction

(iii) Evacuate system, check for leaks, and find light spot zero position in vacuo (S_z)

(iv) Generate nitric oxide and introduce into reaction vessel

(v) Freeze nitric oxide and seal constriction

(vi) Allow nitric oxide to vaporise

(vii) Fill thermostat bath and regulate at 25°C

(viii) Adjust pressure in manometers so that light spot from spiral gauge mirror reaches its zero position

(ix) Read position of upper mercury level by

(α) set microscope approximately in position

(β) Set vernier zero to nearest millimetre division on shaft scale using lens and micrometer screw

Let shaft scale reading = A) refer to specimen
) readings sheet
Let micrometer scale reading = B) (figure 23)

(γ) screw micrometer to meniscus. Rotate microscope and adjust micrometer so that microscope crosswires touch peak of meniscus. Switch off all vibrating machinery to steady meniscus; realign microscope, then restart machinery. Micrometer scale reading = C

$\therefore$ position of meniscus R = A + (C - B) with respect to the shaft scale.

(x) Switch off all motors etc. again and quickly read exact position of light spot. Reading = S. Restart motors. (Reading S was never greater than 1cm from the zero position S_z).

(xi) Note temperature near manometers (T_L)

(xii) Move microscope to lower level meniscus. Repeat readings A,B, C.

(xiii) Repeat image reading S

(xiv) Repeat temperature T_L

(xv) Repeat series of readings (ix) to (xiv) until steady pressure reading is obtained. (Occasionally under conditions of freak weather or rapid change in laboratory temperature readings did not become constant. In these cases the attempt was repeated later).

(xvi) Note precise thermostat bath temperature

(xvii) Empty thermostat bath and break N_2O_4 ampoule

(xviii) Freeze and vaporise contents of reaction vessel several times to ensure thorough mixing

(xix) Refill and regulate thermostat bath and allow two days to come to equilibrium

(xx) Repeat operations (viii) to (xvi) at each temperature 5°C, 15°C, 25°C, 35°C and 45°C allowing at least six hours equilibration time

(xxi) Drain thermostat bath and cut off top of reaction vessel lead in tube

(xxii) Measure volume of detached 'cup' and height to cut

(xxiii) Arrange atmospheric pressure zero position for spiral light spot and compare with (iii)

(xxiv) Remove used N_2O_4 ampoule, find weight of glass and internal volume

(xxv) Reload with new ampoule and repeat

(i) Spectrophotometric Measurements.

In addition to the measurement of pressure to evaluate the desired equilibrium constant it was thought desirable to obtain additional data about it from spectrophotometric measurements. The absorption spectrum of the NO_2/N_2O_4 system is adequately known (139). Nitric oxide and dinitrogen trioxide we assume to be transparent in the range used thus allowing an estimation of the equilibrium concentration NO_2 and the calculation of an equilibrium constant independent of the measured equilibrium pressure.

It was decided that for these measurements the 5461 Å yellow-green line of the mercury spectrum would be most suitable, since it is easy to produce and it avoids the region of photodissociation of NO_2.

The optical density of reaction mixture was compared with that of a solution of iodine in carbon tetrachloride in an identical cell. This solution was chosen because of its stability, freedom from ageing effects, the shape of its absorption spectrum (shown in figure 19) and the value of its extinction coefficient (141 -144).

(j) Spectrophotometric Apparatus.

The layout of this is shown in figure 19a.

(i) Light Source.

The source of light was a low pressure mercury vapour lamp of type: Siemens 230-240 volts 125 watts, with choke: G.E.C. type G31, 125 watts. The current to the lamp was supplied by an 'Advance' constant voltage transformer type MT27A, 1991. The lamp was surrounded by a water cooled jacket. (See figure 20)

Another source of light which was tried prior to the above was the Osira 125 watt L.P.M.V. lamp with its pearl glass outer casing removed. This was run in conjunction with a 125 watt choke and 12½ F condenser. The intensity of illumination was found to be less stable than that from the Siemens lamp.

In an attempt to achieve even greater voltage stability a carbon pile autovoltage stabiliser was also tried, but without success.

(ii) Standard Cell and Filter System.

The absorption strength of the solution in the standard cell was made approximately equal to the highest concentration of NO_2 likely to be obtained in the reaction vessel. It was about 8×10^{-4} molar (i.e. about 0.122g iodine per litre carbon tetrachloride). A series of solutions of iodine in carbon tetrachloride was also made up so that when filled into 1 cm cells and placed in the reaction vessel beam, the intensity of that beam was near to that of the standard beam. These were calibrated in terms of photocurrent.

This simplified, and increased the accuracy of, the measurement of the intensities.

(iii) Optical System.

Light from the mercury vapour lamp was reflected by two optically flat mirrors (see figure 19a) to lenses arranged so that parallel light beams passed through the two cells. Only the central portion of each beam was used. The required spectral line was obtained by a pair of Kodak Wratten No.77 filters which were protected by Ilford heat filters H503.

Shutters prevented light from passing through the cells except when measurements were being taken.

After passing through the cells the beams of light were received on a photomultiplier tube which was mounted on a slide such that in each end stop position of the slide the tube was accurately placed in the beam from the appropriate cell.

(iv) Photometric Measurements.

It was originally intended to compare the ratio of the resultant light intensities (from a common source) simultaneously using an instrument described by Walker and Baker (140) (see figure 21). This would have allowed the comparison measurement to have been made with an accuracy of about 0.1 per cent. However, delivery of this instrument in full working condition was not made during the course of this research and a considerably less accurate method had to be used.

A Mazda 27MI photomultiplier tube received the light to be measured. It was wired at 60 volts per stage by means of high tension batteries; the photocurrent from the tube was passed down a chain of high stability resistors as shown in figure 22. The voltage across the 3.3 KΩ resistor was used as a measure of the photocurrent. It was measured with a Cambridge portable potentiometer.

(k) Spectrophotometric Measurements: Experimental Procedure.

(i) Switch on power supply to light source at least half an hour before intended use. Prevent light passing through reaction vessel and reaching photomultiplier tube.

(ii) After completing pressure measurements at a given temperature, select iodine filter and place in reaction vessel beam.

(iii) Remove light beam shutters and measure standard cell light beam photocurrent at 5 sec intervals over a period of time. Take mean.

(iv) Slide photocell to other beam. Take photocurrent readings as before and take mean.

(v) Repeat (iii) and (iv) rapidly to check.

A similar procedure was used to calibrate the system with known concentrations of NO_2.

3. Calculation.

The readings of pressure described earlier gave rise to data sheets of the form shown in figure **23**. These readings are converted into cm of mercury pressure in the following way.

The observed position of each meniscus is given in column R whence column D is obtained as the difference between each contiguous reading. This is the observed pressure which must now be correlated with the variation of the null instrument from its known zero position (S_z). Although values D frequently showed a drift to higher pressures, this was invariably accompanied by a movement of the optical beam so that a mean value of D ($D_{av.}$) could stand with a mean value for the position of the image (S).

A pressure allowance (C_s) equivalent to (S_z-S) at 0.004 cm of mercury per millimetre scale division was then applied to $D_{av.}$ to give D_s.

Since the temperature of the manometers varied quite considerably a correction was applied at this stage to compensate for the resulting thermal expansion effects and correct to 20°C. The following expression was used:

$$C_T - 1.818\ (20 - T_L)\ D_S \times 10^{-4} \quad \text{cm Hg.}$$

This correction when applied to D_S gave the pressure in the reaction vessel in cm of mercury at 20°C (D_{STL}).

Column D_{SL} was used in only a few experiments where the manometers had a slight slope which necessitated the inclusion of a correction of 1 in 10^4.

Pressure D_{STL} was converted to international atmospheres in the following way, using a method due to Broch; who said that the corrected barometric height at 0°C,

$$H_o = H \frac{(1 - (\beta - \alpha)\ t\ )}{(\ (1 + \beta\ t)\ )}$$

where H, t are the observed height and temperature of the barometer

α is the coefficient of linear expansion for glass (8.5×10^{-6})

β is the coefficient of cubic expansion for mercury (1.818×10^{-4})

Since the D_{STL} values are all at 20°C we find that

$$H_o = 0.992924H$$

Into this we can incorporate a correction for a change in the value for the acceleration due to gravity from 981.370 (Sheffield) to 980.665 (Standard), whence

$$H_o = 0.993638H$$

Our composite factor for D_{STL} to complete the change to atmospheres now becomes 0.1307413.

Taking now the observed temperature and pressure of nitric oxide a correction may be applied to convert this to p_{NO} values for each N_2O_3 equilibrium temperature. This is shown for Run 18 in Table III.

Specimen Calculation for Run 18.

We may summarise the remaining data for this Run as follows:

(i) Height of cut above reference point = 12.1_0cm.

(ii) Volume of detached cup = 4.83ml.

(iii) Volume of glass in ampoule = 1.39ml.

(iv) Internal volume of ampoule = 2.36ml.

(v) Volume of breaker = 2.74ml.

(vi) Mass of N_2O_4 used = 0.52400g.

The cell volume to the 9.0_6cm mark has been found to be 1266.32ml. Volume of the calibrated tube from 9.06 to

12.1_0 can therefore be calculated = 3.43ml.

Volume of the system at N_2O_3 equilibrium

$= 1266.32 - 1.39 - 2.74 + 3.43 + 4.83$ ml

$= 1270.45$ ml

The volume of the system before the breakage of the N_2O_4 ampoule will be less than this by the internal volume of the ampoule,

$= 1270.45 - 2.36$

$= 1268.09$ ml.

At 45.05°C and under the recorded pressure conditions calculation of the equilibrium constant for the $N_2O_4 \rightleftharpoons 2NO_2$ reaction by the method of Giauque and Kemp (85) gives a value of

$$K_{N_2O_4} = 0.59417$$

Equation (8) page now defines the partial pressure of NO_2,

$$p_{NO_2} = \tfrac{1}{2}\left[- K + \sqrt{K^2 + 4K(P - p^{\circ}_{NO})}\right]$$

whence $p_{NO_2} = 0.14826$ atm.

$p_{N_2O_4}$ may be derived simply from the mass of N_2O_4 used and the volume and temperature of the system

$$= \frac{0.52400 \times 22.451 \times 318.21}{92.016 \times 1.27045 \times 273.16}$$

$= 0.11704$atm.

Now $p_{NO} = 2P - 2p^{\circ}_{N_2O_4} - p^{\circ}_{NO} - p_{NO_2}$ Equation (6) page 44

$$= 0.35817 \text{ atm.}$$

And $$p_{N_2O_3} = p^{\circ}_{NO} - p_{NO}$$ Equation (3) page 43

$$= 0.01183 \text{ atm.}$$

Whence $$K = \frac{p_{NO} \cdot p_{NO_2}}{p_{N_2O_3}}$$

$$= 4.48_8$$

A similar procedure was used to find each equilibrium constant. These equilibrium constants are for the measured temperatures which usually differ from the nominal temperature by a few hundredths of a degree. Slight corrections were therefore applied to each K value to align them precisely to temperatures 5.00, 15.00, 25.00, 35.00 and 45.00°C. These corrections were calculated from the van't Hoff equation plot which gave

$$\frac{\log K}{T} = 0.02 \text{ per } ^{\circ}\text{C},$$

that is, corrections to K as shown in figure 25. These corrections are very small and are barely significant.

Calculations from Spectrophotometric Measurements.

The ratio of the photocurrent voltages was used as a measure of the light absorption of the NO_2 in the reaction vessel. This was done in an attempt to compensate for the large random fluctuations in the intensity of the light source. The calibration graph (figure 24) shows the ratio of these voltages as a function of the partial pressure of NO_2. This graph was used to convert measured ratios to partial pressures which were then used in conjunction with the data previously described to calculate the equilibrium constant.

4. Equilibrium Data: Results and Discussion.

Pressure Measurements.

Experimental observations and calculated equilibrium constants are set out in Tables (III to V). The theory behind the method of calculation is given in chapter VIII page 42. and a specimen calculation on page 77. The data for the nitrogen dioxide-dinotrogen tetroxide equilibrium was calculated from the material and by the method recommended by Giauque and Kemp (85).

If we examine K_2, the equilibrium constant for N_2O_3, at any single temperature, we find quite a wide variation in the calculated values. Ideally, of course, K_2 should be independent of concentration.

Now we can seek to rationalise this variation by plotting the equilibrium constant against the concentration of each component of the mixture in turn and also the total pressure. A quite random arrangement of the points is obtained in each case except those involving the partial pressure of NO_2 (or N_2O_4) or the initial concentration of N_2O_4 ($p^{\circ}_{N_2O_4}$). In the former case the plot at each temperature appears to be linear (see figure 25) and for the purpose of calculations from it, has been treated as such. The plot involving $p^{\circ}_{N_2O_4}$ could also be linear but rather suggests a very slight curvature (see figure 26).

Another feature of these plots is that the slope in each case distinctly increases with increasing temperature.

But in spite of these unusual variations, when log K_2, as determined from zero extrapolation of the linear plots is plotted as a function of the reciprocal absolute temperature, a straight line relationship is shown. This confirms that the assumptions and conclusions arising from the van't Hoff equation are valid over the temperature region investigated. Whatever the reason for the isothermal variations in K_2 it seems clear that the extrapolated values are correct.

Factors which will influence the variations in K_2 are:- (i) experimental error, (ii) non-ideality of the gases, (iii) sorption, and (iv) the presence of some molecular species not allowed for in the calculations.

(i) Experimental Error.

The experimental errors arising from measured values are discussed and assessed in chapter VIII , page 65 The calculated experimental error in each single determination of the equilibrium constant K_2 is approximately 4 per cent. This agrees quite well with the spread of points seen on the linear plots described above.

(ii) Non-Ideality.

Using published figures for the van der Waals constants for nitric oxide, nitrogen dioxide and dinotrogen tetroxide (93,94) and assuming the N_2O_4 values to apply approximately to N_2O_3 , we may correct each partial pressure and recalculate the equilibrium constants. Such a calculation as this does in fact reduce the overall spread of the values at each temperature, but there remains the major portion of the spread which cannot wholly be accounted for.

(iii) Sorption.

If the amount of gas adsorbed on the walls of the reaction vessel to form a monolayer, be calculated, it can be seen that only small errors (always less that the experimental error) may arise in the measured partial pressures. At most of the pressures used in these experiments it is thought unlikely that any multimolecular layer adsorption will take place; although even if it did the errors arising from it would hardly be significant.

There is one aspect of sorption which is thought to be quite possibly important. This is adsorption of polar molecules on the inner surface of the glass spiral measuring device. Because of the very sensitive nature of this instrument, adsorption here may give rise to serious changes in zero position of the gauge. Changes in the elastic constants of glass and metal have already been observed by some workers (97 - 100). Extrapolation to zero pressure should eliminate these deviations.

(iv) Other Molecules.

Whichever of the "rational" methods of plotting the results is adopted we see the same trend in the slope of the line. At higher temperatures the slope is greater, presumably indicating that the deviation from ideality is greater when temperatures are higher. This being so, it seems unlikely that the deviations could be caused by association of the molecules of N_2O_3 in any manner, since such association would not be favoured by increasing temperature. However, association is not wholly precluded by the numerical data. If we examine equations (11),(15), (16) and (17) (chapter VIII page 47) we can see that the existance of N_4O_6 molecules would qualitatively influence the experimental deviation in the required direction.

To illustrate this more quantitatively table VI has been drawn up to show the recalculated values of K_1 after making the following assumptions:

(α) That $K_4 \simeq 1, 0{\cdot}1$.

(β) That K_4 is independent of concentration, since both $p_{N_2O_3}$ and $p_{N_4O_6}$ are always very low.

(γ) That $p_{N_4O_6}$ is negligibly small, since $p_{N_2O_3}$ is already small and $p_{N_4O_6} = p^2_{N_2O_3}$

The trend obtained is illustrated graphically in figure 27.

Whilst the assumptions almost certainly are false, the trend in the recalculated values will be the same whatever the precise value of K_4 , and should therefore be quite real.

The presence of N_4O_6 molecules in the equilibrium mixture cannot therefore be excluded.

It therefore seems likely that the slope of the equilibrium constant/concentration line is due to some combination of all of the above mentioned factors. Because of the nature of these factors in that their influence diminishes at lower pressure and concentration, it seems certain that the extrapolation is valid.

Comparison of these results with those of Verhoek and Daniels (figure 26) shows that although the difference is rather wide, when the circles of error are drawn their overlap over the lines drawn for this work lends agreeable support.

It should be remembered here that the graphs (figure 2) which these workers drew for their publication (54) show even greater deviations from the best straight line.

The plots of the logarithm of the extrapolated equilibrium constants of Abel and Proisl, Verhoek and Daniels and this work are shown in figure 28. Extremely good agreement exists between the Austrian and this latest work (9600 and 9530 cal. mole^{-1}).

Spectophotometric Measurements.

These are shown in Tables VI and the resulting equilibrium constants shown in figure 28d.

These measurements and results are not at all satisfactory. The errors in them are high and it cannot be said that they give more than an idea of the order of magnitude of the equilibrium constants. The use of the cathode follower bridge circuit described on page 74 and figure 21 could have made a great improvement in the accuracy and usefulness of these results.

5. Thermodynamic Functions.

A summary of thermodynamic functions for both single molecular species and equilibria is given below in Tables I and II. Other nitrogen compounds are included for comparison.

Table I. Standard Molar Entropies at 298.16°K and 1 atm.

	$S_{cal.}$	$S_{abs.}$
NO	50.34	
NO_2	57.47	59.65
N_2O_4	72.73	77.10
N_2O_3	74.56	
NOF	59.24	
NOCl	62.4	
NOBr	65.2	

entropy units

(S_{abs} is the Standard Molar Entropy under the above conditions and fully corrected for the effects of nuclear spin and random orientation of the crystal at absolute zero. S_{cal} is this entropy in its more usual form, without correction).

It is interesting to compare the standard molar entropies of N_2O_4 and N_2O_3 . In any homologous series it is usual for entropies to increase with increasing molecular size but in this case the standard entropy N_2O_3 is greater than that of N_2O_4 by 1.83 units. Too much should not be deduced from this however. It would be better to compare the S_{abs} values as the differences betweeh the nuclear spin and random orientation factors might reverse the difference between the S_{cal} values.

Table II. Molar Thermodynamic Functions for Equilibria at

at 298.16°K

Function	$N_2O_4 \rightleftharpoons 2NO_2$	$N_2O_3 \rightleftharpoons NO_2 + NO$	units
ΔH^o	13,693	9527	calories
ΔF^o	1110	385.2	calories
ΔS^o	42.21	33.25	entropy units

CHAPTER IX.

LOW TEMPERATURE CRYOSCOPY.

1. General.

Before the chemical properties of dinitrogen trioxide can be properly investigated its limits of stability must be thoroughly understood. If pure N_2O_3 does exist in the absence of its dissociation products, it must do so at temperatures approaching its freezing point. The precise shape of the freezing point/composition diagram near 100 per cent N_2O_3 will give a measurement of the extent of the dissociation, as will the vapour pressures and analysis of the vapour in this region.

As a preliminary to a more exact study of the low temperature behaviour of N_2O_3 a programme was begun to delineate the low temperature phase diagram of the system. It was also intended that some vapour pressures would be measured, but this proved impossible in the time available.

2. The Measurement of Temperature.

Throughout this cryoscopic work, temperatures were measured using a 5-junction Copper/Constantan thermocouple. The E.M.F. from this was measured with a Cambridge

Instrument Company portable potentiometer. From the standard E.M.F. tables it can be seen that for this 5-junction thermocouple at about -100°C a one degree temperature change is equivalent to about 0.15 mV which can be measured on the potentiometer to 0.01 mV. This accuracy was thought adequate for the investigation.

The thermocouple, each set of junctions embedded in naphthalene in a thin glass tube, was calibrated at 5 standard temperatures.

(i) Ice Point.

A bath of clean ice with distilled water was arranged in a Dewar vessel. When both sets of thermocouple junctions were placed in this bath, no E.M.F. was recorded. Such an ice bath was used as the fixed temperature for all subsequent measurements.

(ii) Sublimation of Solid Carbon Dioxide.

This method of obtaining a standard temperature was taken from a Reinhold publication: "Temperature, Its Measurement and Control".(145)

A coil of lacquered nichrome wire was arranged at the bottom of a Dewar vessel so that by varying the input voltage up to 30 watts of heat could be generated. The vessel was half filled with fresh pulverised solid carbon dioxide, the set of junctions placed in position and packed centrally with more pulverised "Cardice". The opening was sealed with cotton wool (see figure **29**).

Heating the solid carbon dioxide at 30 watts for ten minutes vaporised sufficient gaseous carbon dioxide to displaced all the air from the system. When heating was continued at about 7 watts the sublimation of solid CO_2 in an atmosphere of CO_2 was steadily maintained. The E.M.F. obtained was noted, as was the atmospheric pressure. The sublimation temperature was calculated from

$$T^\circ A = \frac{1349}{9.8114 - \log_{10} p}$$

where p is the atmospheric pressure in mm of mercury.

(iii) Melting Point of Carbon Disulphide.

Calibration of the thermocouple at this temperature was carried out in the apparatus shown in figure **30**.

Pure carbon disulphide was redistilled twice before being placed in the central boiling tube. With the thermocouple tube and stirrer in position the liquid was frozen to the temperature of liquid nitrogen, then put into the Dewar vessel which had also been cooled with

liquid nitrogen. The system was allowed to warm up slowly whilst time/E.M.F. readings were taken. The E.M.F. was steady at the melting point, the figure for which was taken from Brown and Manor (146) M. Pt = $-112.05\ ^\circ C$.
The melting was repeated several times.

(iv) Boiling Point of Oxygen.

The E.M.F. produced between junctions at the boiling point of oxygen and the ice point was measured within one hour of its collection from the plant at the works of The British Oxygen Co.Limited, Rotherham.

The boiling point was calculated from

$$t^\circ C = -182.970 + \frac{(21.94 \log_{10} r)}{(1-0.261 \log_{10} r)}$$

$$\text{where } r = \frac{\text{atmospheric pressure (mm Hg.)}}{760.0}$$

(v) Boiling Point of Nitrogen.

The E.M.F. produced between junctions at the boiling point of nitrogen and the ice point was also measured within one hour of collection.

The above two measurements were carried out quickly so as to minimise the uptake of atmospheric impurities which might affect the boiling points. The phenomenon is thought to be more significant in the case of liquid nitrogen an open vessel of which rapidly picks up oxygen from the air.

E.M.F's and temperatures are summarised below.

Method	Temperature °C	E.M.F. mV.
ice point	0	0
CO_2 point	-78.50	13,940
CS_2 point	-112.05	18.910
liquid oxygen	-182.89	27.275
liquid nitrogen	-195.80	28.390

From 0°C to -112°C we find that the temperature is given by

$$2.628 \times 10^{-4}t + 0.1982t + E = 0$$

that is $$t = \frac{-0.1982 \pm \sqrt{3.929 \times 10^{-2} - 10.51 \times 10^{-4}E}}{5.255 \times 10^{-4}}$$

where t is the temperature in degrees centigrade and E is the E.M.F. in millivolts.

3. Cryoscopy: Experiment I.

In this experiment it was hoped first to obtain a quantity of N_2O_3 in the cryoscope by freezing out nitric oxide from a known volume and pressure, and allowing it to react with a quantity of nitrogen dioxide from ampoules of the type described previously. After obtaining a freezing point successive small portions of NO_2 would be added and further freezing points obtained.

(i) Generation of Nitrogen Dioxide.

Some quantities of nitrogen dioxide were made by the method already described but most was made by the method of Addison et al (147) being more suited to the production of larger quantities. This entailed the heating of well dried 'Analar' lead nitrate in a steel bomb and passing the gases produced down through a water condenser fitted with a drain flask at the bottom (see figure **31**). Oxygen and NO_2 passed on and were well dried by a long column packed with phosphorus pentoxide. The product was collected in the receiving vessel as liquid N_2O_4 at -10°C.

The receiver was placed on a vacuum apparatus (see figure **32**) where the oxygen was removed, the N_2O_4 redistilled and the ampoules filled. These ampoules for cryoscopy differed from the earlier type in that they possessed a skirt which allowed them to be sealed on to a vacuum system (see figure **10b**).

(ii) The Generation of Nitric Oxide.

The nitric oxide was produced by the method already described. It was collected in the identical reaction vessel and the same spiral gauge and manometer system was used to measure its pressure. The apparatus differed in that a 3-way tap was mounted at the head of tube A (see figure 11) such that it remained beneath the water of the thermostat bath. This tap was of the mercury seal type: it was greased with Florube W grease and the crown filled with silicone grease for waterproofing. Since the volume of the system was known; for a given pressure the exact quantity of nitric oxide enclosed could be calculated.

The quantity of nitric oxide was adjusted so that when combined with the definite quantity of N_2O_4 available in certain ampoules, the resultant composition would be approximately N_2O_3.

(iii) Apparatus.

The cryoscopic apparatus for this experiment is shown in figure **34**. It was connected to the side arm of the bulb containing the measured quantity of nitric oxide.

The cryoscope itself was designed to withstand an internal pressure of at least 10 atmospheres with a safety factor of 5. This was done because it was hoped to obtain perhaps one or more freezing points of N_2O_3 enriched with NO, the pressure above which it has been stated (89) never falls below two atmospheres. It was also hoped to use the cryoscope in later experiments when the pressure would also be measured.

Naphthalene was not used in this case to hold the junctions of the thermocouple. In order to facilitate the filling of the thermocouple tube benzene was used instead. This benzene remained solid at all measured temperatures.

The cryoscope was suspended by its arms in the central Dewar vessel which was to contain liquid nitrogen. Since this Dewar was surrounded with solid CO_2 in another Dewar it could not be emptied of liquid nitrogen in the usual way; instead therefore the liquid was evaporated by a bubbling tube carrying a stream of cool dry air. As the nitrogen left the vessel it cooled the cryoscope. In this way, with small quantities of liquid nitrogen, the degree of cooling was controlled. Stirring was electro-magnetic.

(iv) Procedure.

(a) Construct apparatus with train of N_2O_4 ampoules, join to vacuum and NO system: evacuate and test for leaks.

(b) Generate required measured quantity of NO and introduce into cryoscope. Freeze out with liquid nitrogen and seal off system.

(c) Break required N_2O_4 ampoules with magnetic breaker and distil over to frozen NO.

(d) Allow system to warm to solid CO_2 temperature. Maintain at this temperature with stirring for several hours.

(e) Solidify with the evaporation of a quantity of liquid nitrogen.

(f) Allow to warm up naturally and take time-temperature readings till shape of curve indicates a wholly liquid system.

(g) Repeat (e) and (f).

(h) Break another N_2O_4 ampoule when cryoscope is at liquid nitrogen temperature and repeat (d),(e),(f) and (g).

(i) Repeat (h) etc.

4. Experiment I: Results and Discussion.

These results are shown in Table **VII** and graphically in figure **35**. A typical time and temperature curve is shown in figure **36**.

Undoubtedly the greatest error involved in the conversion of melting points to a temperature/composition diagram is that whereas the phase diagram shows the temperature at which solid first appears from the liquid phase the melting point does not give this easily. When a liquid freezes its composition just before the solid first separates is usually homogeneous when stirring is adequate. A frozen solid may not be homogeneous but may consist of discrete volumes of solid components and/or solid of eutectic composition. The precise arrangement will depend to some extent on the method of freezing: for example the disparity in composition would be amplified by a slow fall in temperature in the absence of stirring. Although in this work rapid freezing was carried out it is thought that the points may be weighted towards the eutectic temperature since over this composition region more eutectic composition would be present by itself than discrete pure solid.

The interpretation of the melting point curve also presented a probem; namely, which point on the curve represented the temperature required for the phase diagram?

In figure 37 curve AB represents the increase in temperature of the mixed solid. At B the stirrer was able to free itself and begin to move upon which the temperature fell to C and remained there for a short time whilst the rest of the solid melted. The liquid then warmed up to D.

The temperature at C was taken to be the melting point. If the solid is quite homogeneous it does represent the temperatue required for the phase diagram.

Another criticism which can be levelled against this experiment is that the main source of heat input is the thermocouple wires. About six inches away from the thermocouple junctions the temperature of the wire was about 20°C giving a temperature gradient of over 100°C over this short distance and provided with a good conductor. Elsewhere the cryoscope was provided with insulation in the form of Dewar vessels, glass and cotton wool. Ideally these wires should pass through a medium of high specific heat at temperatures near those being measured.

These criticisms were removed in the following experiment.

4. Cryoscopy: Experiment 2.

This experiment undertook to measure the freezing points of N_2O_3 - N_2O_4 mixtures starting with pure N_2O_4 and adding NO. The cryoscope was redesigned and the method of addition of the nitric oxide was changed from volumetric to gravimetric.

(i) Addition of Nitrogen Dioxide.

This was done in precisely the same way that has been described although the weighed ampoules were usually larger, containing about 20 mls of liquid N_2O_4.

(ii) Addition of Nitric Oxide.

Nitric oxide was generated as before. It was collected in ampoules of the type shown in figure 38 where the size of the bulb varied between 300 ml and 650 ml. Both designs worked well although type B proved easier to construct. The method of collection was similar to that used for N_2O_4. The ampoules were accurately weighed before and after filling and full buoyancy corrections applied to determine the precise weight of nitric oxide. Up to 3 atmospheres pressure was allowed in each bulb.

(iii) Apparatus.

The cryoscope design is shown in figure 40 . Four specimens were made before obtaining one perfect example. One cryoscope was found to fracture in rather a curious way when its contents of N_2O_3 was frozen with liquid nitrogen. The main body tube showed about 30 long fine cracks all parallel to the axis of the tube. This could perhaps be caused by strong adhesion of the N_2O_3 to the glass wall followed by contraction of the solid.

A side tube with platinum wire contact was fitted to provide a cold finger seed to prevent super cooling.
It was found unnecessary.

The thermocouple pocket was arranged to enter the liquid from beneath so that the metal leads could more easily pass through a cooler area.

The electromagnetic stirrer operated in the lead in tube.

The overall appearance of the apparatus is shown in figure 41. The large Dewar vessel was arranged in a lagged box such that it could be surrounded on all sides with solid CO_2. To cool the bath liquid (petroleum ether 40°-60°C) rapidly a copper tube containing liquid nitrogen was inserted in it and the supply of liquid nitrogen maintained. Smaller changes in temperature of the bath were arranged by varying the rate of flow of air at the temperature of liquid nitrogen through the alloy coils shown.

The bath liquid was stirred with a glass spiral stirrer connected to a remotely situated motor by Bowden Cable.

(iv) Procedure.

(a) Construct apparatus with train of bulbs, join to vacuum system, evacuate and check for the absence of leaks.

(b) Seal off.

(c) Break N_2O_4 ampoule and distil into cryoscope.

(d) Take time/temperature readings as bath liquid is cooled. First change in the slope of the cooling curve gives freezing point.

(e) Break first nitric oxide bulb. Distil into cryoscope.

(f) Cool and warm many times to ensure thorough mixing and reaction.

(g) Repeat (d), (e) and (f) with all bulbs of nitric oxide.

5. Experiment 2: Results and Discussion.

The idealised shape of the time/temperature curve is shown in figure **42**. This last curve may be explained as follows. Line AB shows the cooling of the liquid phase. At B the rate of cooling changes as the pure solid of one component begins to appear. Traversing BC follows the formation of all of the pure solid component until at C solid of the eutectic composition begins to form. Here (CD) the temperature stays steady until all the liquid of this composition has solidified, after which time the temperature once again falls (DE).

A steady temperature was usually obtained at B for at least 3 minutes. In the case of pure N_2O_4 , BCD was horizontally linear for about 20 minutes.

A typical curve is shown in figure **43**. The freezing points are shown in Table **VIII** and also in figure **44**.

The N_2O_4 end of the curve agreed well with the results of Whittaker et al and Baume and Robert (see figure **45**). Towards the N_2O_3 end of the curve the results obtained tend to deviate more from those of Baume and Robert which seem rather high. Von Wittorff's results on the other hand seem somewhat low.

Throughout the two cryoscopic experiments no freezing or melting point has been obtained below -107°C and many experiments led to the same figure of about -106°C for the eutectic temperature. This is in marked contrast to the agreement between von Wittorff and Baume and Robert at -112°C. However examination on their results shows that they did not measure any temperature below -108°C (von Wittorff) or -107°C (Baume and Robert). The measurement of freezing point near the eutectic point is always rather difficult since the true freezing point may be confused with the steady temperature as the eutectic forms. It could very well be that the lowest temperatures obtained by these earlier workers represent their measurement of the eutectic temperature. However, this must necessarily remain a matter of conjecture only, since concrete evidence cannot now be obtained.

It is considered that the extrapolated value giving the freezing point of N_2O_3 from this experiment represents the most accurate value available at this time. The experiment provides self consistent measurements which are placed reasonably with respect to the experiment 1 values described earlier. No other worker has provided adequate data to allow the extrapolation to be made. It is unfortunate, though, that the accuracy of this work did not allow a more accurate curve to be drawn from which an estimation of the degree of dissociation of N_2O_3 at its freezing point could be obtained.

The composition of the eutectic found from this work differs little from that found by the earlier workers.

But it should not be thought that the apparatus and method described in this experiment represents adequate development . The following criticisms of it should be mentioned.

(i) The temperature of the N_2O_3 tended to follow the temperature of the bath rather too quickly giving too little time to observe and measure the freezing point. A jacket of some material with poor heat conductivity could with advantage be placed round the cryoscope and thermocouple leads.

(ii) The method used to cool the bath liquid slowly is not considered ideal. A better system would be to circulate through the coil a liquid, refrigerated and thermostated in a controllable manner.

(iii) The fitting of a platinum cold finger is considered unnecessary and is also undesirable since it weakens the structure and provides points of undue strain in the glass when cooled.

CHAPTER X.

MISCELLANEOUS EXPERIMENTS.

When the region of stability of N_2O_3 becomes known more precisely, the chemical behaviour of that molecule may be investigated more easily. At the moment this chemical behaviour is complicated by the possible presence of the dissociation products of N_2O_3. Any chemical reactions performed now, must first find out the behaviour of the dissociation products under similar conditions. These reactions will continue to be relevant when the behaviour of pure N_2O_3 is known.

With this end in view a few chemical reactions were performed.

Reactions of Liquid Nitric Oxide.

In each case the contact was maintained for several hours. Analyses were by UV or IR spectroscopy.

(1) With Sodium. The course of the reaction between sodium and nitric oxide is liquid ammonia has been investigated (153,154) and the product shown to be sodium nitrosyl NaNO (154).

No reaction of this or any other kind was detected in this work.

(2) With Zinc. No reaction detected.

(3) With Diethylammonium Chloride. No reaction detected.

(4) With Diethylammonium Nitrite. No reaction detected.

Reactions of Dinitrogen Tetroxide.

Competent reviews of this topic are available (149, 150) and much work can be found in the papers of Addison and others published in the Journal of the Chemical Society from about 1949.

Reactions of Dinitrogen Trioxide.

These were carried out at the temperature of a solid CO_2/acetone bath in dry anaerobic conditions and in the presence of an excess of nitric oxide above the N_2O_3 composition (see figure 46). The duration of each reaction was about two hours. Analyses were by UV or IR spectroscopy usually, confirmed in certain doubtful cases by qualitative and quantitative analysis.

(1) With Sodium. No reaction detected.

(2) With Zinc. No reaction detected.

(3) With Copper. No reaction detected.

(4) With Diethylammonium Chloride. Substance dissolves in N_2O_3 . Residue after vacuum removal of N_2O_3 was a yellow oil which on prolonged evacuation solidfied. IR spectroscopy showed the presence of diethylammonium nitrate only.

(5) With Sodium Nitrite. No reaction detected.

(6) With Diethylammonium Nitrite. Substance dissolves in N_2O_3 . All nitrite converted to nitrate.

(7) With Zinc and Diethylammonium Nitrite. Reaction product was washed with water, the zinc removed by filtration and the solution taken down to dryness. The presence of zinc was confirmed in this residue, and also nitrate and the diethylammonium group. Nitrite was found to be absent. The IR trace is shown in figure **47** .

DISCUSSION.

No reactions have been observed with liquid nitric oxide. This may be due to the low reactivity of this oxide and/or the extremely low temperature used.

Dinitrogen tetroxide itself readily reacts with metals and this reaction rate at 0°C is increased when N_2O_3 is added up to 40 per cent (164). To account for the lack of reactions under the conditions described therefore, the most likely explanation seems to be that the rate of reaction is negligibly slow at circa -80°C.

Diethylammonium chloride with N_2O_4 reacts (165) to give diethylnitrosamine and nitrosyl chloride

$$\begin{tikzcd} Et_2N.Cl + N_2O_4 \arrow[r] & Et_2N.NO \arrow[d, "N_2O_4"] \\ & (Et_2N.NO)_2NO^{+}NO_3^{-} \end{tikzcd}$$

and eventually the addition compound shown. In the work carried out here with N_2O_3, infra-red spectroscopy did not show the presence of any nitrosamine structure; only the diethylammonium trace with the addition of nitrate peaks. Although the presence of an oil at one stage of the product recovery indicates complexity, the simplest representation of the overall change is

$$Et_2N^{+}.Cl^{-} + NO^{+}NO_3^{-} \longrightarrow Et_2N^{+}NO_3^{-} + NOCl$$

This supports the suggestion put forward by Addison et al (164) thatthe known increase in dielectric constant of N_2O_3/ N_2O_4 mixture yields more $NO^{+}NO_3^{-}$ ion pairs.

The absence of nitrite in this reaction and in that involving diethylammonium nitrite seems to indicate that N_2O_3 shows no tendency to ionise to $NO^{+}NO_2^{-}$. This provides a mechanism for the elimination of nitrite ion from

$$Et_2N^+NO_2^- + NO^+NO_3^- \longrightarrow Et_2N^+NO_3^- + N_2O_3\text{(undissociated)}$$

yet this mechanism does not seem powerful enough to bring about the oxidation of sodium nitrite.

The last of the exploratory experiments looked at the reaction of zinc with diethylammonium nitrite and N_2O_3. Here we could possibly form diethylnitrosamine as

$$Et_2N^+NO_2^- \xrightarrow[N_2O_3]{N_2O_4\text{ or}} Et_2N.NO + N_2O_3$$

whence a reaction similar to

$$Zn + 4N_2O_4 + 4Et_2\ NNO \longrightarrow 2\left[(Et_2NNO)_2NO\right]^+ + \left[Zn\ (NO_3)_4\right]^= + 2NO$$

may follow (166). However, since the products of the reaction were difficult to identify no firm conclusions can be reached about this .

CONCLUSIONS.

It should be emphasised that all the reactions described above are purely exploratory and can in no way be considered final. It is thought that they may prove useful in planning more definitive experiments at a later date.

CHAPTER XI.

FUTURE WORK ON DINITROGEN TRIOXIDE.

With the knowledge of initial concentrations and the equilibrium pressure of the vapour phase N_2O_3 system we are limited in the number of unknowns which may be calculated. Before any additional information can be obtained another parameter must be measured. Spectrophotometric measurements should provide this. A more accurate version of the method described in this work with the concomitant measurement of pressure should be adequate for the final complete elucidation of the vapour phase equilibrium.

It should then be possible to extend the method by an extension of the wavelengths used to cope with measurements of the low temperature liquid equilibrium. This has already been done for the $N_2O_4 \rightleftharpoons 2NO_2$ system by Steese and Whittaker (155).

The determination of the shape of the phase diagram in the region of pure N_2O_3 is worth repeating with more accurate apparatus. Some idea of the dissociation of N_2O_3

can be obtained from the shape of this curve. At the same time the pressure and composition of the vapour in this region can be found, which will define more closely the stability of N_2O_3. The shape of the phase diagram for the NO rich system is also of great interest.

Plots of the UV and visible absorption spectrum of liquid of N_2O_3 composition at different temperatures in the region of its freezing point will show by their constancy whether N_2O_3 is stable. Changes in the shape of these curves will show changes in the concentration of dissociation products.

The object of all this work is to define the conditions under which N_2O_3 is stable by itself both in the solid and particularly the liquid states. The conditions of stability in the presence of NO and in the absence of N_2O_4 are also of interest from the point of view of certain reactions. Once these limits have been established precise physical measurements can be made and the chemical behaviour of the molecular species N_2O_3 (or perhaps its dimer) found.

Of particular interest is the low temperature calorimetry of pure N_2O_3 . This would be the basis of extensive thermodynamic calculations.

Magnetochemical measurements on material which is known to be pure N_2O_3 would help to decide the structure of the molecule as would its dipole moment.

Chemically, N_2O_3 may behave as an interesting solvent in which "acid-base" type reactions may occur. These reactions have been found in N_2O_4 (149,150) which may act as $NO^+ NO_3^-$(i.e. nitrosyl nitrate): N_2O_3 could act as $NO^+ NO_2^-$(nitrosyl nitrite) which behaviour has already been suggested in anhydrous sulphuric acid solution (135,136).

CHAPTER X11

SUMMARY.

The chemistry of dinitrogen trioxide is reviewed.

By use of an all glass apparatus the equilibrium between nitrogen dioxide, dinitrogen tetroxide, nitric oxide and dinitrogen trioxide has been studied in the gas phase by two methods at 5°, 15°, 25°, 35° and 45°C. The equilibrium constant at each temperature has been determined over a wide concentration range, enabling thermodynamic constants to be obtained by extrapolation to zero pressure. Values of S and H are given. The significance of the results is discussed.

The melting and freezing points of mixtures of dinitrogen trioxide with dinitrogen tetroxide have been measured at concentrations 70% to 100% N_2O_3 giving temperatures in the region of -100°C. The freezing point of pure N_2O_3 was obtained by extrapolation. Criticisms of the work are made and suggestions for improvements put forward.

Some reactions of the dinitrogen trioxide system have been investigated.

CHAPTER XIII.

REFERENCES.

1. Gay-Lussac: Ann.Chim.Phys. (2), 1, 400 (1816).
2. Dulong: Ann.Chim.Phys. (2), 2, 320 (1816).
3. Lunge: Ber. 11, 1229, 1641 (1878).
4. Stenhouse, Groves: J. (1877) 544.
5. Nylander: Z. Chem. (2), 2, 66 (1866).
6. Luck: Z. analyt.Chem. 8, 402 (1869).
7. Hasenbach: J. prakt. Chem. (2), 4, 2 (1871).
8. Ramsay,Cundall: J. (1885), 188, 672.
9. Geuther: Annalen, 245, 96 (1888).
10. Ramsay: J. (1890), 590.
11. Ramsay: Z. phys. Chem. 5, 221 (1890).
12. Klemenc; Pollak: Z. anorg.Chem. 115,131 (1921).
13. Peligot: Ann.Chim.Phys. (3), 2, 66 (1841).
14. Peligot: Annalen, 39, 335 (1841).
15. Geuther, Michaelis: Ber. 4, 767 (1871).
16. Hofmann, Zedwitz: Ber. 42, 2032 (1909).
17. Meister: Ber. 5, 285 (1872).
18. Rammelsberg: Ber. 5, 310 (1872).
19. Lunge, Porschnew: Z. anorg.Chem. 7, 209 (1894).
20. Neuman, Manke: Z. Elektrochem. 35, 754 et seq. (1929).
21. Barnes: J.Indian Chem.Soc. 9, 332 (1932).
22. Thorpe, Tutton: J. (1891), 1028.
23. Helbig: Atti.Accad.naz.Lincei, (5), 11, 57 and 311 (1902).
24. Helbig: Atti.Accad.naz.Lincei, (5), 12, I, 166, (1903).
25. Helbig: Gazzetta, 33, I, 454 (1903).
26. Helbig: Z.Elektrochem. 16, 205 (1910).
27. Helbig: Z.angew. Chem. 24, 1179 (1911).
28. Fischer; Braehmer: Ber. 39, 944 et seq. (1906).
29. Briner, Durand: Compt.rend. 145, 248 (1907).
30. Briner, Durand: J. Chim.Phys. 7, 7 (1909).
31. Scarpa: Gazzetta, 37, II, 185 (1907).
32. Muller: Z. angew.Chem. 24, 1179 (1911).
33. Muller: Z. anorg.Chem. 76, 324,334 (1912).
34. Raschig: Z. angew.Chem. 24, 1320,1912 (1911).

35. Raschig: Chem. -Ztg. 35, 1096 (1911).
36. Raschig: Z. anorg.Chem. 84, 115 (1914).
37. Bodenstein et al: Z. Elektrochem. 24, 183 (1918).
38. Bodenstein et al: Z. phys.Chem. 100, ca 106 (1922).
39. Hasche: J.A.C.S. 47, 2143 (1925).
40. Francesconi, Sciacca: Gazzetta, 34, I, 417 (1904).
41. Herzfeld: Z. Physik. 8, 132 (1922).
42. Steiner: Z. phys. Chem. B15, 249 (1932).
43. Rabinowitch: Trans.Faraday Soc. 33, 283 (1937).
44. Gershinowitz; Eyring: J.A.C.S. 57, 985 (1935).
45. Trantz, Schluter: Z. anorg. Ch. 136, 1 (1924).
46. Glasstone, Laidler, Eyring: The Theory of Rate Processes McGraw-Hill, New York, N.Y.1941.
47. Gray, Yoffe: Chem. Rev. 55, 1069 et seq. (1955).
48. I.R.Beattie: Private communication.
49. Addison, Lewis: J. (1951) 2833.
50. Addison, Lewis, Thompson: J. (1949) 5211.
51. Addison, Lewis, Thompson: J. (1951) 2829.
52. Wourtzel: Compt. rend. 170, 109 (1920).
53. Abel, Proisl:Z. Elektrochem. 35, 712 (1929).
54. Verhoek, Daniels: J.A.C.S. 53, 1250 (1931).
55. Klemenc: Z. anorg.Chem. 280,100 (1955).
56. Leifer: J.Chem.Phys. 8, 301 (1940).
57. Ramsay: Chem.N. 70, 187 (1894).
58. Dixon, Peterkin: Proc. 15,115 (1899).
59. Dixon, Peterkin: J. (1899) 613.
60. Luck: Z. analyt.Chem. 8, 402 (1869).
61. Raschig: Z.angew. Chem. 17, 1783 (1904).
62. Raschig: Z.angew.Chem. 18, 1281 (1905).
63. Raschig: Z.angew.Chem 20,699,1809 (1907).
64. Lunge: Ber. 12, 357 (1879).
65. Lunge: Ber. 15, 495 (1882).
66. Lunge: Dingl.J. 233, 74 (1879).
67. Lunge: J. (1885), 457.
68. Lunge: Z.angew.Chem. 19, 1932 (1906).
69. Lunge; Berl: Z.angew.Chem. 19, 881 (1906).
70. Le Blanc: Z. Elektrochem. 12, 544 (1906).
71. Guye: Bull.Soc.Chim. France (4),5,(1909) Supplement p.61.
72. Foester,Blich: Z.angew.Chem. 23, 2025 (1910).
73. Sanfourche: Compt.rend. 172, 1573 (1921).

74. Sanfourche: Ann.Chim.(France) (10),1,49 (1924).
75. Briner,Niewiazski,Wiswald: J.Chim.phys. 19, 290 (1921).
76. Briner,Niewiazski,Wiswald: Helv.Chim.Acta. 5, 432 (1922).
77. Wieland: Ber. 54, 1776 (1921).
78. Foerster: Ber. 55, 490 (1922).
79. Baker, Baker: J. (1907) 1862.
80. Baker, Baker: J. (1912) 2341.
81. Jones: J. (1914) 2310.
82. Wourtzel: Compt.rend. 169, 1397 (1919).
83. Richardson: J. (1887) 397.
84. Bodenstein, Katayama: Z.phys.Chem. 69, 26 (1909).
85. Giauque,Kemp: J.Chem.Phys. 6, 40 (1938).
86. Ogg, Richardson, Wilson: J.Chem.Phys. 18, 573 (1950).
87. Ogg, Wilson: J.Chem.Phys. 18, 900 (1950).
88. Perrine,Johnstone: J.Chem.Phys. 21, 2202 (1953).
89. Purcell, Cheeseman: J. (1932) 834.
90. Ingold, Ingold: Nature 159, 743 (1949).
91. Begun, Melton: J.Chem.Phys. 25, 1292 (1952).
92. Reed, Lipscomb: Acta Cryst. 6, 781 (1953).
93. Kaye,Laby: 'Tables of Physical and Chemical Constants', Longmans, 1949.
94. 'Handbook of Chemistry and Physics', Chemical Rubber Publishing Co., Cleveland, Ohio, 30th Edition.
95. Hughes, Ingold, Ridd: Nature 166, 642 (1950).
96. Li, Ritter: J.A.C.S. 75, 5823 (1953).
97. Coelingh: Kolloid Z. 87, 251 (1939).
98. McBain, Bakr: J.A.C.S. 48, 690 (1926).
99. Chipalkatti, Giles: Nature, 165, 735 (1950).
100. Edelson,Robertson: Acta Met. 2, 583 (1954).
101. Ramsay, Cundall: J. (1890) 590.
102. Ramsay, Cundall: J. (1891) 1076.
103. von Wittorff: Z.anorg.Chem. 41, 91 (1904).
104. von Wittorff: J.Russ.Ges (Chem) 36, 862 (1904).
105. Berl, Winnocker: Z.anorg.Chem. 212,123 (1933).
106. d'Or, Tarte: Bull.Soc.roy.Sci.Liege: 20, 685 (1951).
107. d'Or, Tarte: Bull.Soc.roy.Sci.Leige: 22, 276 (1953).
108. Baume,Robert: Compt.rend. 169, 970 (1919).
109. Whittaker, Sprague,Skolnik,Smith: J.A.C.S. 74, 4794 (1952).

110. Gmelin: Hanbuch der anorg.Chem, Stickstoff p.742.
111. Guye, Drouginine: J.Chim.phys. 8, 500 (1910).
112. Freeman,Gordon: J.A.C.S. 78, 1813 (1956).
113. Noyes: J.A.C.S. 47, 2159 (1925).
114. Boh: Ann.Chim (France) 20, 421 (1945).
115. Backman, Hokama: J.A.C.S. 79, 4370 (1957).
116. Ssaposhnikow: J.Russ.Ges. (Chem): 32, 380 (1900).
117. Reihlen,Hake: Annalen, 452, 57 (1927).
118. Ingold: 'Structure and Mechanism in Organic Chemistry', Bell & Sons Ltd., London, 1953. pp 283, 398.
119. Pearson,Henry, Bergmann, Basols: J.A.C.S. 76, 5920 (1954).
120. Hammett: 'Physical Organic Chemistry', McGraw-Hill, New York, N.Y., 1940, p 294.
121. Dusenberg, Powell: J.A.C.S., 73, 3266, 3269 (1951).
122. Melvin, Wulf: Phys.Rev. (2), 38, 2294 (1931).
123. Melvin, Wulf: Phys.Rev. (2), 45, 751 (1934).
124. Melvin, Wulf: Bull.Amer.Phys.Soc. 9, 19 (1934).
125. Wulf: J. Opt.Soc.Amer. 25, 236 (1935).
126. Ramsay: Z.phys.Chem. 5, 225 (1890).
127. Ramsay: J. (1890) 598.
128. Pascal: Compt. rend. 148, 414 (1909).
129. Pascal: Ann.Chim.Phys. (8), 19, 20 (1910).
130. Sone: Sci. Reports Tohoku Univ.11, I, 154 (1922).
131. Wieland: Ber. 54, 1783 (1921).
132. Johnston: Disc. Faraday Soc. 17, 20 (1954).
133. Johnstone, Giauque: J.A.C.S. 51, 3194 (1929).
134. Nightingale, Downie, Rotenberg, Crawford, Ogg: J. Phys.Chem, 58, 1047 (1954).
135. Gillespie, Graham, Hughes, Ingold, Peeling: Nature, 158, 480 (1946).
136. Gillespie, Graham, Hughes, Ingold, Peeling: J.(1950) 2514.
137. Yorke: J.Sci.Instr. 22, 196 (1945).
138. Yorke: J.Sci.Instr. 28, 16 (1951).
139. Dixon: J.Chem.Phys. 8, 157 (1940).
140. Walker, Baker: J.Sci. Instr. 30, 328 (1953).
141. Gillam,Morton: Proc.Roy.Soc. A124, 604 (1929).
142. Gillam,Morton: Proc.Roy.Soc. A132, 152 (1931).
143. Walker: Trans.Faraday Soc. 31, 1432 (1935).
144. Landolt-Bornstein, Springer-Verlag, Berlin.142033.

145. 'Temperature, its measurement and control',
Amer.Inst. P., N.Y., Reinhold, 1941.
146. Brown, Manor: J.A.C.S. 59, 500 (1937).
147. Addison, Thompson: J. (1949) S211.
148. Levy, Scaife: J. (1946) 1093.
149. Gray, Yoffe: Quart.Rev. 9 (4) (1955)
150. Gray, Yoffe: Chem.Rev. 55, 1069 (1955).
151. Moeller: 'Inorganic Chenistry', Wiley, 1952,
p 63 et seq.
152. Klemenc: Zanorg.Chem. 280, 100 (1955).
153. Joannis: Ann.Chim.Phys.(8), 7, 84 (1906).
154. Zintl, Harder: Ber. 66,730 (1933).
155. Steese,Whittaker: J.Chem.Phys. 24, 776 (1956).
156. Stoddart: J. (1937) 1991.
157. Chapman,Chapman: J.(1945) 448.
158. Ephraim: 'Inorganic Chemistry', Gurney & Jackson,
London, 5th Edition (1949) p.702.
159. Addison,Lewis,Thompson: J. (1951) 2838.
160. Addison,Lewis: Quart.Rev. 9, 122 (1955).
161. Meyer,Wagner: J.A.C.S. 44, 1032 (1922).
162. Lehmann,Kluge: Z.anorg.Chem. 264, 120 (1951).
163. Gerding,Eriks: Rec.Trav.chim. 71, 773 (1952).
164. Addison, Lewis, Thompson: J.(1951) 2838.
165. Addison,Conduit,Thompson: J. (1951) 1297.
166. Addison,Hodge,Thompson: J. (1954) 1143.
167. Wayne, Yost: J.Chem.Phys. 18, 767 (1950).
168. Wayne, Yost: H.Chem.Phys. 19, 41 (1951).
169. Frankland,Farmer: J. (1901) 1356.
170. Smith: J.A.C.S. 69, 1741 (1947).

Table III.

Experimental Observations on the Dinitrogen Trioxide Equilibrium.

Run No.	N_2O_4 g.	NO atm.	Vol.* ml.	T °C	Equilib. Pressure atm.
1	1.48728	0.30129 at 25.04°C	1265.5 (1268.3)	4.96	0.58548
				15.00	0.63033
				25.04	0.68017
				35.08	0.73626
				45.12	0.79774
2	1.21744	0.34391 at 25.04°C	1263.8 (1266.9)	4.96	0.56971
				15.00	0.61060
				25.04	0.55754
				35.08	0.70769
				45.12	0.76315
4	0.84238	0.05488 at 25.04°C	1264.5 (1267.6)	4.96	0.24187
				15.00	0.26480
				25.04	0.29187
5	0.47498	0.63231 at 25.04°C	1271.5 (1274.5)	4.96	0.67870
				15.00	0.71589
				25.04	0.75555
				35.08	0.79579
				45.12	0.83678
6	0.53386	0.56959 at 25.07°C	1269.2 (1272.4)	5.03	0.63475
				15.08	0.67120
				25.07	0.70951
				35.11	0.74995
				45.12	0.79087
7	0.45360	0.67577 at 25.07°C	1268.4 (1271.4)	5.05	0.71440
				15.03	0.75387
				25.07	0.79364
				35.04	0.83449
				45.21	0.87689

*Vol. of cell containing NO, with vol. of cell containing the equilibrium mixture in parentheses.

Table III contd.

Run No.	N_2O_4 g.	NO atm.	Vol.* ml.	T °C	Equilibrium Pressure atm.
8	0.87667	0.67986 at 25.07°C	1268.0 (1271.0)	5.01	0.79707
				15.01	0.84459
				25.07	0.89641
				35.08	0.45055
				45.08	1.00728
9	0.08535	0.26059 at 25.04°C	1268.6 (1270.1)	4.86	0.26347
				15.01	0.27587
				25.04	0.28880
				35.08	0.30098
				45.12	0.31274
10	0.50110	0.36709 at 25.12°C	1269.1 (1271.9)	5.00	0.44680
				15.01	0.47492
				25.12	0.50559
				35.02	0.53658
				45.10	0.56892
11	2.10492	0.12580 at 24.97°C	1272.1 (1274.5)	15.00	0.60501
				24.97	0.65907
				35.01	0.72206
				45.01	0.79228
13	1.34501	0.05856 at 24.96°C	1273.1 (1275.5)	4.95	0.34848
				14.92	0.37960
				24.96	0.41736
				35.12	0.46101
				45.12	0.50843
14	1.33390	0.49548 at 25.04°C	1270.7 (1273.1)	4.95	0.72332
				14.97	0.77215
				25.04	0.82707
				34.99	0.88559
				45.04	0.94984
16	2.10885	0.38256 at 25.01°C	1271.6 (1274.2)	15.00	0.83070
				25.01	0.89544
				35.07	0.96888

Table III contd.

Run No.	N_2O_4 g.	NO atm.	Vol.* ml.	T °C	Equilibrium Pressure atm.
17	2.22996	0.38471 at 24.04°C	1270.9 (1273.3)	14.95	0.85894
				25.04	0.92652
				35.05	1.00249
18	0.52400	0.34674 at 25.04°C	1268.1 (1270.4)	4.99	0.43329
				15.00	0.46101
				25.04	0.49133
				35.16	0.52313
				45.05	0.55526
19	0.97346	0.47831 at 25.04°C	1268.3 (1270.7)	4.86	0.63796
				14.95	0.68003
				25.04	0.72638
				35.02	0.77586
				45.21	0.82918

Table IV.

Calculated Values of Equilibrium Partial Pressures and Constants.

Run No.	T °C	$p^{o}_{N_2O_4}$ atm.	p^{o}_{NO} atm.	p_{NO} atm.	p_{NO_2} atm.	$p_{N_2O_3}$ atm.	K_2 atm.
1	4.96	0.29085	0.28100	0.23490	0.07335	0.04610	0.374
	15.00	0.30135	0.29115	0.25282	0.11400	0.03832	0.752
	25.04	0.31185	0.30129	0.26775	0.16761	0.03354	1.34
	35.08	0.32233	0.31143	0.28260	0.23383	0.02883	2.29
	45.12	0.33285	0.32158	0.29746	0.31074	0.02412	3.83
2	4.96	0.23834	0.32075	0.27644	0.06555	0.04432	0.409
	15.00	0.24694	0.33233	0.29409	0.10090	0.03824	0.776
	25.04	0.25554	0.34391	0.31146	0.14862	0.03245	1.43
	35.08	0.26415	0.35549	0.32638	0.20522	0.02911	2.30
	45.12	0.27275	0.36707	0.34239	0.27134	0.02468	3.76
4	4.96	0.16482	0.05119	0.04520	0.05772	0.00599	0.435
	15.00	0.17077	0.05304	0.04756	0.08747	0.00548	0.759
	25.04	0.17672	0.05488	0.05073	0.12468	0.00415	1.52
5	4.96	0.09243	0.58973	0.54829	0.03451	0.04144	0.457
	15.00	0.09577	0.61102	0.57533	0.05390	0.03569	0.869
	25.04	0.09911	0.63231	0.60295	0.07762	0.02936	1.59
	35.08	0.10244	0.65360	0.62885	0.10425	0.02475	2.65
	45.12	0.10578	0.67488	0.65621	0.13089	0.01867	4.60
6	5.03	0.10409	0.53132	0.49176	0.03826	0.03956	0.476
	15.08	0.10785	0.55051	0.51680	0.05940	0.03371	0.911
	25.07	0.11159	0.56959	0.54096	0.08530	0.02863	1.61
	35.11	0.11534	0.58876	0.56526	0.11519	0.02350	2.77
	45.19	0.11911	0.60802	0.58891	0.14659	0.01911	4.52
7	5.05	0.08851	0.63041	0.58782	0.03355	0.04259	0.463
	15.03	0.09169	0.65302	0.61897	0.05238	0.03406	0.952
	25.07	0.09488	0.67577	0.64667	0.07508	0.02911	1.68
	35.04	0.09805	0.69836	0.67392	0.10059	0.02445	2.77
	45.21	0.10129	0.72141	0.70198	0.12781	0.01943	4.62

Table IV contd.

Run No.	T °C	$p^o_{N_2O_4}$ atm.	p^o_{NO} atm.	p_{NO} atm.	p_{NO_2} atm.	$p_{N_2O_3}$ atm.	K_2 atm.
8	5.01	0.17110	0.63413	0.56844	0.04937	0.06569	0.427
	15.01	0.17725	0.65693	0.59994	0.07781	0.05699	0.819
	25.07	0.18344	0.67986	0.63122	0.11485	0.04864	1.49
	35.08	0.18959	0.70268	0.66056	0.15866	0.04212	2.49
	45.08	0.19575	0.72548	0.69004	0.20754	0.03544	4.04
9	4.86	0.01666	0.24296	0.23775	0.01291	0.00521	0.590
	15.01	0.01727	0.25183	0.24687	0.01849	0.00496	0.921
	25.04	0.01787	0.26059	0.25720	0.02405	0.00339	1.83
	35.08	0.01847	0.26937	0.26683	0.02882	0.00254	3.03
	45.12	0.01907	0.27814	0.27637	0.03281	0.00177	5.12
10	5.00	0.09773	0.34233	0.31608	0.03974	0.02626	0.478
	15.01	0.10124	0.35465	0.33270	0.06000	0.02195	0.909
	25.12	0.10480	0.36709	0.34911	0.08539	0.01798	1.66
	35.02	0.10827	0.37928	0.36405	0.11328	0.01523	2.71
	45.10	0.11182	0.39168	0.37958	0.14296	0.01211	4.48
11	15.00	0.42441	0.12159	0.09864	0.14097	0.02296	0.606
	24.97	0.43910	0.12580	0.10608	0.20807	0.01972	1.12
	35.11	0.45388	0.13004	0.11305	0.29328	0.01699	1.95
	45.01	0.46861	0.13426	0.11966	0.39343	0.01460	3.23
13	4.95	0.26154	0.05463	0.04516	0.07410	0.00947	0.353
	14.92	0.27091	0.05659	0.04870	0.11208	0.00789	0.692
	24.96	0.28035	0.05856	0.05196	0.16348	0.00660	1.29
	35.12	0.28991	0.06056	0.05503	0.22661	0.00553	2.26
	45.12	0.29931	0.06252	0.05796	0.29775	0.00456	3.79
14	4.95	0.25986	0.46210	0.39921	0.06561	0.06289	0.417
	14.97	0.26922	0.47875	0.42407	0.10305	0.05468	0.799
	25.04	0.27863	0.49548	0.44855	0.15286	0.04693	1.46
	34.99	0.28793	0.51201	0.47036	0.21297	0.04166	2.41
	45.04	0.29732	0.52871	0.49326	0.28308	0.03545	3.94
16	15.00	0.42532	0.36972	0.30685	0.13419	0.06287	0.655
	25.01	0.44009	0.38256	0.32734	0.20080	0.05522	1.19
	35.07	0.45494	0.39547	0.34739	0.28502	0.04808	2.06

Table IV contd.

Run No.	T °C	$\overset{o}{p}_{N_2O_4}$ atm.	$\overset{o}{p}_{NO}$ atm.	p_{NO} atm.	p_{NO_2} atm.	$p_{N_2O_3}$ atm.	K_2 atm.
17	14.95	0.44995	0.37169	0.30820	0.13807	0.06349	0.670
	25.04	0.46572	0.38471	0.32940	0.20749	0.05530	1.24
	35.05	0.48135	0.39762	0.34980	0.29486	0.04782	2.16
18	4.99	0.10231	0.32342	0.29749	0.04105	0.02593	0.471
	15.00	0.10599	0.33506	0.31313	0.06185	0.02193	0.883
	25.04	0.10968	0.34674	0.32860	0.08795	0.01814	1.59
	35.16	0.11341	0.35850	0.34326	0.11768	0.01525	2.65
	45.05	0.11704	0.37000	0.35817	0.14826	0.01183	4.49
19	4.86	0.18993	0.44594	0.39461	0.05549	0.05133	0.427
	14.95	0.19683	0.46213	0.41776	0.08652	0.04437	0.815
	25.04	0.20372	0.47831	0.44084	0.12616	0.03747	1.48
	35.02	0.21054	0.49432	0.46160	0.17473	0.03272	2.46
	45.21	0.21750	0.51066	0.48314	0.22956	0.02753	4.03

Summary by least squares plot.

T°C	$K_{N_2O_3}$	Standard deviation
5.00	0.595	± 0.018
15.00	1.082	± 0.025
25.00	1.916	± 0.027
35.00	3.097	± 0.041
45.00	5.193	± 0.059

$\Delta H = + 9527 \pm 96$ cal./mole.

Table V.

Modification of Equilibrium Constant.

Run No.	T °C	$p^o_{NO}-p_{NO}$ $=p_{N_2O_3}$ atm.	$p_{N_2O_3}$ mod. atm.	K_2 mod. atm.
For $K_4 = 1$				
1	5	0.04610	0.0425	0.404
	25	0.03354	0.0316	1.42
	45	0.02412	0.0231	4.00
2	5	0.04432	0.0409	0.443
	25	0.03245	0.0306	1.51
	45	0.02468	0.0235	3.95
4	5	0.00599	0.0059	0.442
	25	0.00415	0.0041	1.54
5	5	0.04144	0.0386	0.490
	25	0.02936	0.0278	1.68
	45	0.01867	0.0180	4.77
6	5	0.03956	0.0368	0.511
	25	0.02863	0.0271	1.70
	45	0.01911	0.0189	4.57
7	5	0.04259	0.0395	0.499
	25	0.02911	0.0276	1.76
	45	0.01943	0.0189	4.75
8	5	0.06569	0.0588	0.477
	25	0.04864	0.0447	1.62
	45	0.03544	0.0333	4.30
9	5	0.00521	0.0052	0.590
	25	0.00339	0.0034	1.82
	45	0.00177	0.0018	5.12

Table V contd.

Run No.	T °C	$p^{o}_{NO}-p_{NO}$ $=p_{N_2O_3}$ atm.	$p_{N_2O_3}$ mod. atm.	K_2 mod. atm.
10	5	0.02626	0.0250	0.503
	25	0.01798	0.0177	1.69
	45	0.01211	0.0119	4.50
11	25	0.01972	0.0190	1.16
	45	0.01460	0.0142	3.32
13	5	0.00947	0.0093	0.360
	25	0.00660	0.0066	1.29
	45	0.00456	0.0042	4.10
14	5	0.06289	0.0565	0.464
	25	0.04693	0.0433	1.58
	45	0.03545	0.0333	4.20
16	25	0.05522	0.0502	1.31
17	25	0.05530	0.0503	1.36
18	5	0.02593	0.0246	0.496
	25	0.01814	0.0175	1.65
	45	0.01183	0.0116	4.59
19	5	0.05133	0.0470	0.466
	25	0.03747	0.0351	1.58
	45	0.02753	0.0261	4.25
For K_4 = 0.1				
1	25	0.03354	0.023	1.95
2	25	0.03245	0.023	2.01
4	25	0.00415	0.003_7	1.71

Table V contd.

Run No.	T °C	$p^{o}_{NO}-p_{NO}$ $=p_{N_2O_3}$ atm.	$p_{N_2O_3}$ mod. atm.	K_2 mod. atm.
5	25	0.02936	0.021	2.23
6	25	0.02863	0.020	2.26
7	25	0.02911	0.023	2.10
8	25	0.04864	0.030	2.40
9	25	0.00339	0.003	2.05
10	25	0.01798	0.014	2.12
11	25	0.01972	0.012	1.91
13	25	0.00660	0.005_9	1.44
14	25	0.04693	0.030	2.28
16	25	0.05522	0.033	1.99
17	25	0.05530	0.033	2.07
18	25	0.01814	0.014	2.05
19	25	0.03747	0.025	2.23

Table VI

Spectrophotometric Measurements.

Calibration.

$\log_{10}10R$	p_{NO_2} calculated atm.	Filter
0.752	0	in
1.085	0.086	in
1.292	0.144	in
0.525	0.144	out
0.898	0.184	out
1.175	0.219	out
1.322	0.240	out
1.481	0.271	out
1.635	0.304	out
1.811	0.348	out
1.978	0.399	out

Equilibria.

Run	T °C	Filter	log10R	p_{NO_2} atm.	p_{NO} atm.	$p_{N_2O_3}$ atm.	$K_{N_2O_3}$
1	5	in	1.384	0.170	0.137	0.144	0.16
	25	out	1.346	0.245	0.190	0.111	0.42
	15	out	0.340	0.125	0.240	0.051	0.59
	35	out	1.619	0.300	0.215	0.096	0.67
	45	out	1.857	0.362	0.247	0.074	1.2

Table VI contd.

Run	T °C	Filter	log10R	p_{NO_2} atm.	p_{NO} atm.	$p_{N_2O_3}$ atm.	$K_{N_2O_3}$
2	5	in	1.387	0.173	0.169	0.152	0.19
	15	out	0.483	0.140	0.255	0.077	0.46
	25	out	1.040	0.201	0.259	0.085	0.61
	35	out	1.390	0.252	0.280	0.065	1.1
	45	out	1.773	0.338	0.276	0.091	1.0
4	5	in	1.141	0.102	0.001	0.044	0.002
	15	in	1.470	0.198	-	-	-
	25	out	0.940	0.189	-	-	-
5	5	in	0.947	0.052	0.531	0.059	0.47
	15	in	1.055	0.080	0.549	0.062	0.71
	25	in	1.217	0.124	0.557	0.075	0.92
	35	in	1.409	0.179	0.554	0.100	0.99
	45	out	0.332	0.125	0.662	0.013	6.4
6	5	in	1.151	0.105	0.425	0.106	0.42
	15	in	1.139	0.102	0.474	0.077	0.63
	25	in	1.328	0.154	0.472	0.098	0.74
	35	out	0.305	0.121	0.559	0.030	2.3
	45	out	0.509	0.142	0.594	0.014	6.0
7	5	in	0.993	0.083	0.538	0.092	0.48
	15	in	1.097	0.091	0.580	0.073	0.72
	25	in	1.474	0.199	0.523	0.153	0.68
	35	out	0.243	0.116	0.659	0.039	1.96
	45	out	0.450	0.136	0.694	0.027	3.5

Extrapolated Values of $K_{N_2O_3}$ at zero pressure.

T°C	$K_{N_2O_3}$
5	0.68
15	1.03
25	1.33

Table VII.

CRYOSCOPY: EXPERIMENT 1.

wt. % N_2O_3	Melting Point $^{\circ}C$
71.7	- 74.5
80.0	- 94.6
88.2	- 107.5
92.8	- 106.0
95.0	- 105.0
96.3	- 103.9
97.5	- 102.8
98.5	- 102.7

Table VIII.

CRYOSCOPY: EXPERIMENT 2.

wt. % N_2O_3	Freezing Point °C
75.55	- 81.0
78.74	- 89.0
82.35	- 98.7
85.88	- 105.8
88.46	- 104.3
92.21	- 102.6
96.16	- 101.0
98.17	- 100.7
98.96	- 100.2

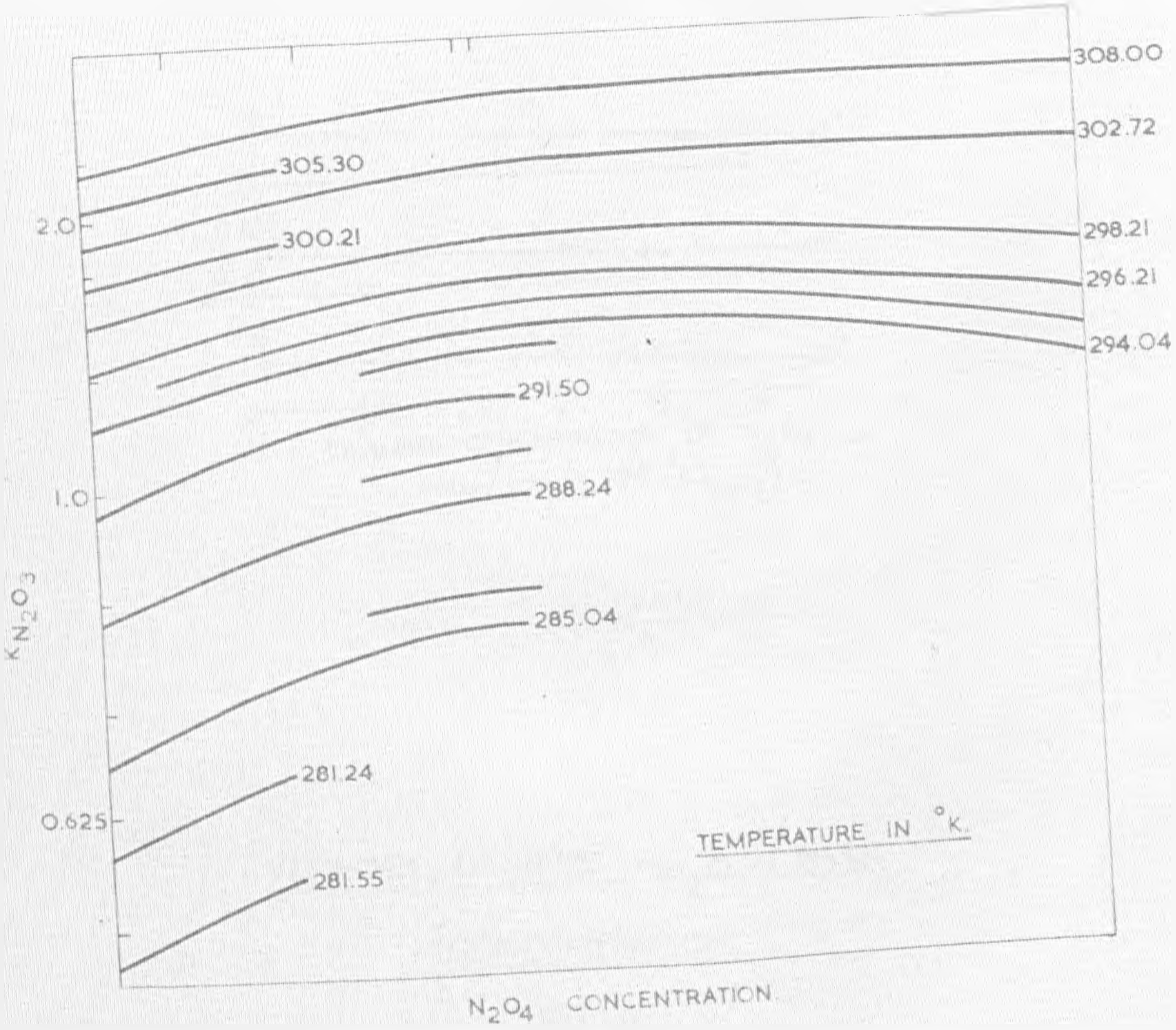
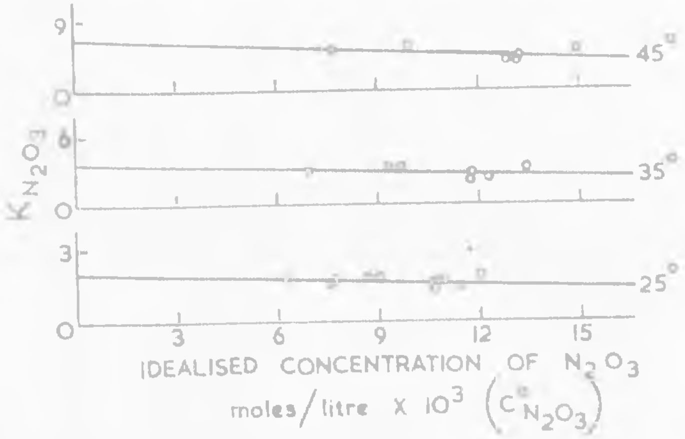


FIG. I. ABEL, PROISL : $K_{N_2O_3}$ / N_2O_4 CONCENTRATION.



VERHOEK, DANIELS $K_{N_2O_3}$ / N_2O_3

CONCENTRATION.

FIG. 2.

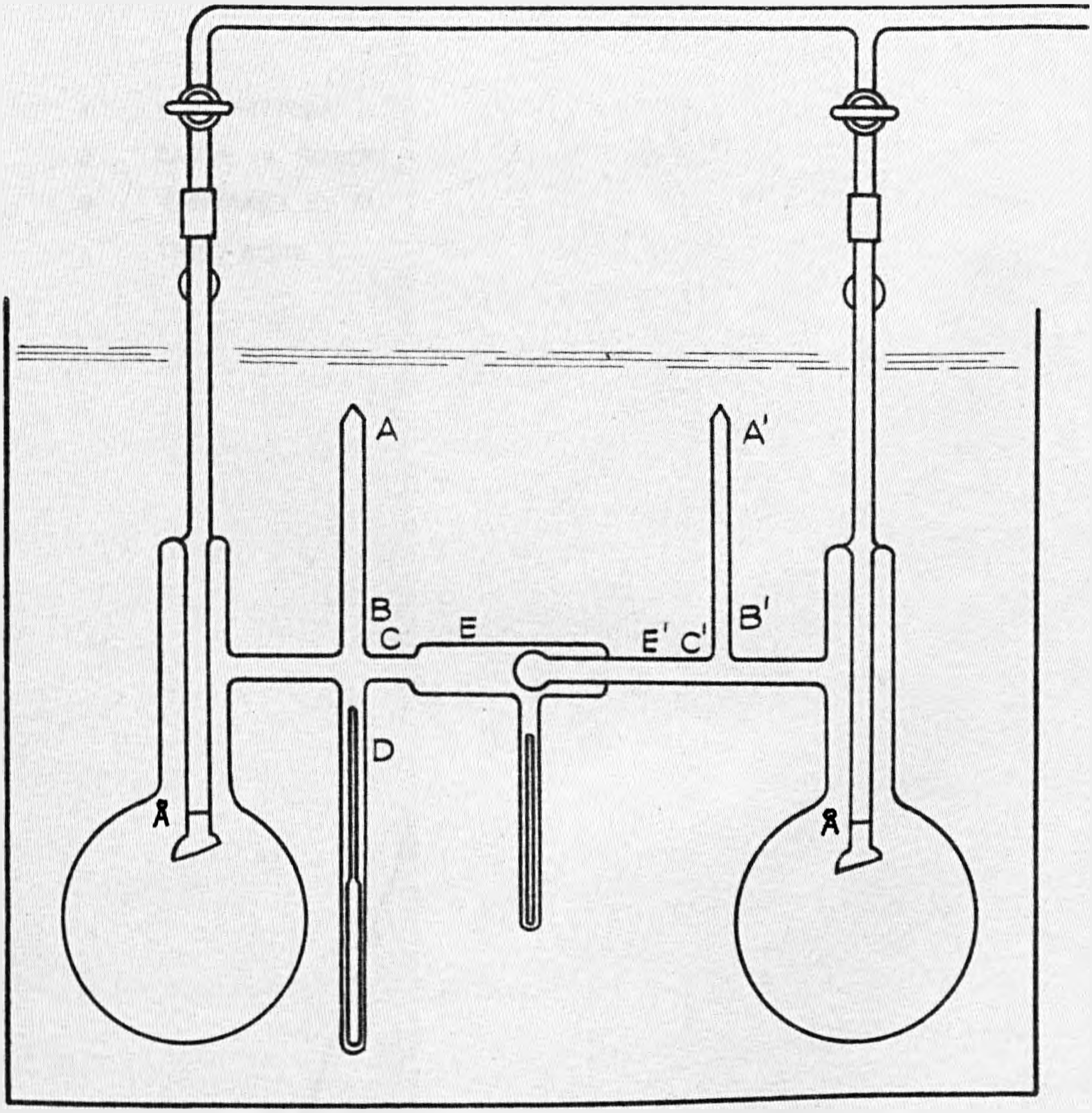


FIG. 3. APPARATUS OF VERHOEK AND DANIELS.

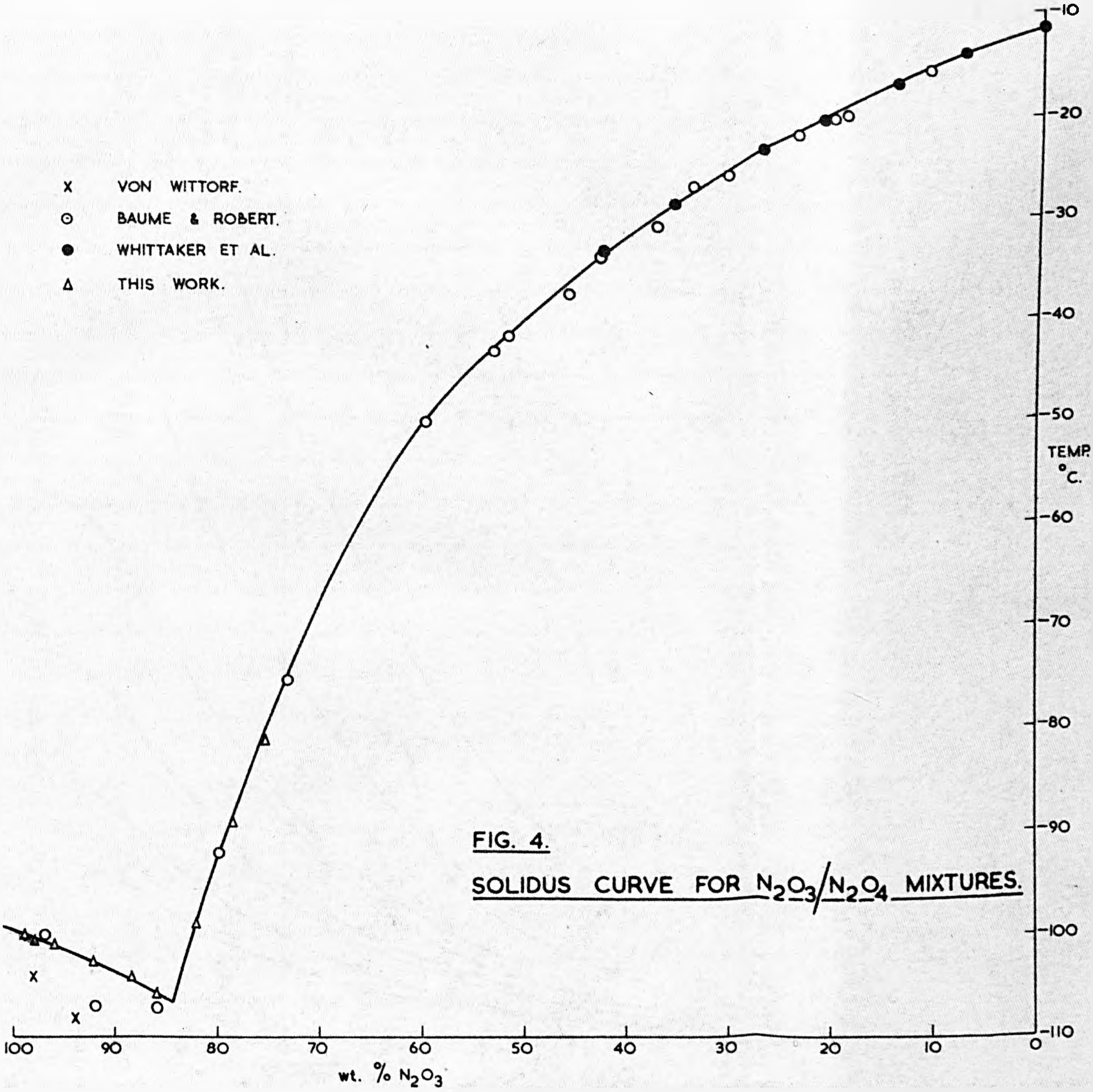


FIG. 4.

SOLIDUS CURVE FOR N_2O_3/N_2O_4 MIXTURES.

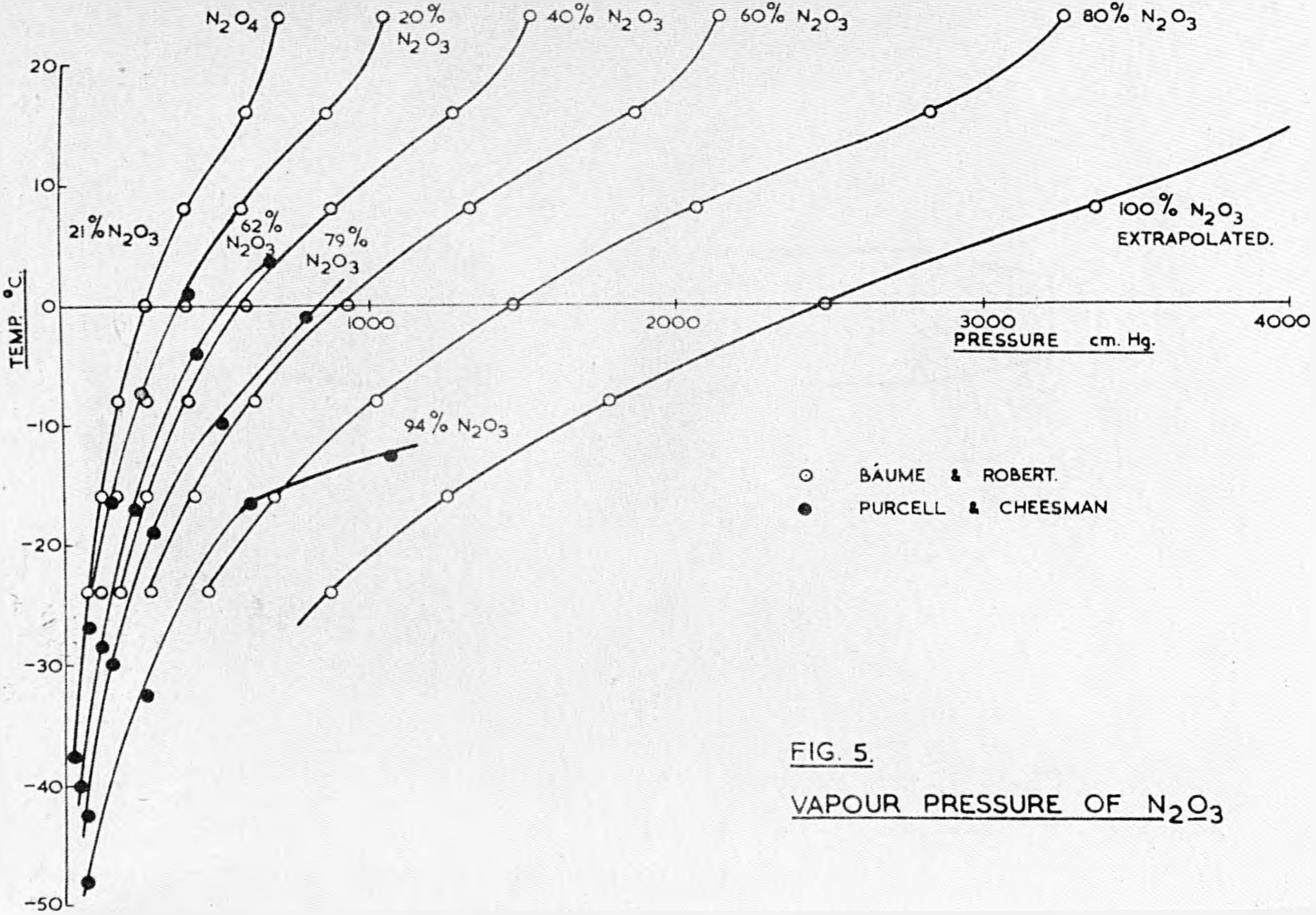
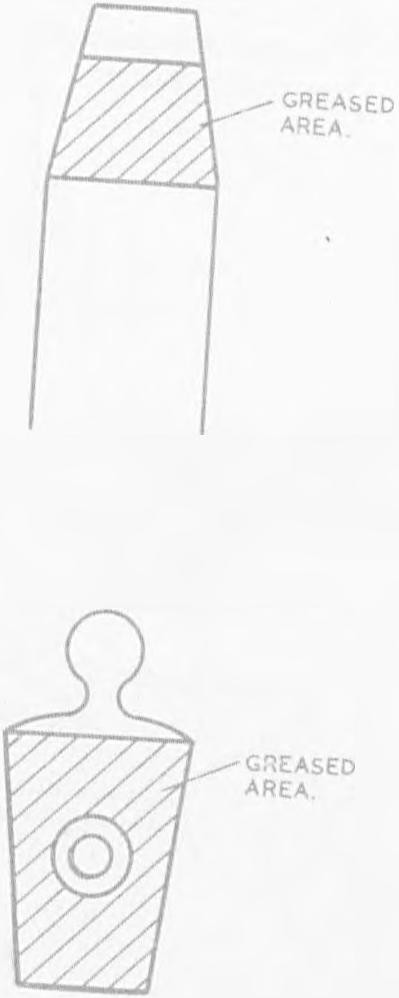


FIG. 5.

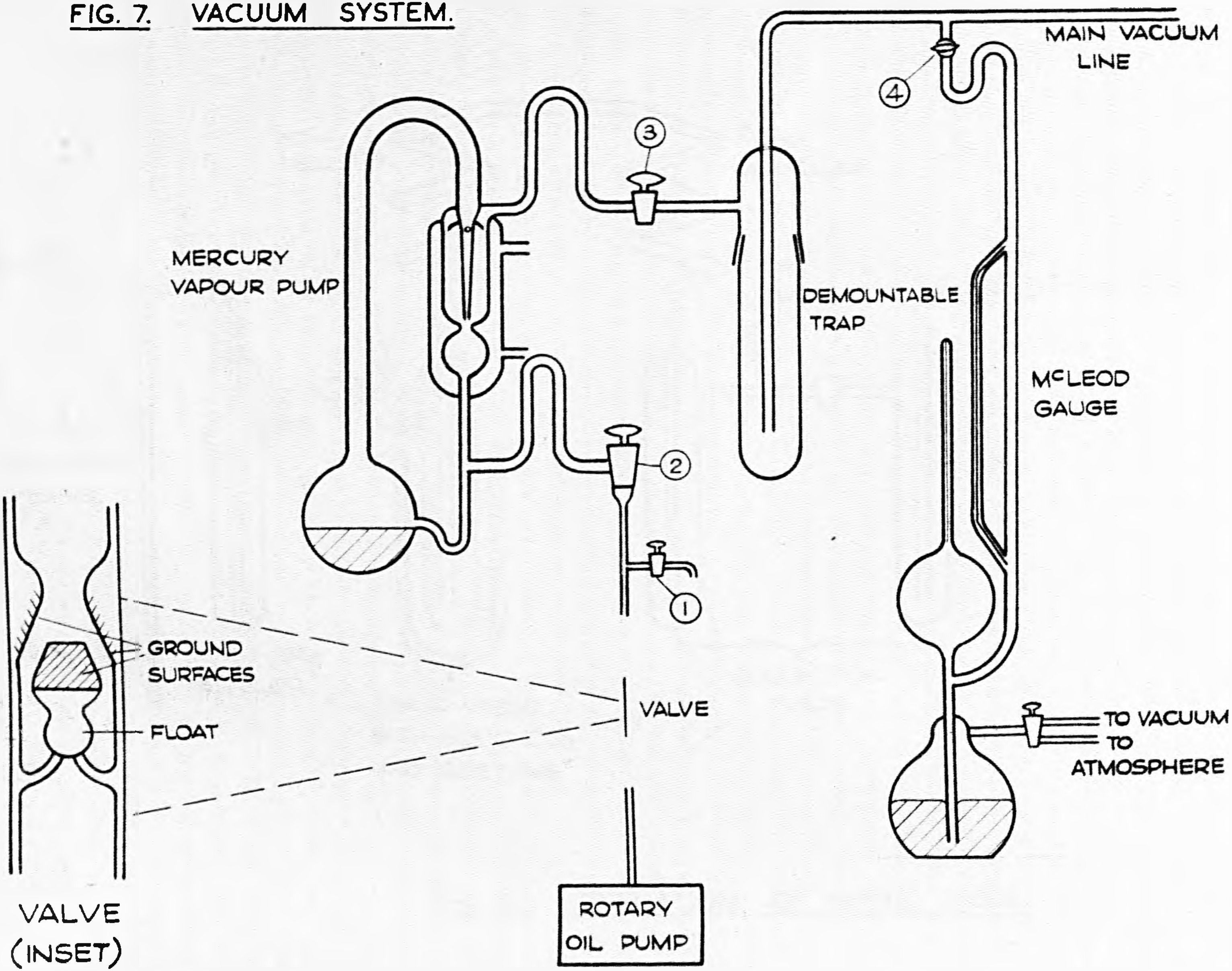
VAPOUR PRESSURE OF N_2O_3



METHOD OF GREASING.

FIG. 6.

FIG. 7. VACUUM SYSTEM.



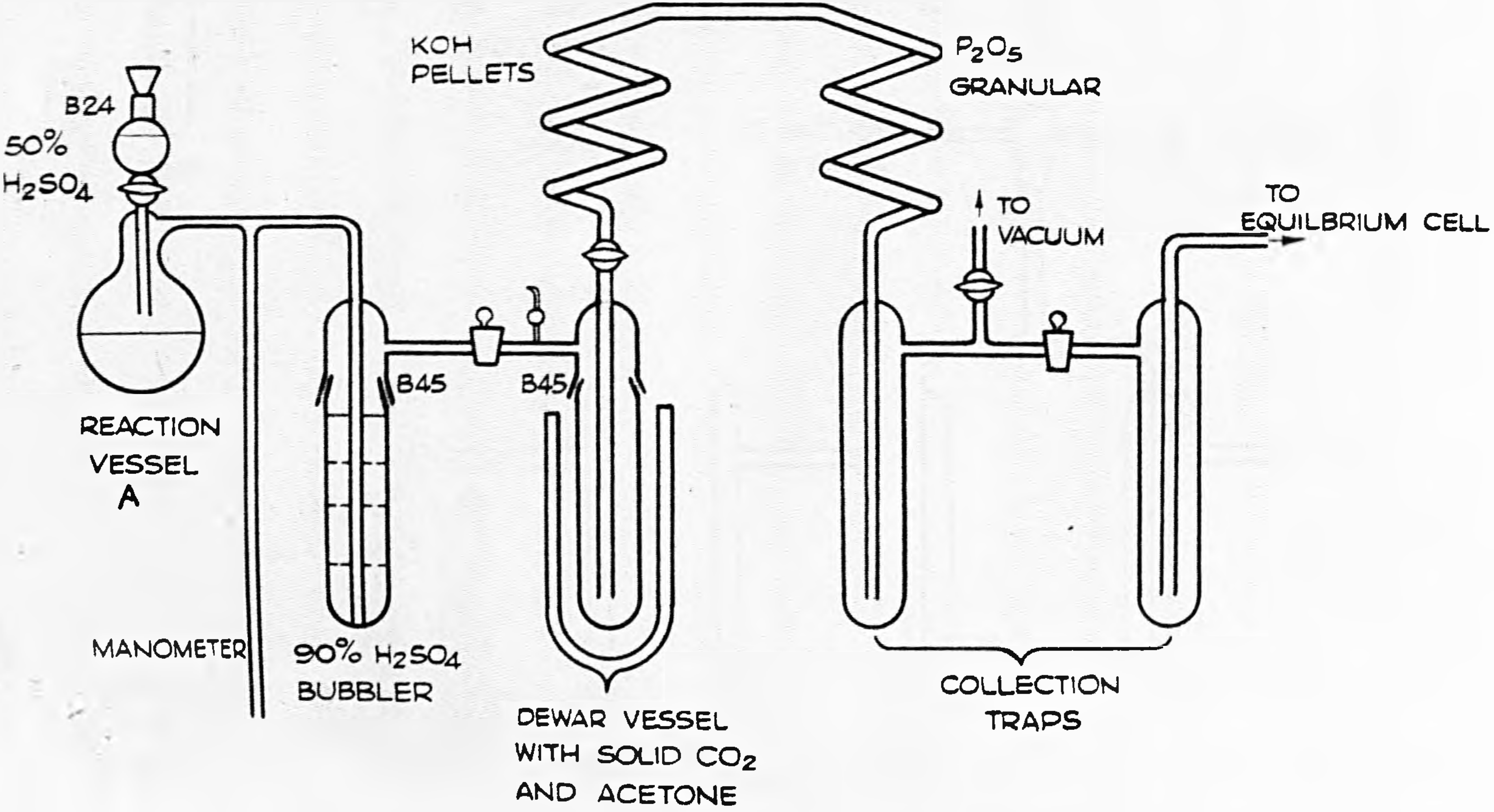


FIG. 8. GENERATION OF NITRIC OXIDE.

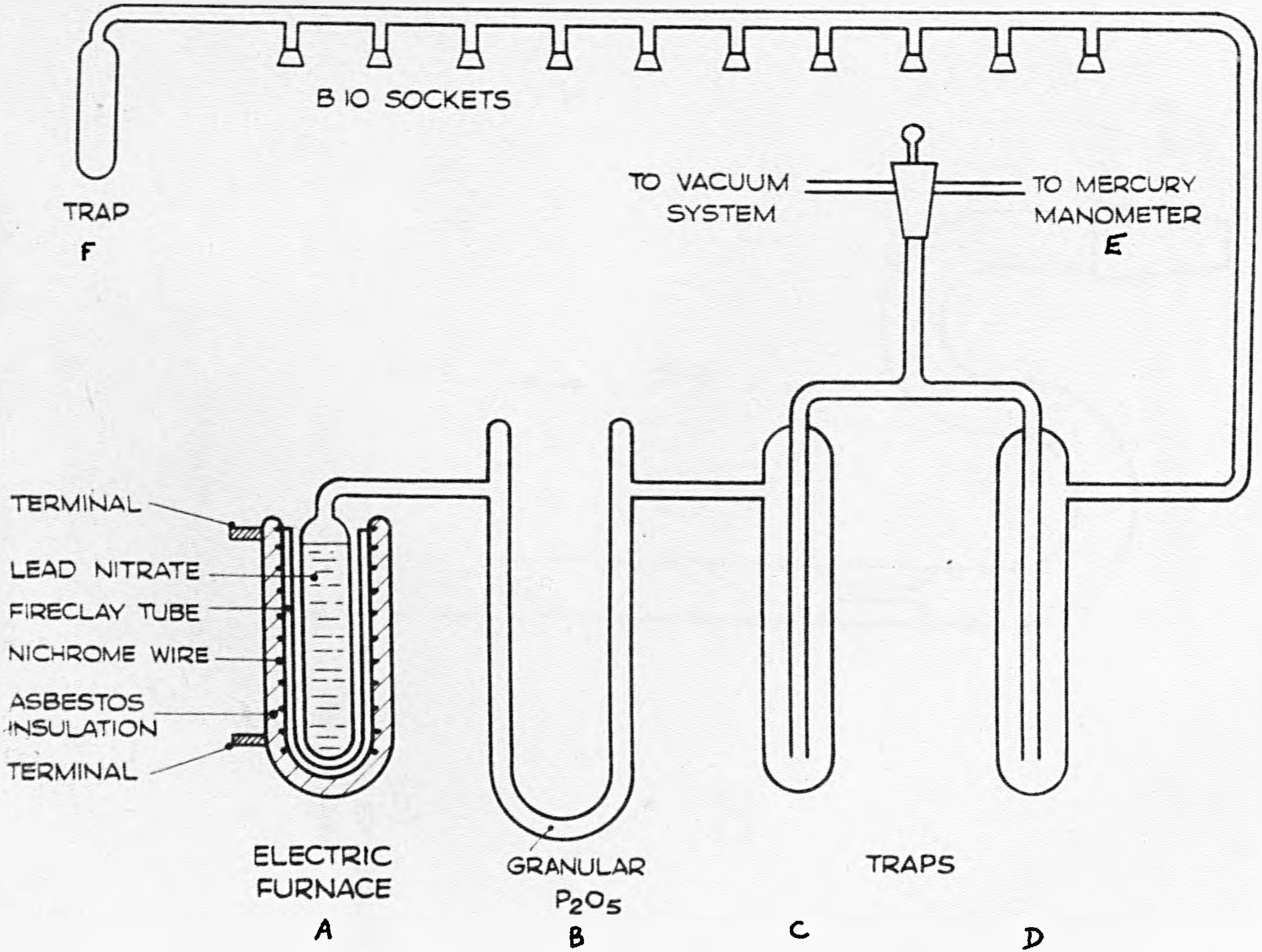


FIG. 9. GENERATION OF NITROGEN DIOXIDE.

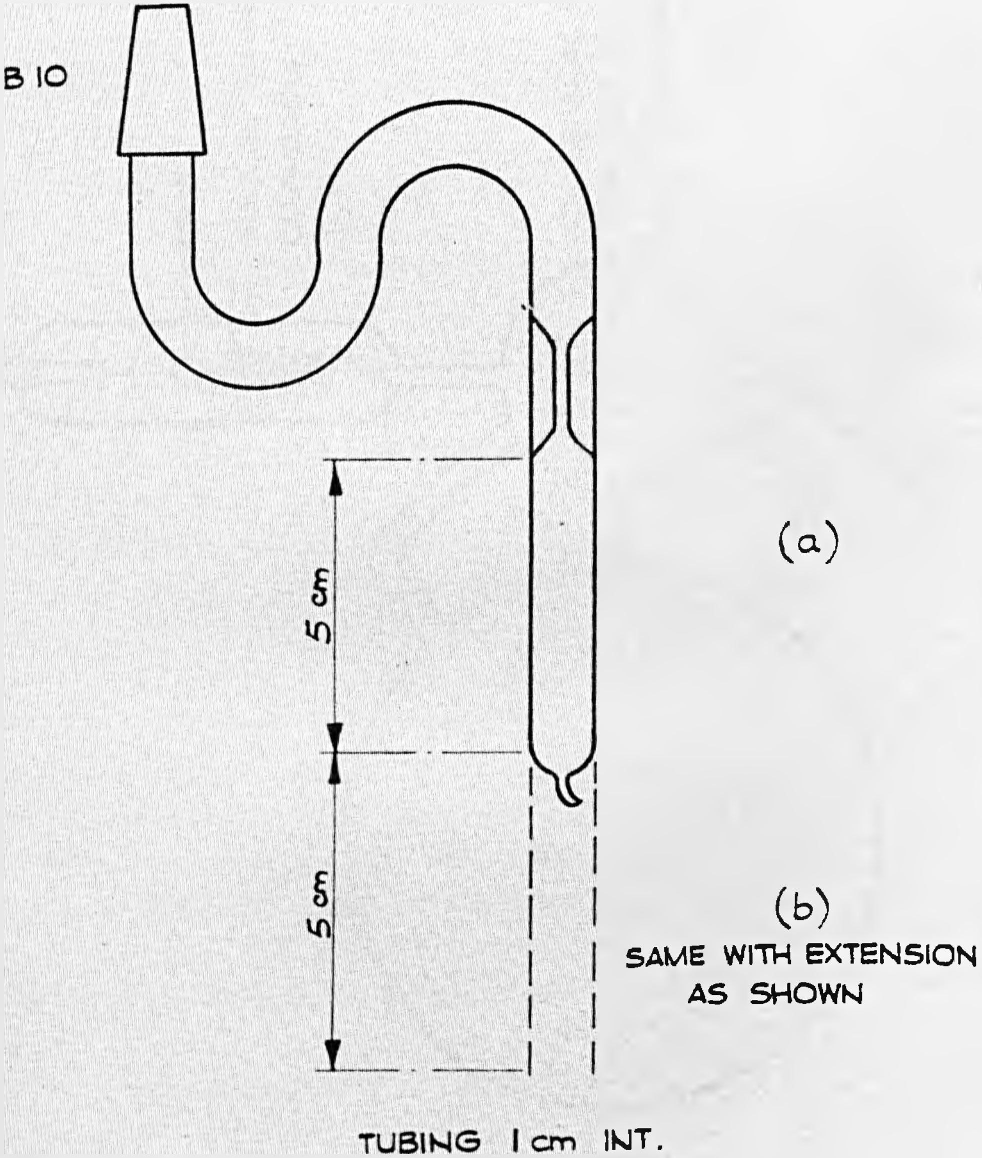


FIG. 10. N_2O_4 AMPOULES.

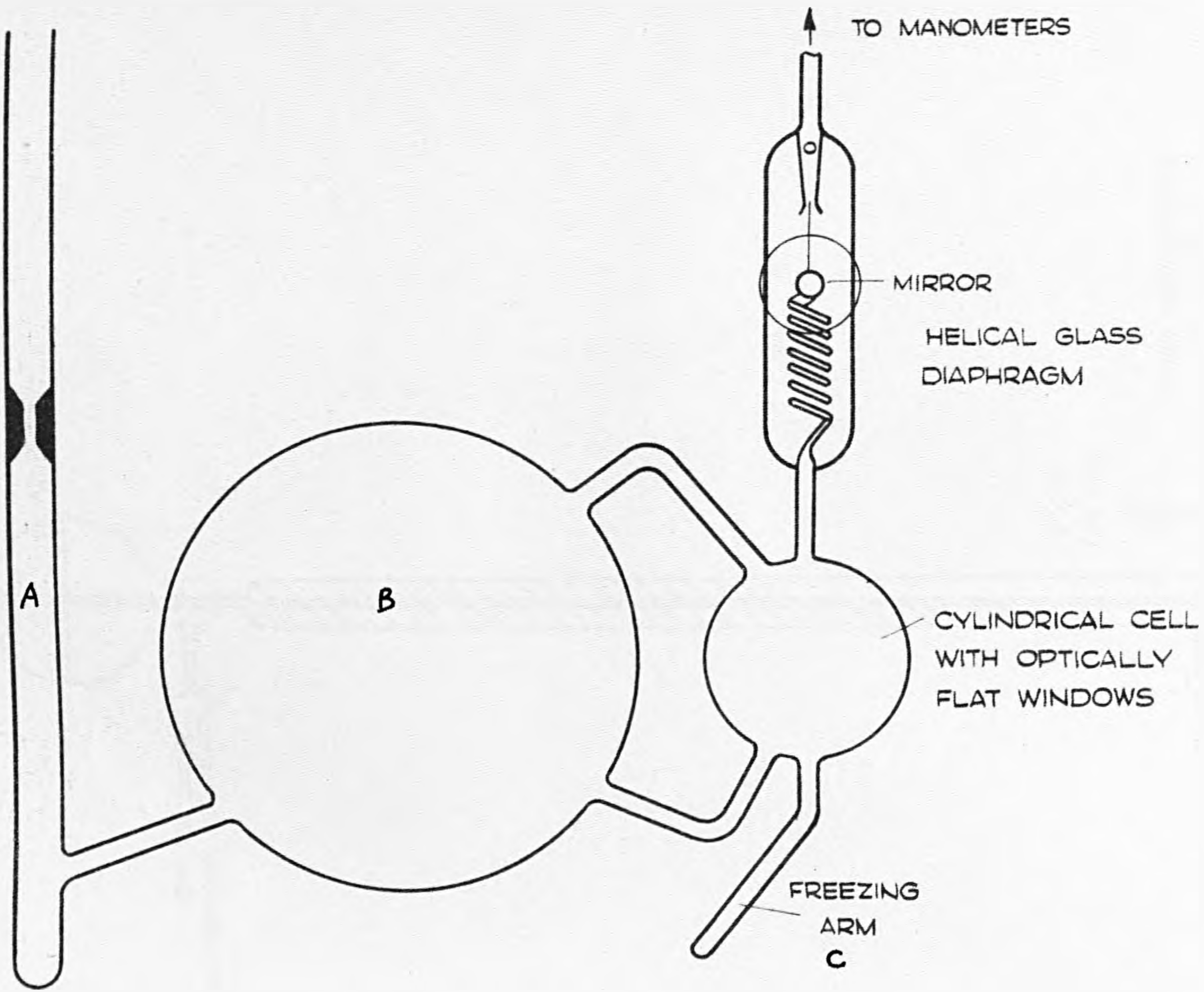


FIG. 11. EQUILIBRIUM CELL.

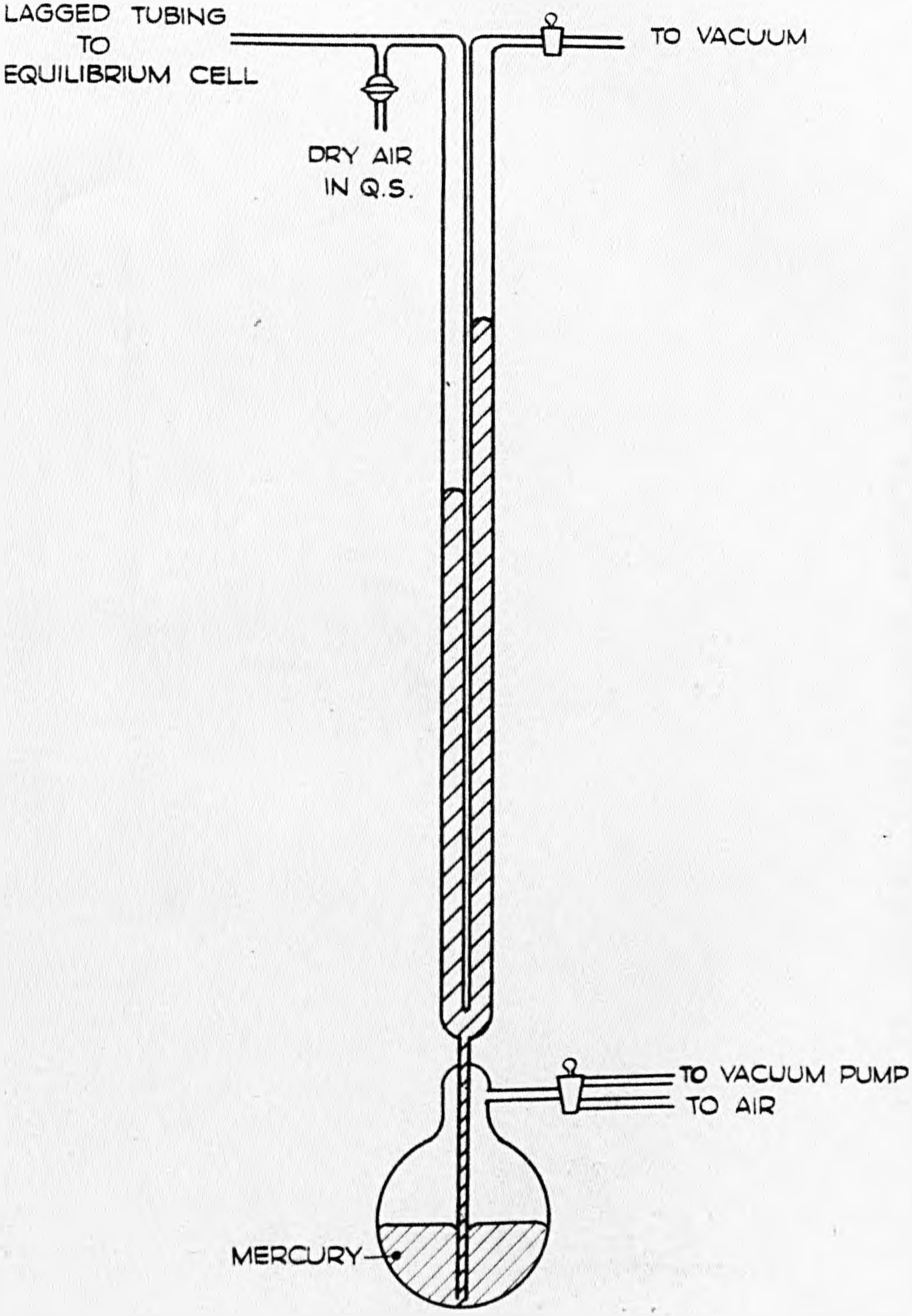


FIG. 12. MANOMETER SYSTEM.

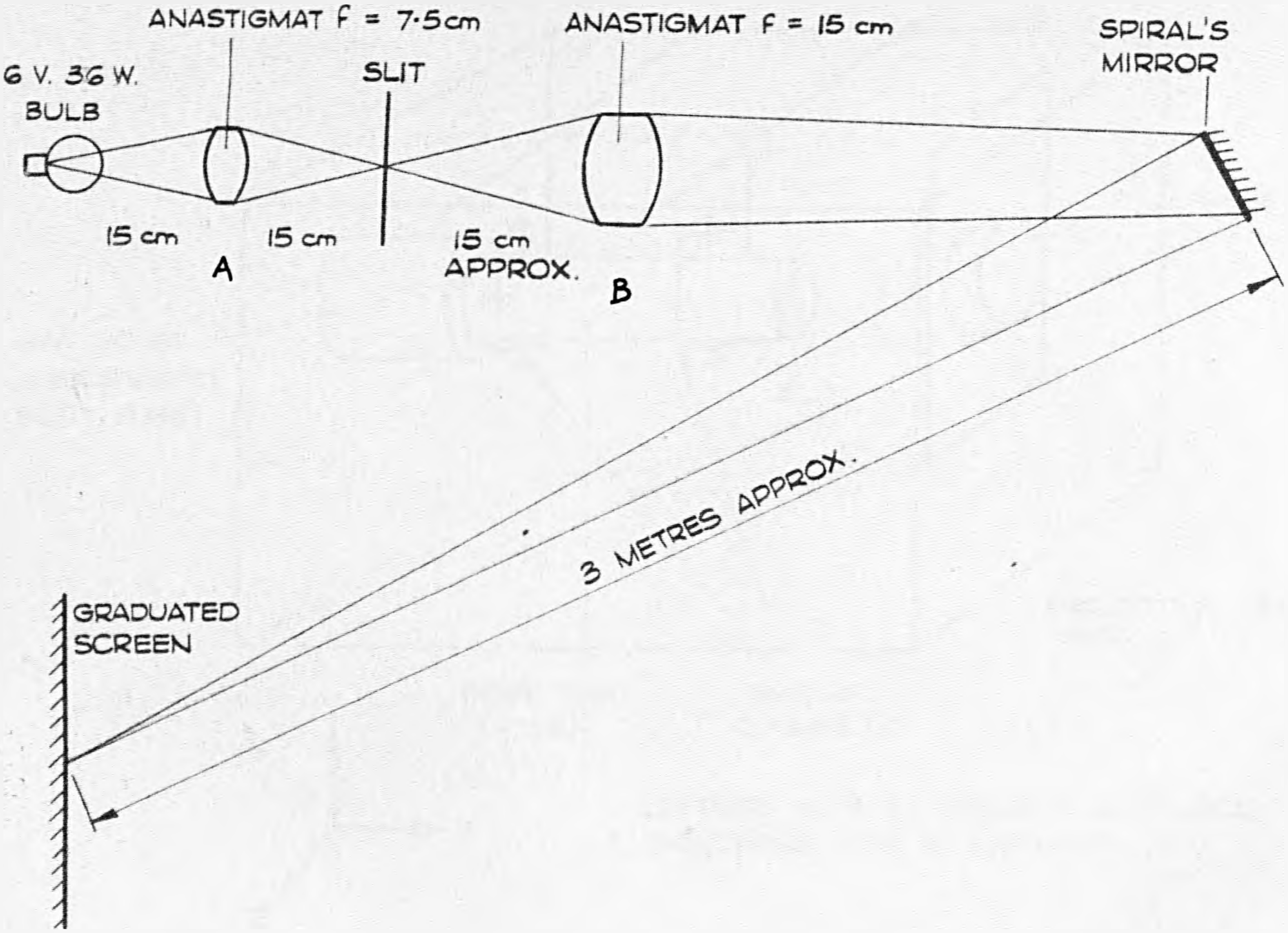
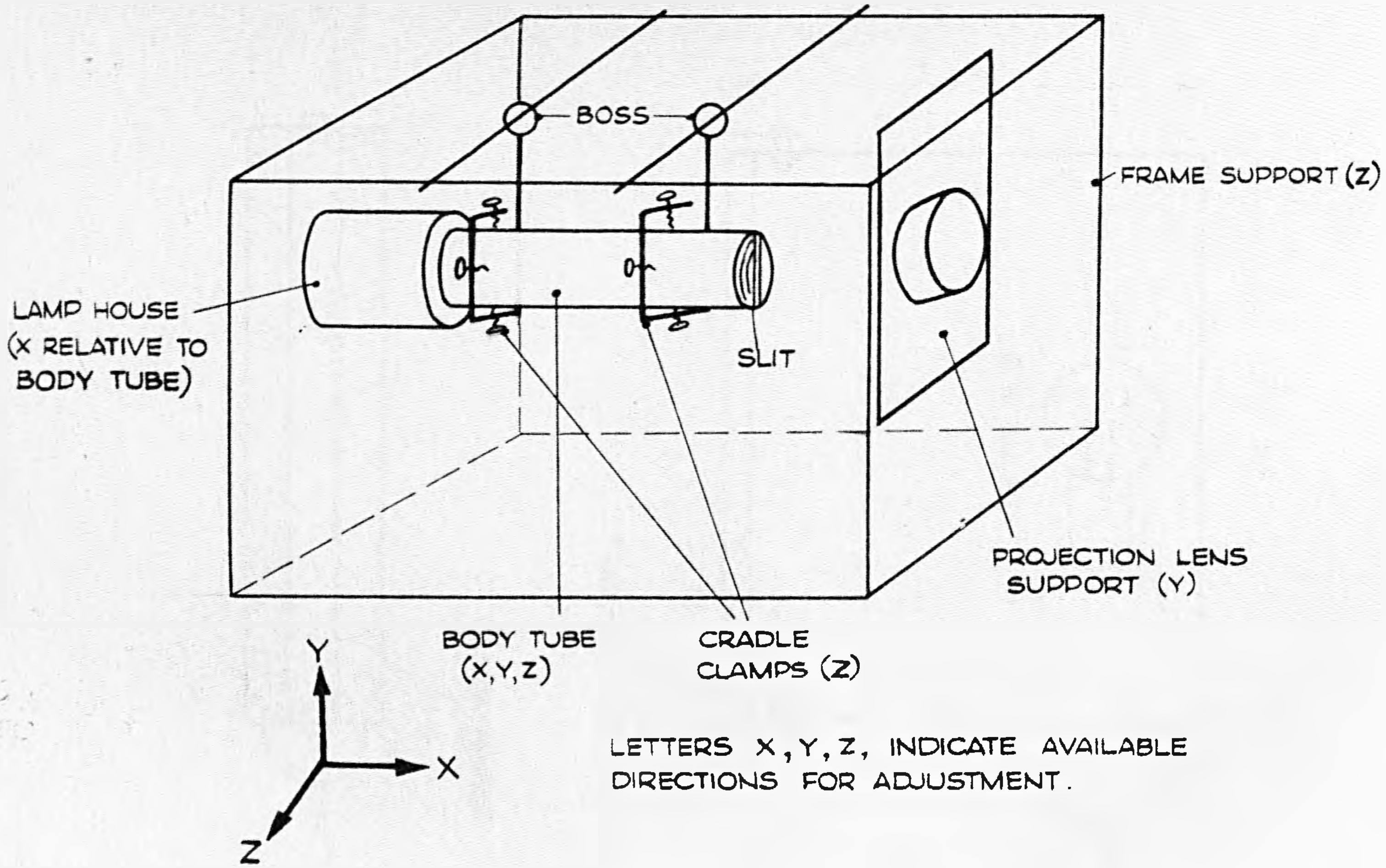


FIG. 13. OPTICAL SYSTEM FOR MIRROR ILLUMINATION.



LETTERS X, Y, Z, INDICATE AVAILABLE DIRECTIONS FOR ADJUSTMENT.

FIG. 14. SPIRALS ILLUMINATION: MECHANICAL DIAGRAM.

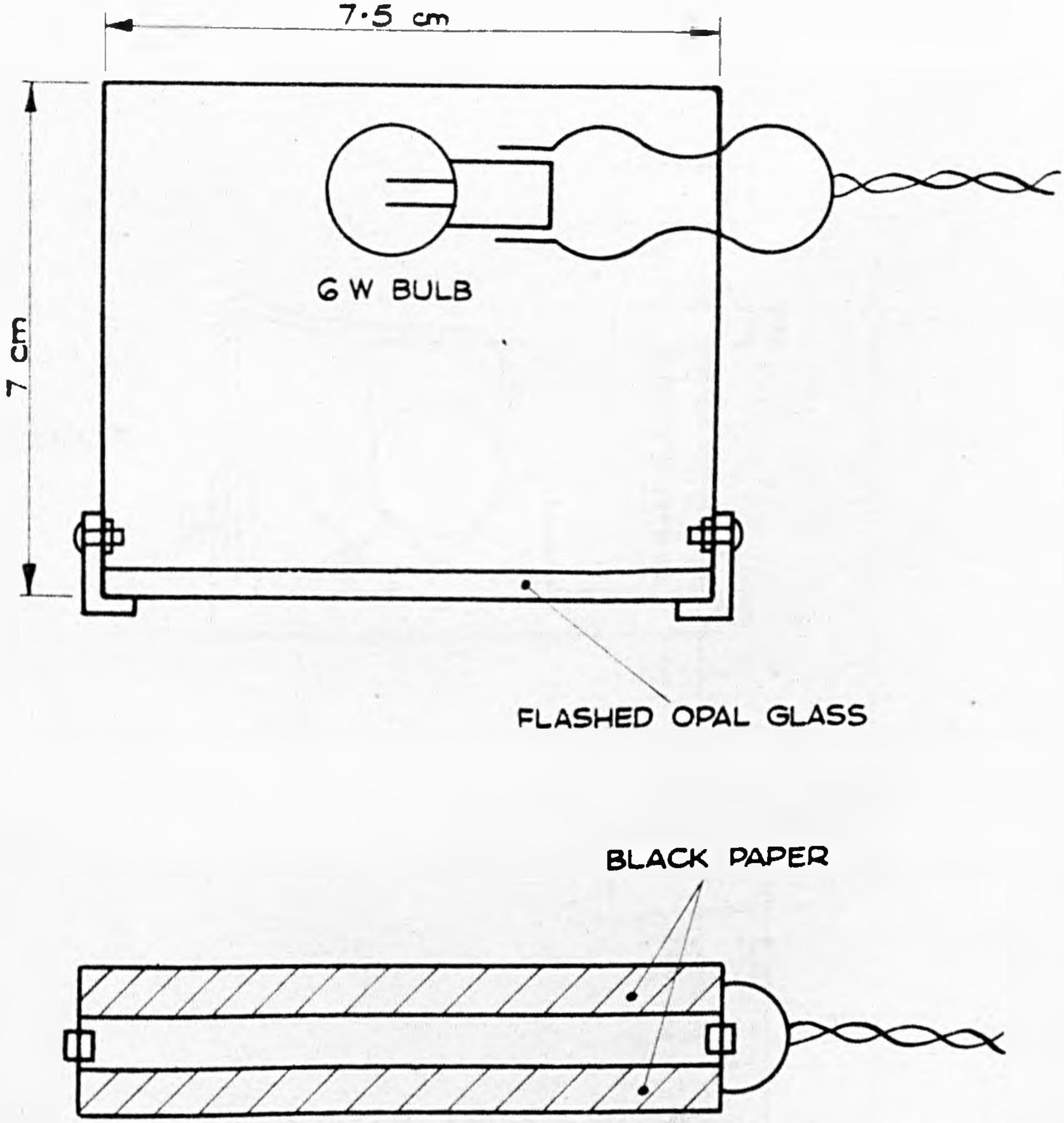


FIG. 15. MENISCUS LIGHT.

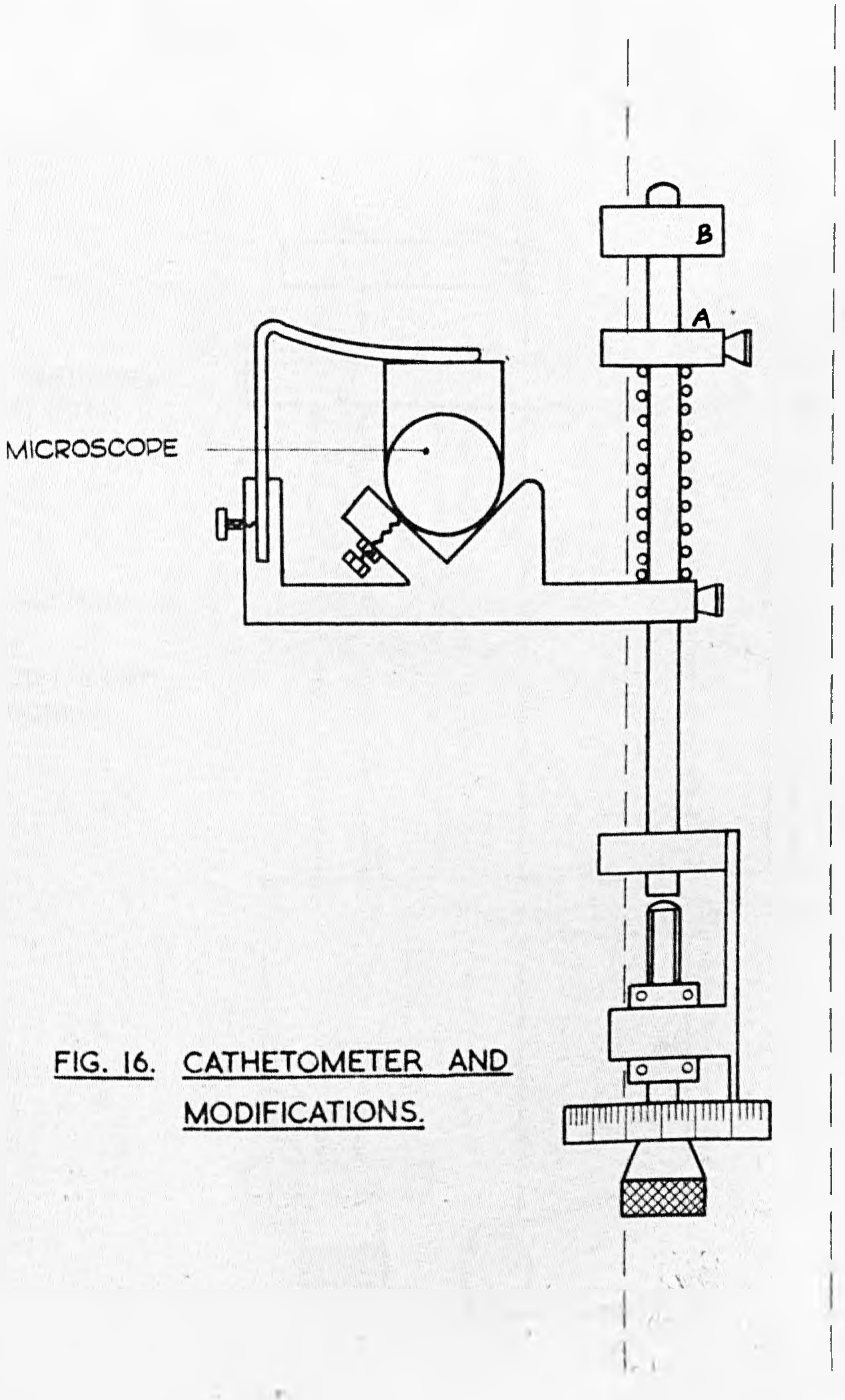
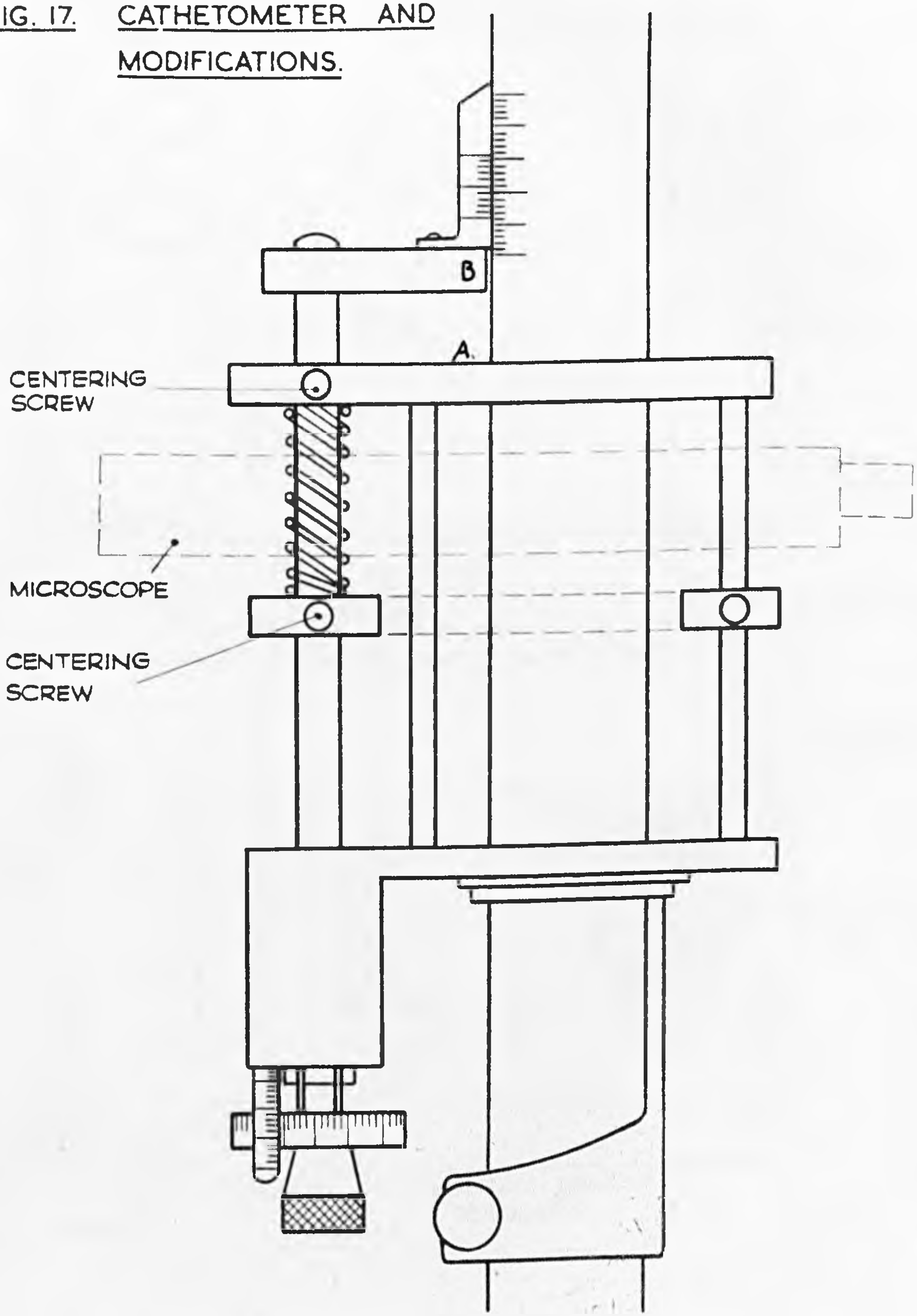


FIG. 16. CATHETOMETER AND MODIFICATIONS.

FIG. 17. CATHETOMETER AND MODIFICATIONS.



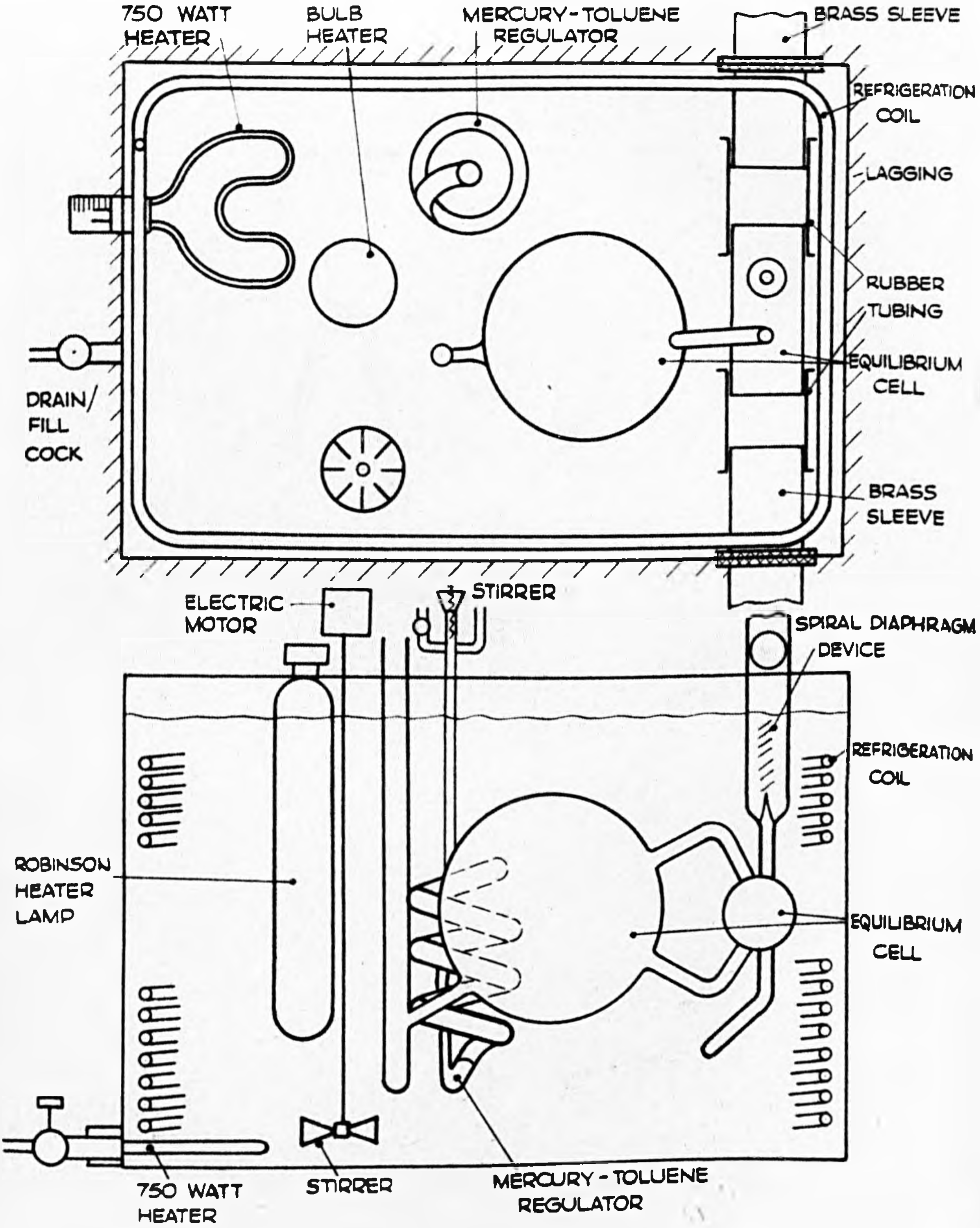
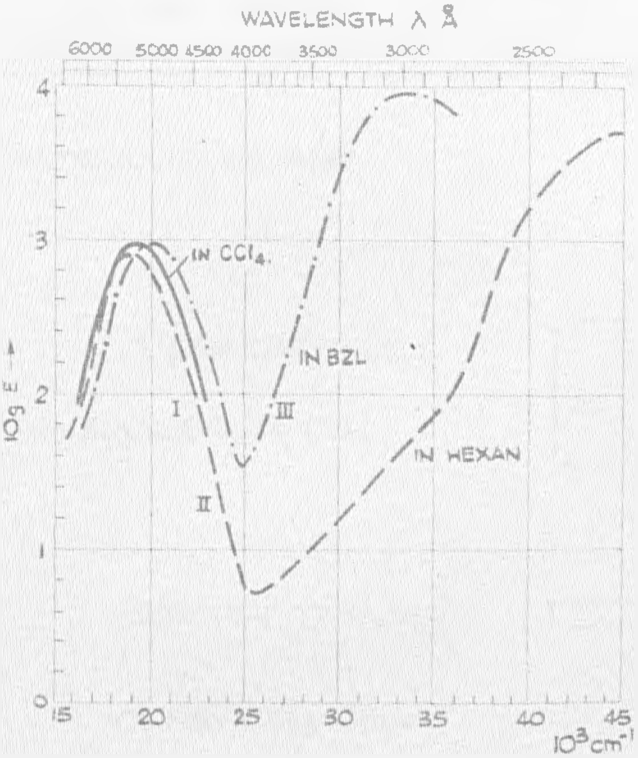


FIG. 18. THERMOSTAT BATH AND CONTENTS.



ABSORPTION SPECTRUM OF IODINE.

FIG. 19.

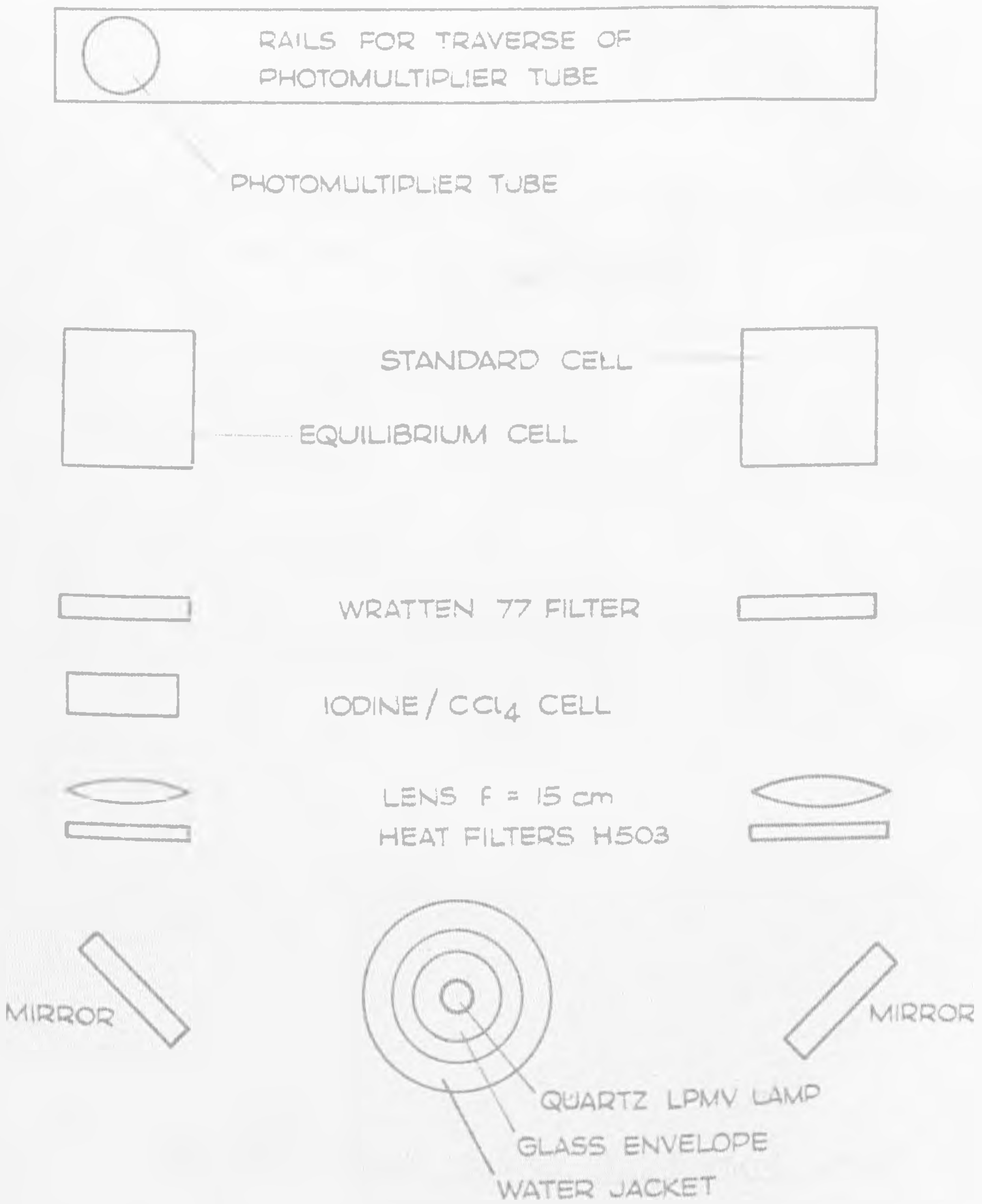


FIG. 19a. SPECTROPHOTOMETRIC APPARATUS.

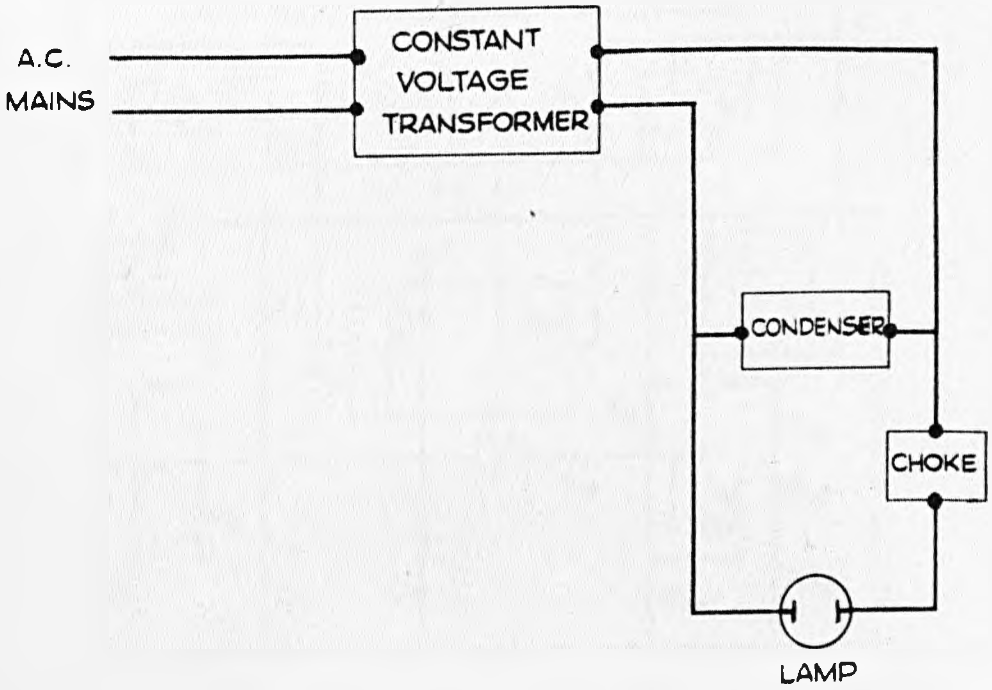
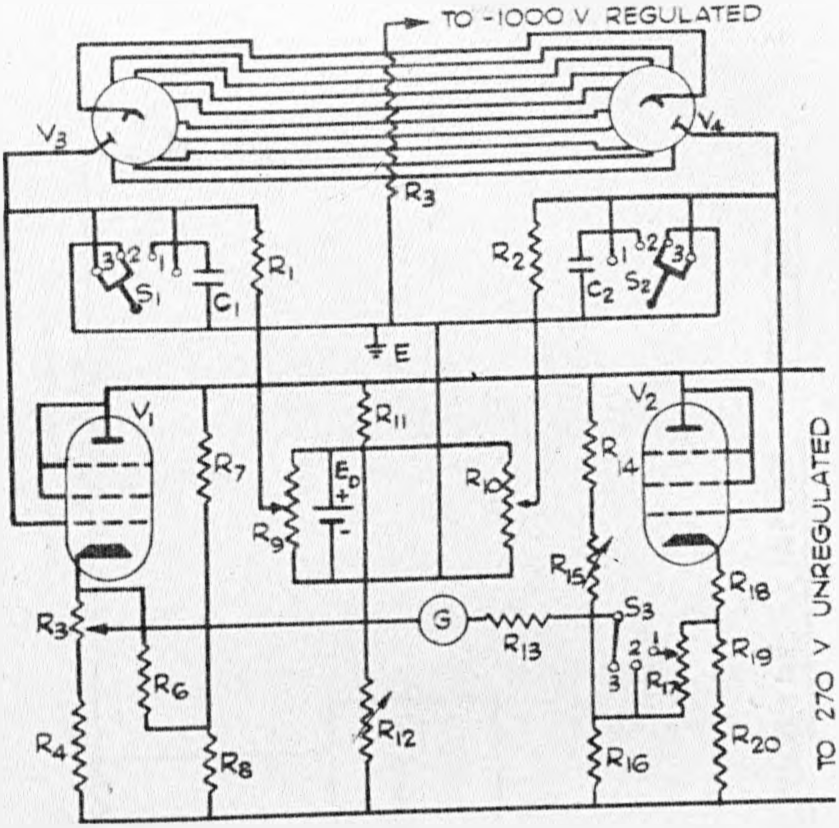


FIG. 20. POWER SUPPLY TO L.P.M.V. LAMP



R_1, R_2 = 15 MΩ

R_3 : 11 × 10 kΩ, 2 W.

R_4 : 10 kΩ, 2 W, w/w.

R_5 = 400 Ω, w/w.

R_6 : 10 kΩ

R_7 : 3 × 1 kΩ, 5 W, w/w
+ 500 Ω, 2 W, w/w

R_8 : 2 × 1 kΩ, 3 W.

R_9 : 500 kΩ var.

R_{10} = 500 kΩ var.

R_{11} : 50 kΩ

R_{12} : 50 kΩ var

R_{13} : 15 kΩ

R_{14} : 3 × 1 kΩ, 5 W, w/w

R_{15} : 1 kΩ, 5 W, w/w

R_{16} : 2 × 1 kΩ, w/w

R_{17} : 10 kΩ, w/w CALIBRATED
POTENTIOMETER.

R_{18} : 200 Ω

R_{19} : 200 Ω

R_{20} : 10 kΩ, 2 W, w/w

V_1 V_2 : TYPE 6AC7/1852

V_3 V_4 : TYPE 931A PHOTO-
MULTIPLIERS.

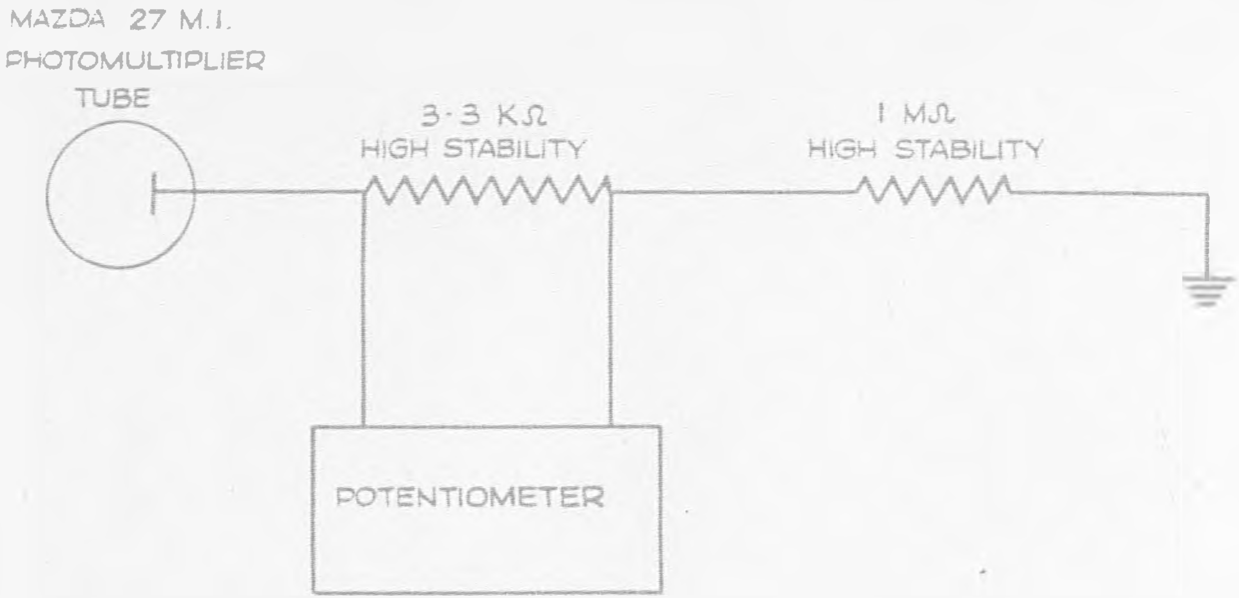
C_1 C_2 : 1 µF

G : 250-0-250 µA MOVING
COIL METER.

E_D : 4.5 V DRY BATTERY

S_1 S_2 : HIGHLY INSULATED.

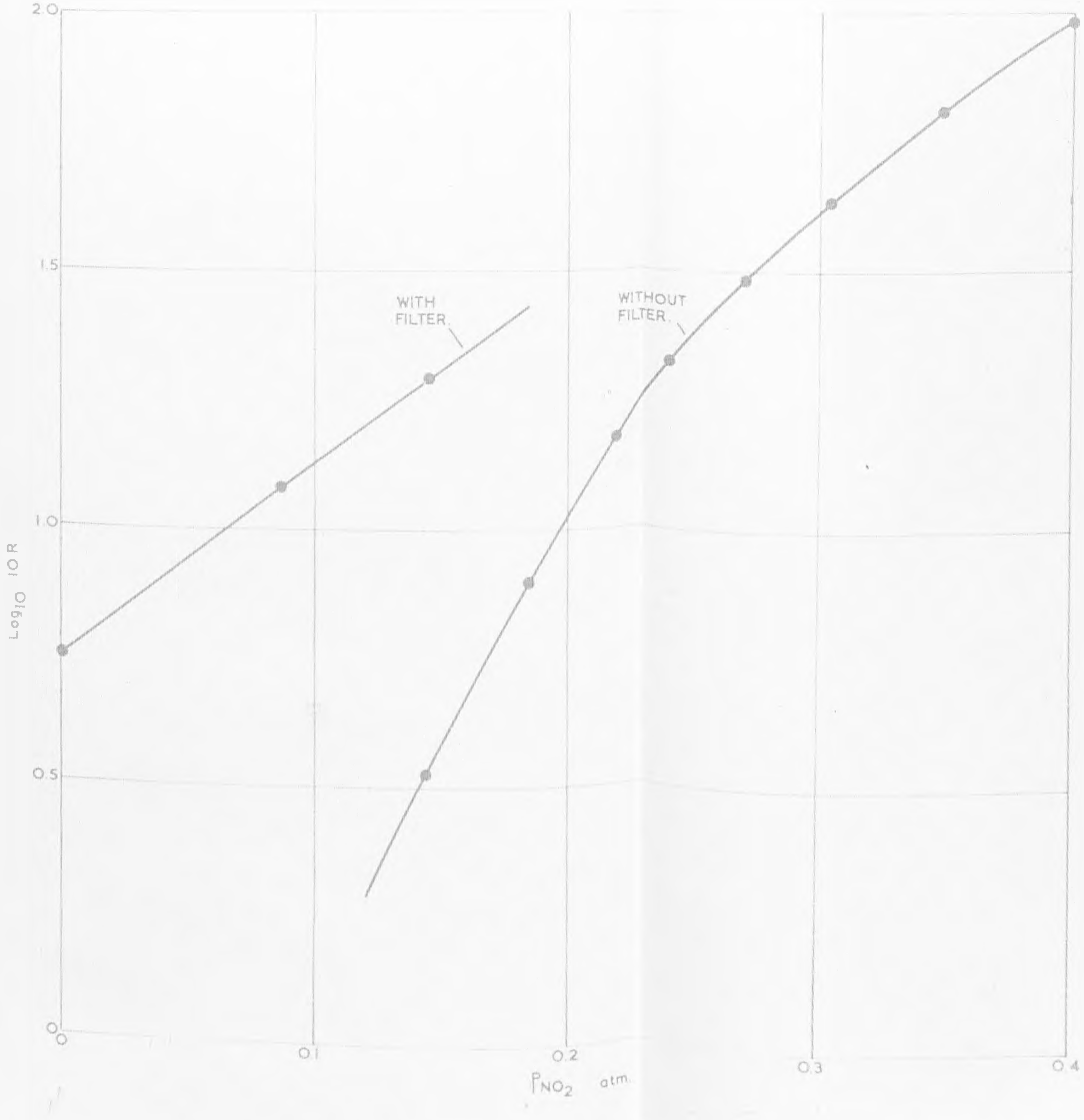
CIRCUIT DIAGRAM FOR CATHODE FOLLOWER. FIG. 21.



MODIFIED SPECTROPHOTOMETRIC CIRCUIT. FIG. 22.

A	B	S	R	D	S_2	S	D_{AV}	S_{AV}	$S_{AV}-S_M$	C_S	D_S	T_L	C_T	D_{SL}	D_{STL}
No at 25·00°c					-1·0							20·7			
53·5	298	339	53·541			-0·15									
79·9	375	348	79·873	26·332		-0·4									
53·5	303	352	53·549	26·324		-0·45						21·2			
79·9	369	354	79·885	26·336		-0·45									
79·9	369	368	79·899			-0·6						21·2			
53·5	330	380	53·550	26·349		-0·6			+	+			—		
79·9	386	395	79·914	26·364		-0·5₀	26·363	-0·6	4	0·015	26·378	21·3	0·006	26·375	26·369
53·5	360	413	53·553	26·361		-0·6			m						
53·5	368	428	53·568			-0·5						21·0			
79·9	403	440	79·937	26·369		-0·65			+	+					
53·6	466	437	53·571	26·366		-0·7	26·369	-0·7	3	0·011	26·380	21·3	— 0·006	26·377	26·371
79·9	413	459	79·946	26·375		-0·75			m						
N_2O_3 at 25·00												21·0			
81·0	487	476	80·989			-1·0			+	+			—		
30·7	514	499	30·685	50·304		-1·0									
81·0	500	495	80·995	50·310		-0·8	50·305	-0·9	1	0·004	50·309	21·2	0·011	50·304	50·293
30·7	537	530	30·693	50·302		-0·9			m						

B	W	R	Mean	2R1
				1030/23/4/55
mV/5	mV/5			
449				
464	449			
464	451			no filter
478	~~[illegible]~~			
478	~~[illegible]~~	4595 x5		
478	420			
475	420	= 22·975		
438	416		✓	
445	418			
452	~~410~~			
469	416	4·19 x5		
449	422	= 20·95		
447	420			$\log 10R = 1{\cdot}040_2$
456				
462		1·097		
448				



PHOTOCURRENT CALIBRATION. FIG. 24.

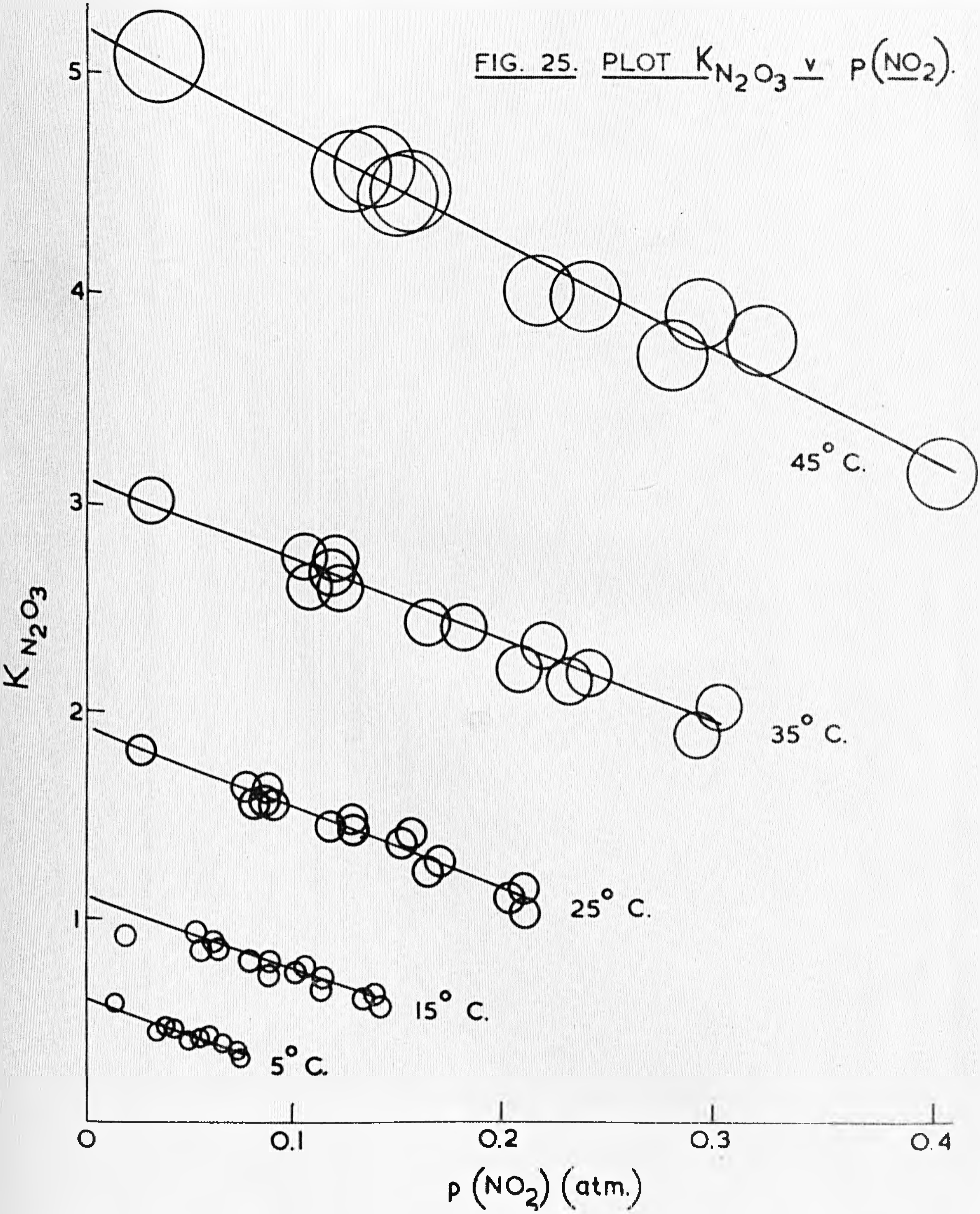
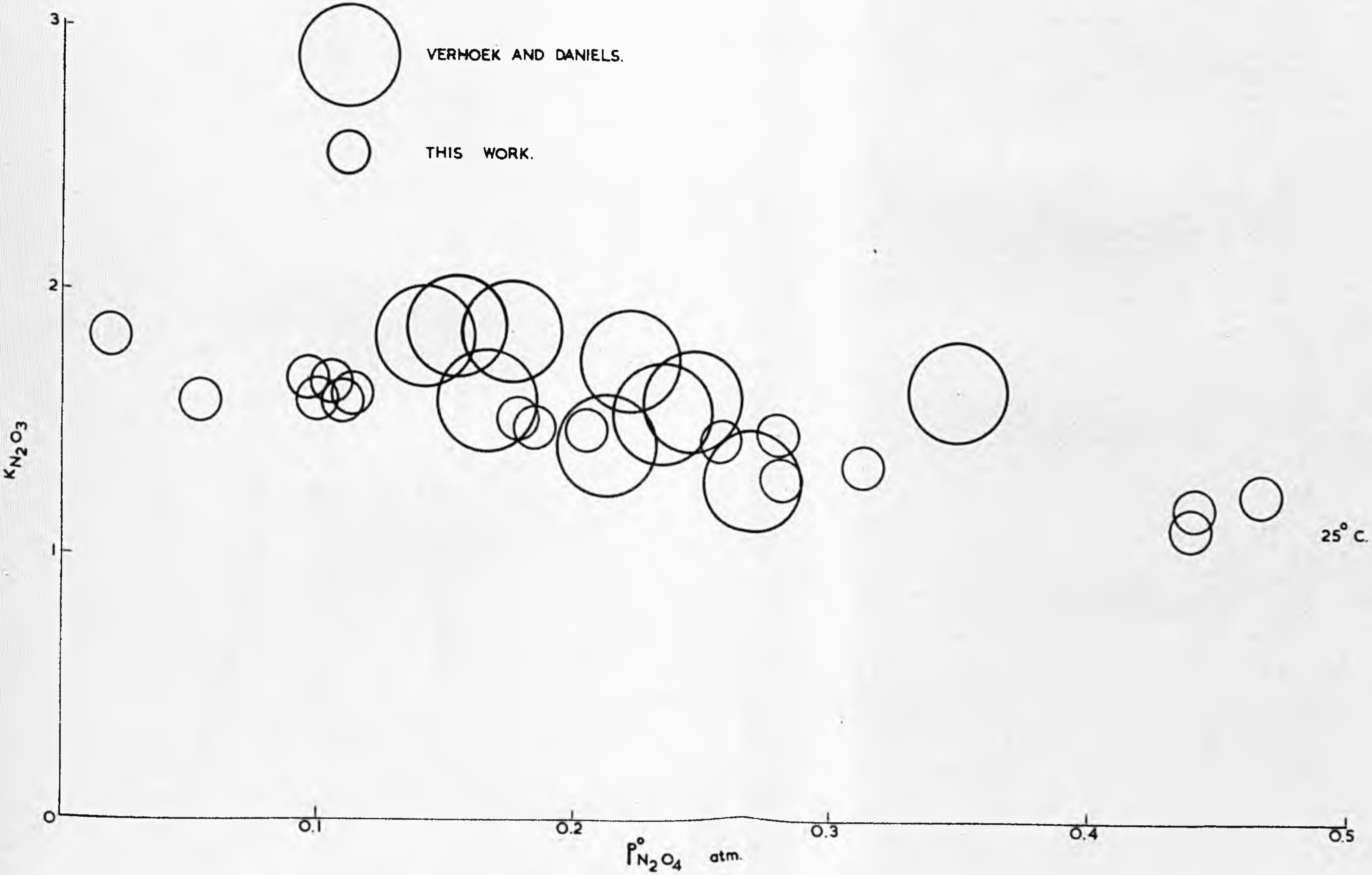
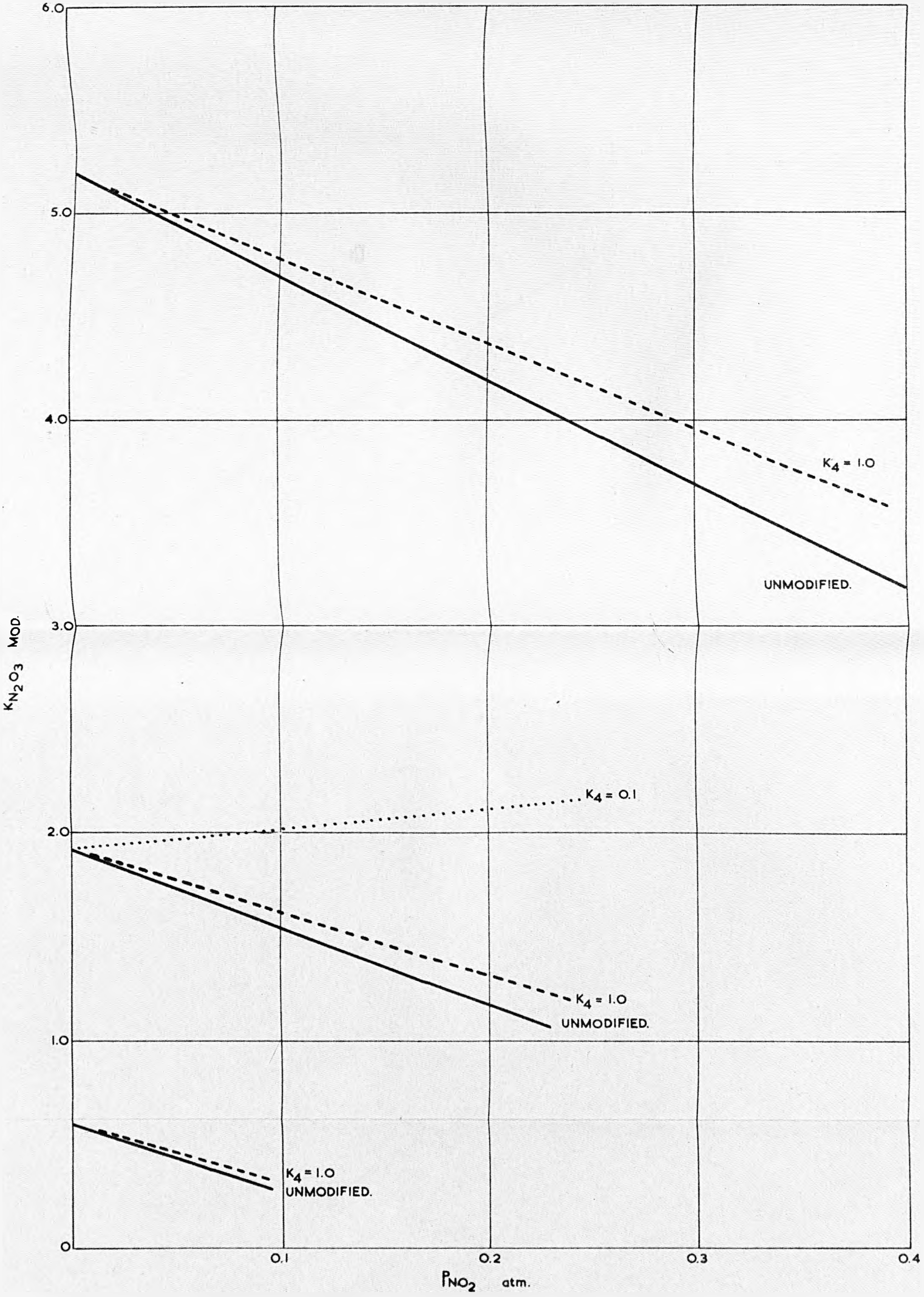


FIG. 25. PLOT $K_{N_2O_3}$ v $p(NO_2)$.

FIG. 26.

EQUILIBRIUM CONSTANT COMPARISON.





MODIFICATION OF $K_{N_2O_3}$ BY N_4O_6. FIG. 27.

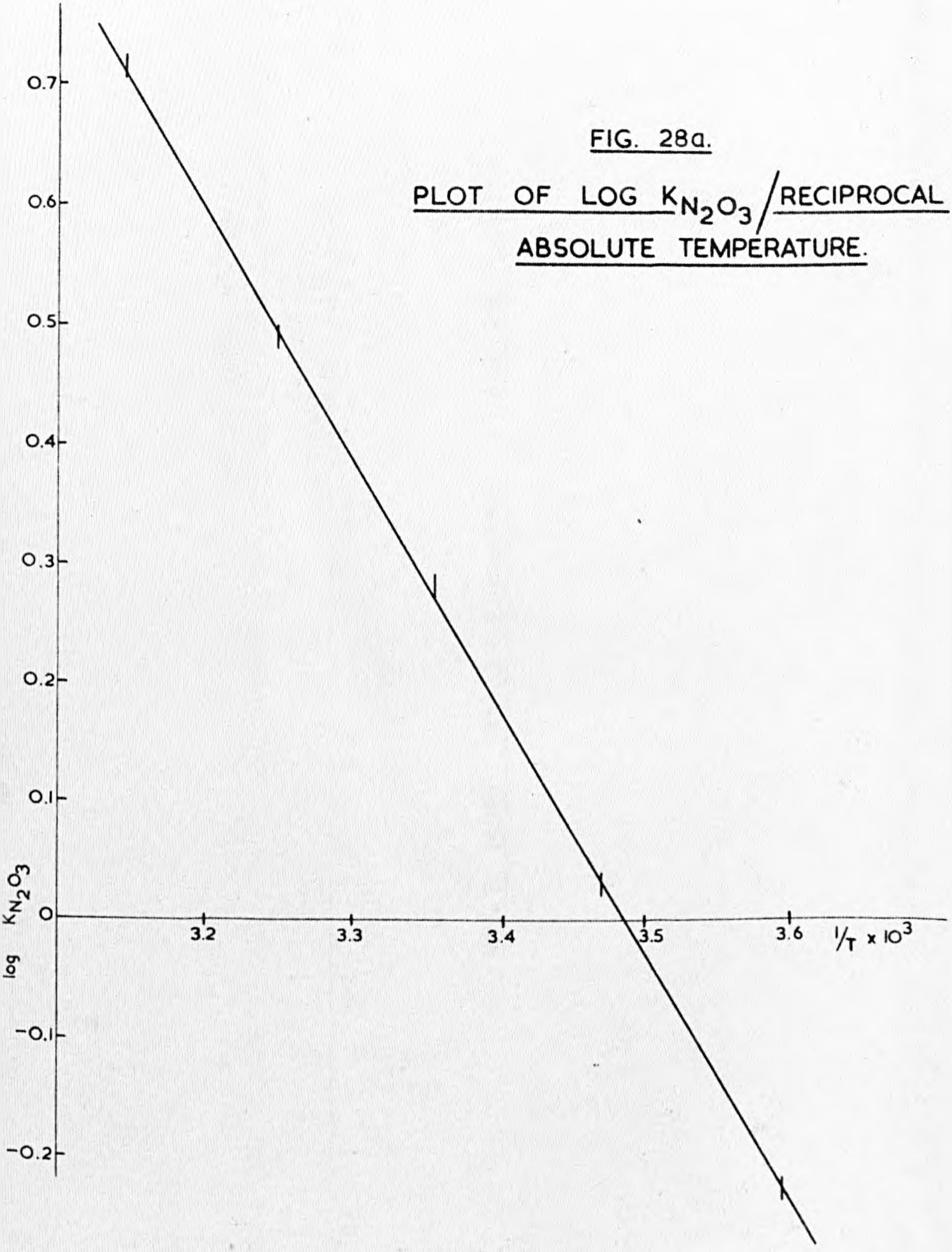
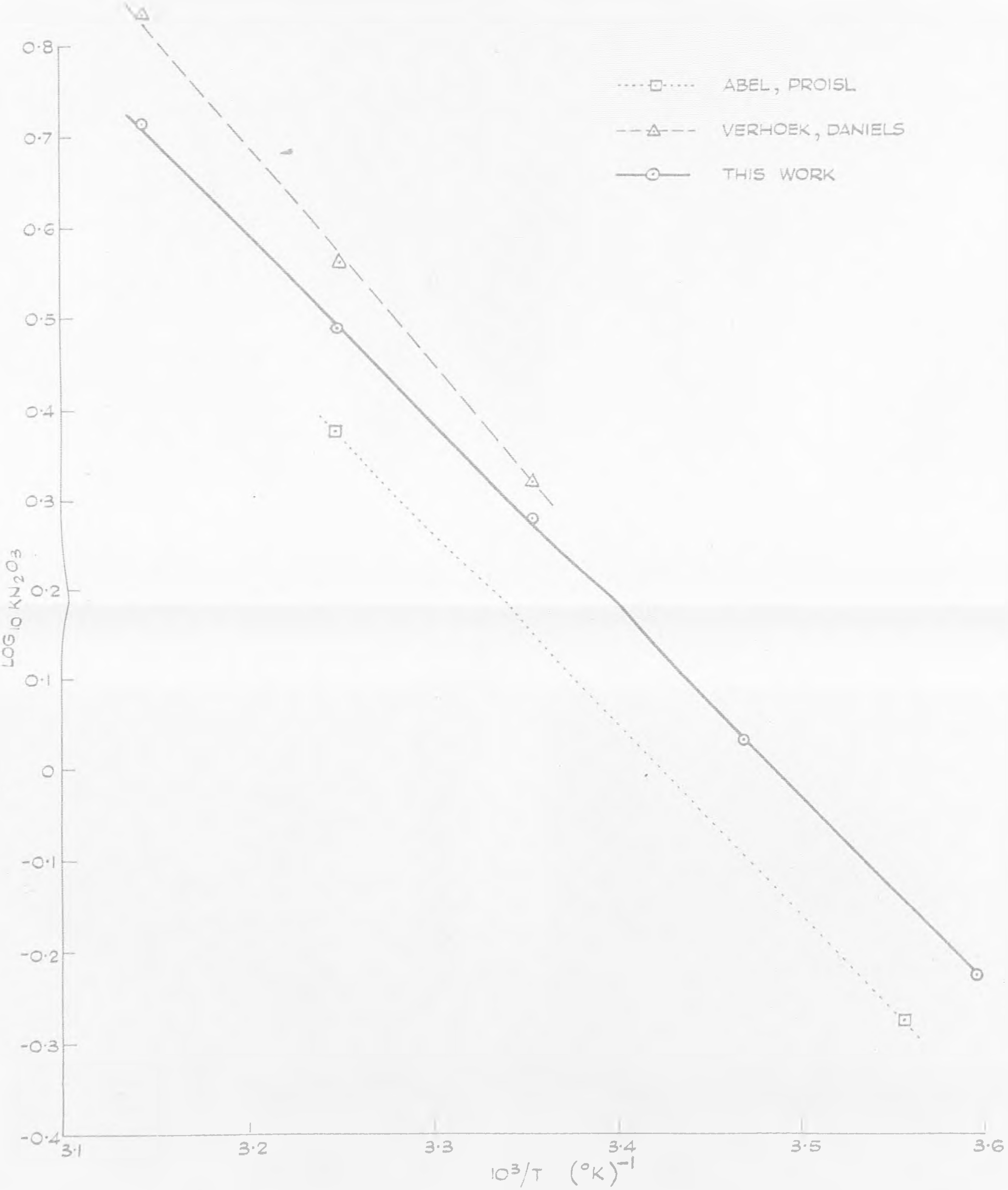
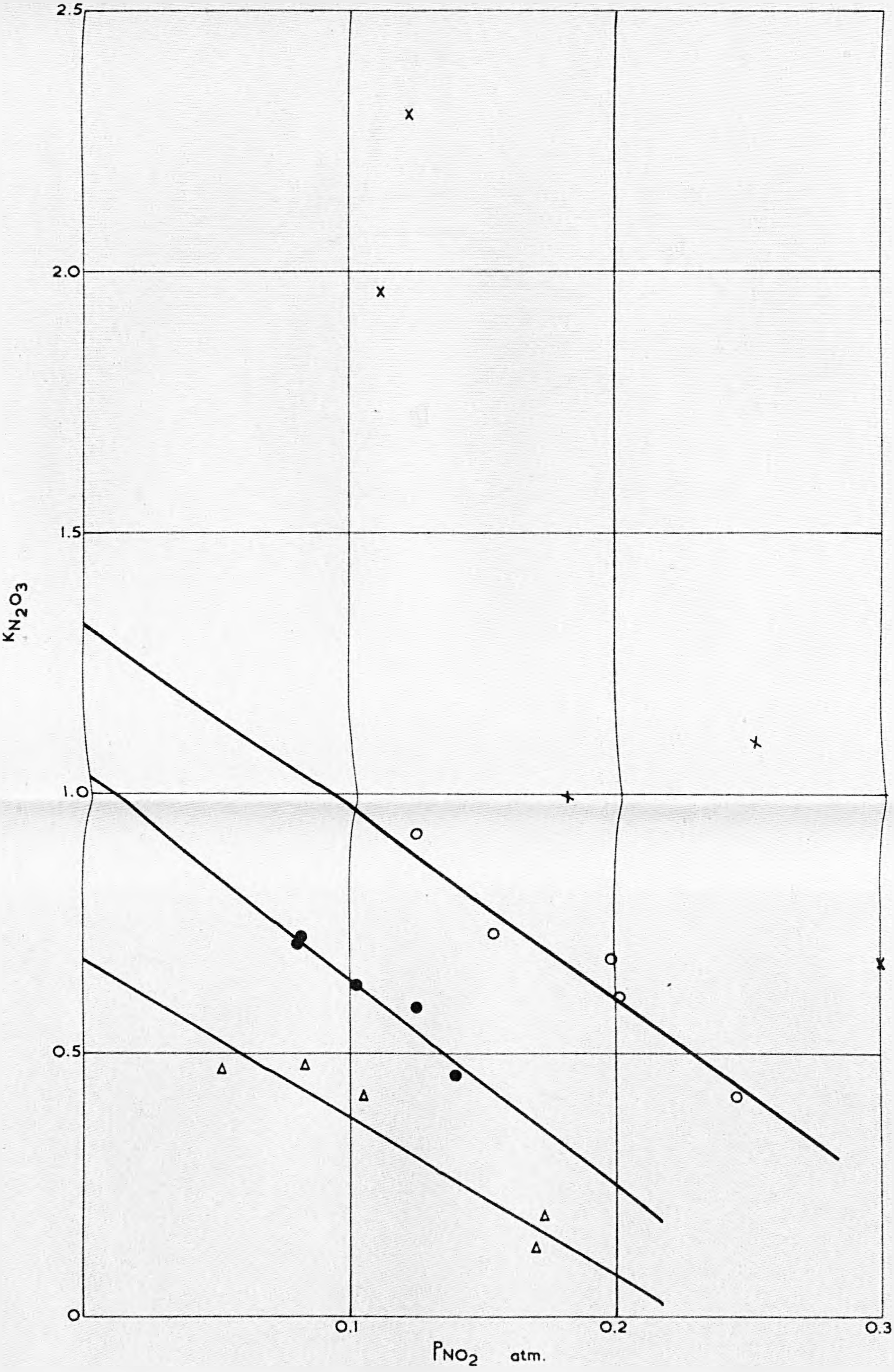


FIG. 28a.

PLOT OF LOG $K_{N_2O_3}$/RECIPROCAL ABSOLUTE TEMPERATURE.

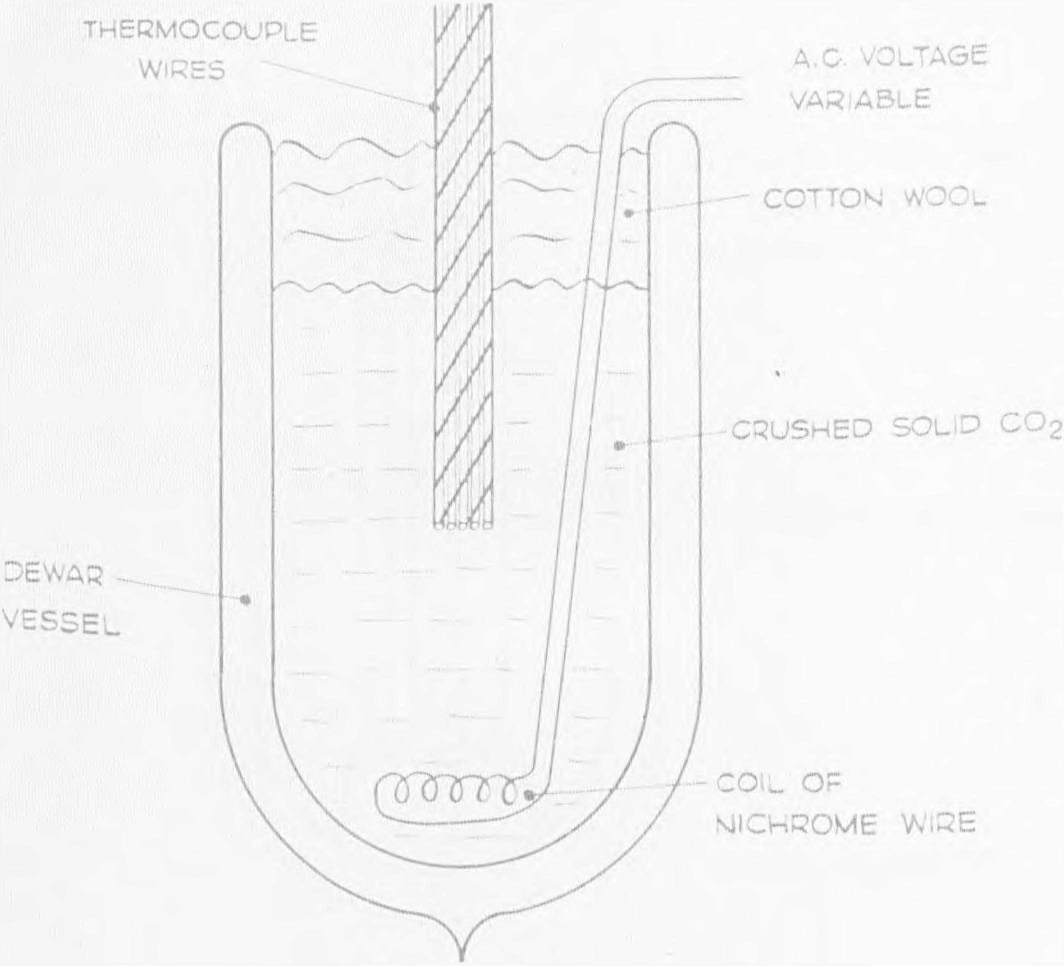


VAN'T HOFF PLOTS : SUMMARY. FIG. 28.



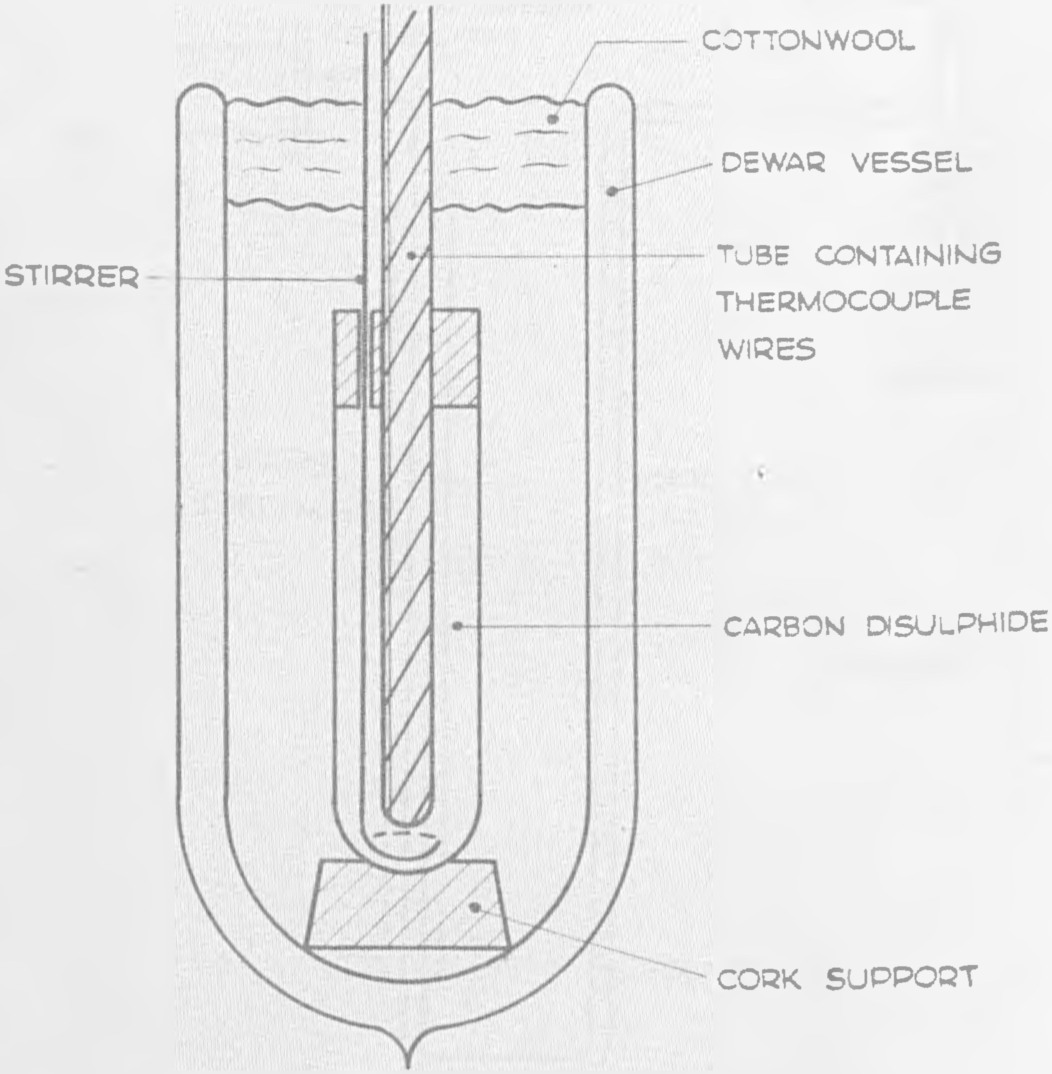
$K_{N_2O_3}$ FROM SPECTROPHOTOMETRIC MEASUREMENTS.

FIG. 28c.



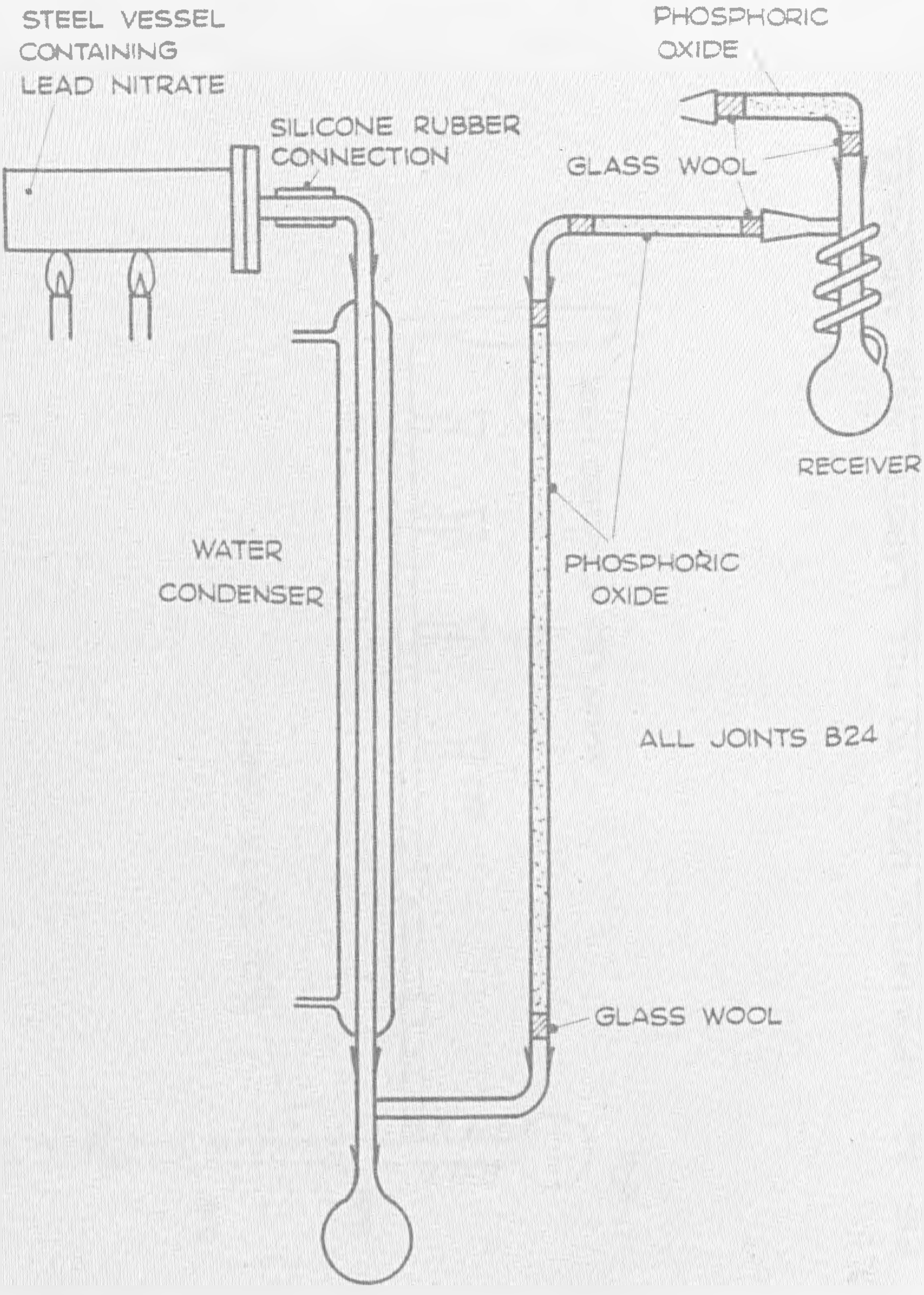
SUBLIMATION TEMPERATURE OF CO_2 APPARATUS

FIG. 29



MELTING POINT OF CS_2: APPARATUS.

FIG. 30.



GENERATION OF NO_2 : LARGE SCALE. FIG. 31.

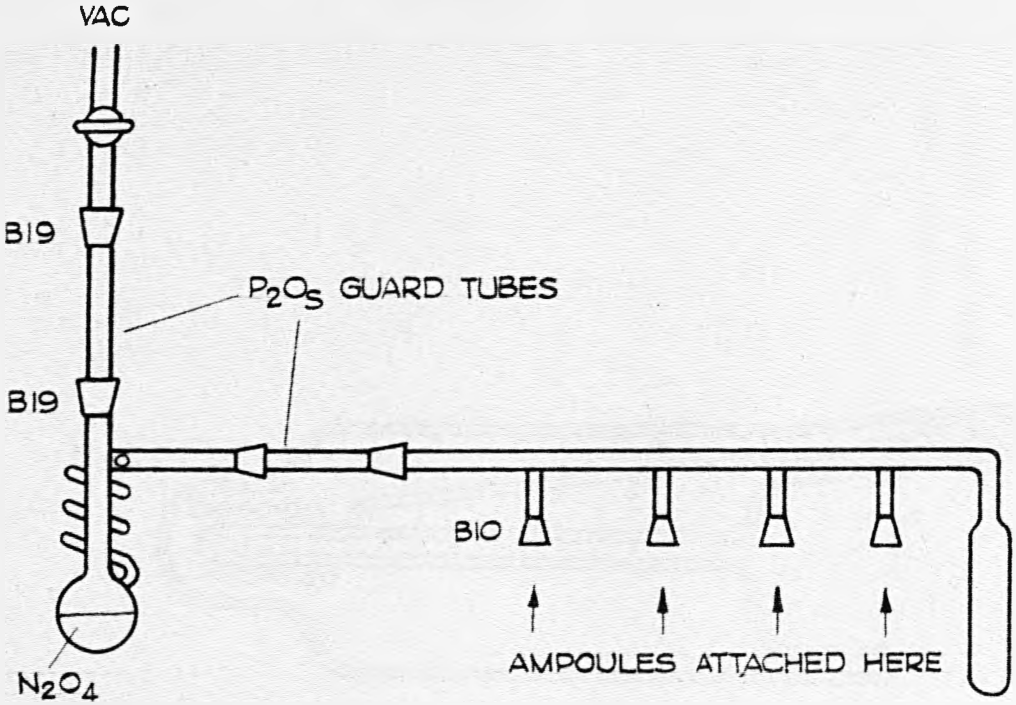


FIG. 32. APPARATUS USED TO FILL LARGER N_2O_4 AMPOULES.

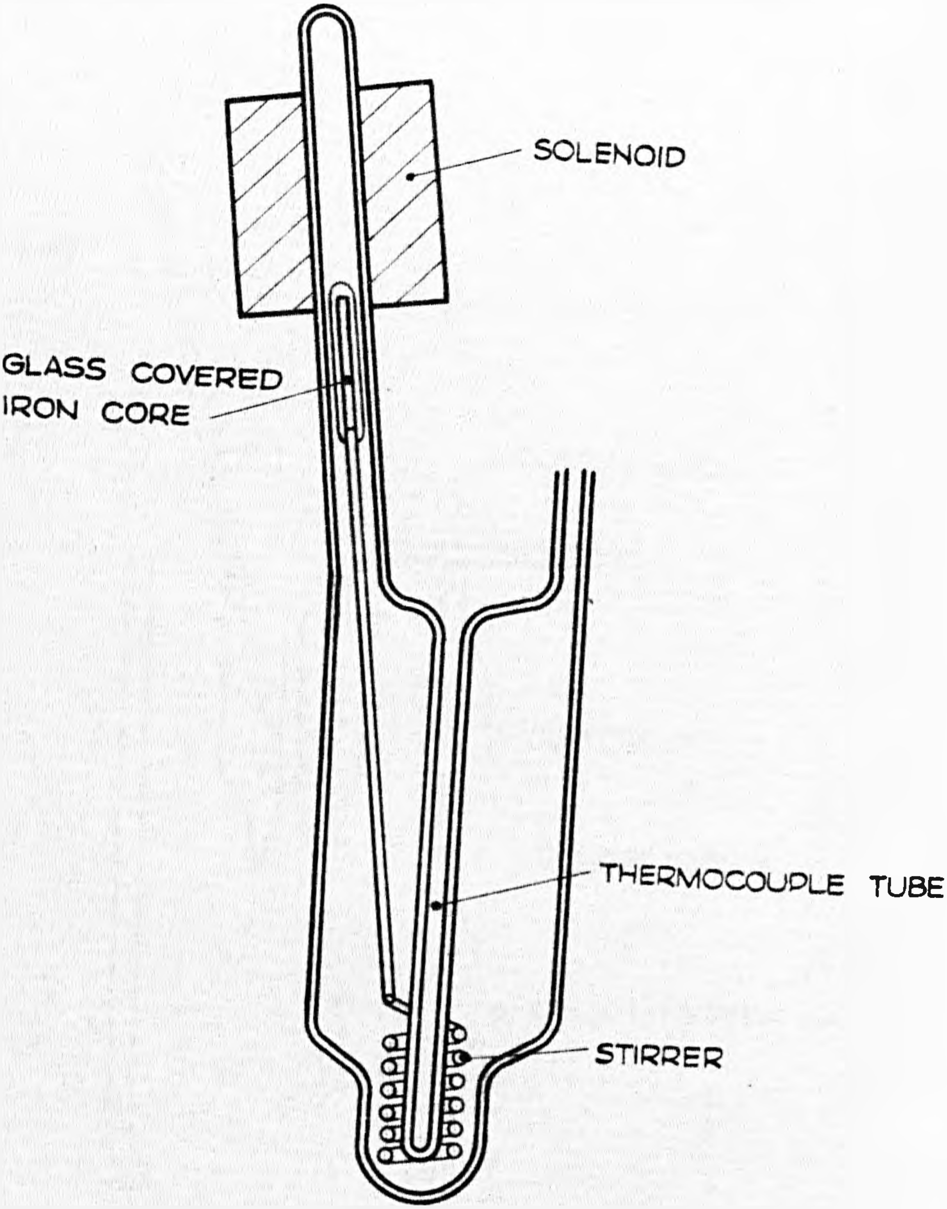
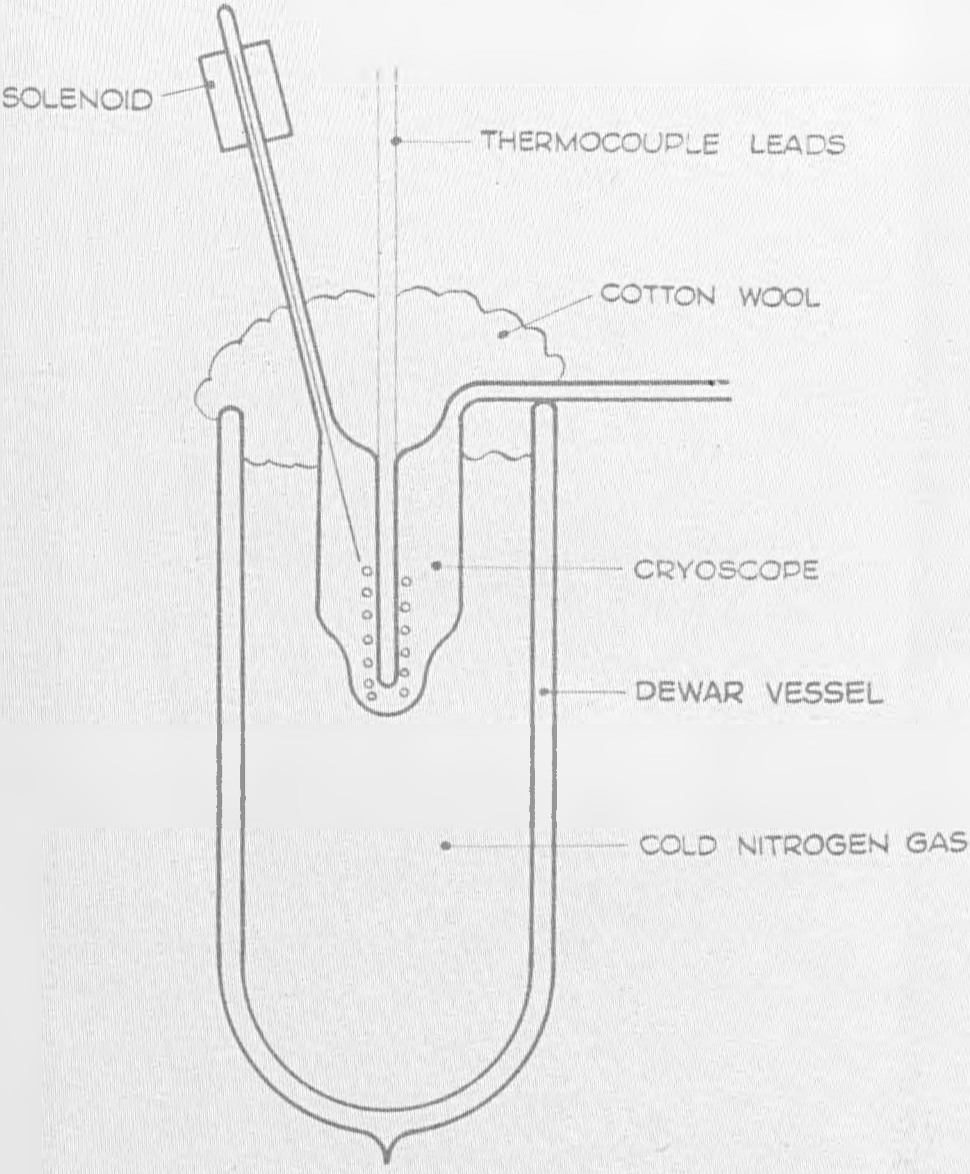
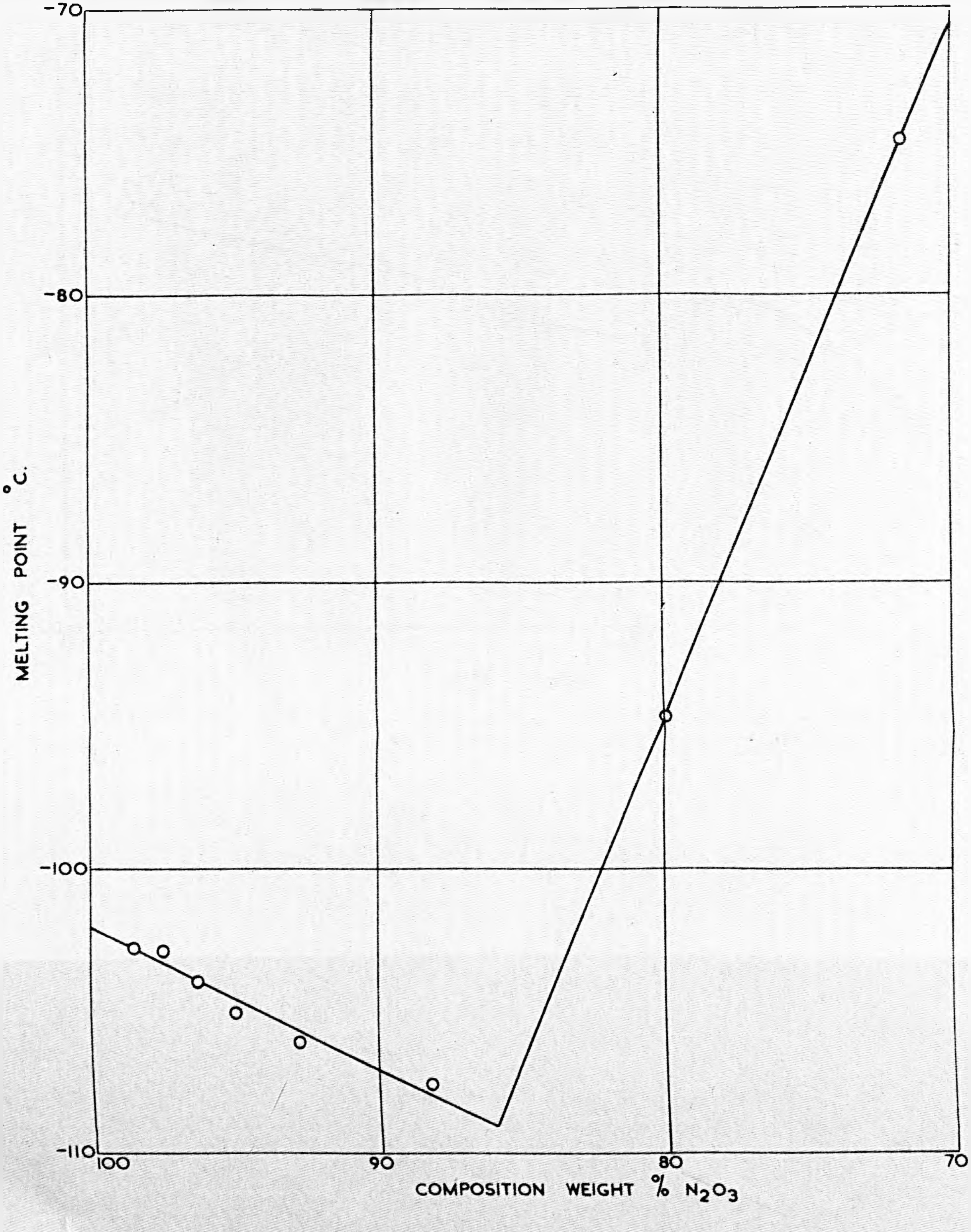


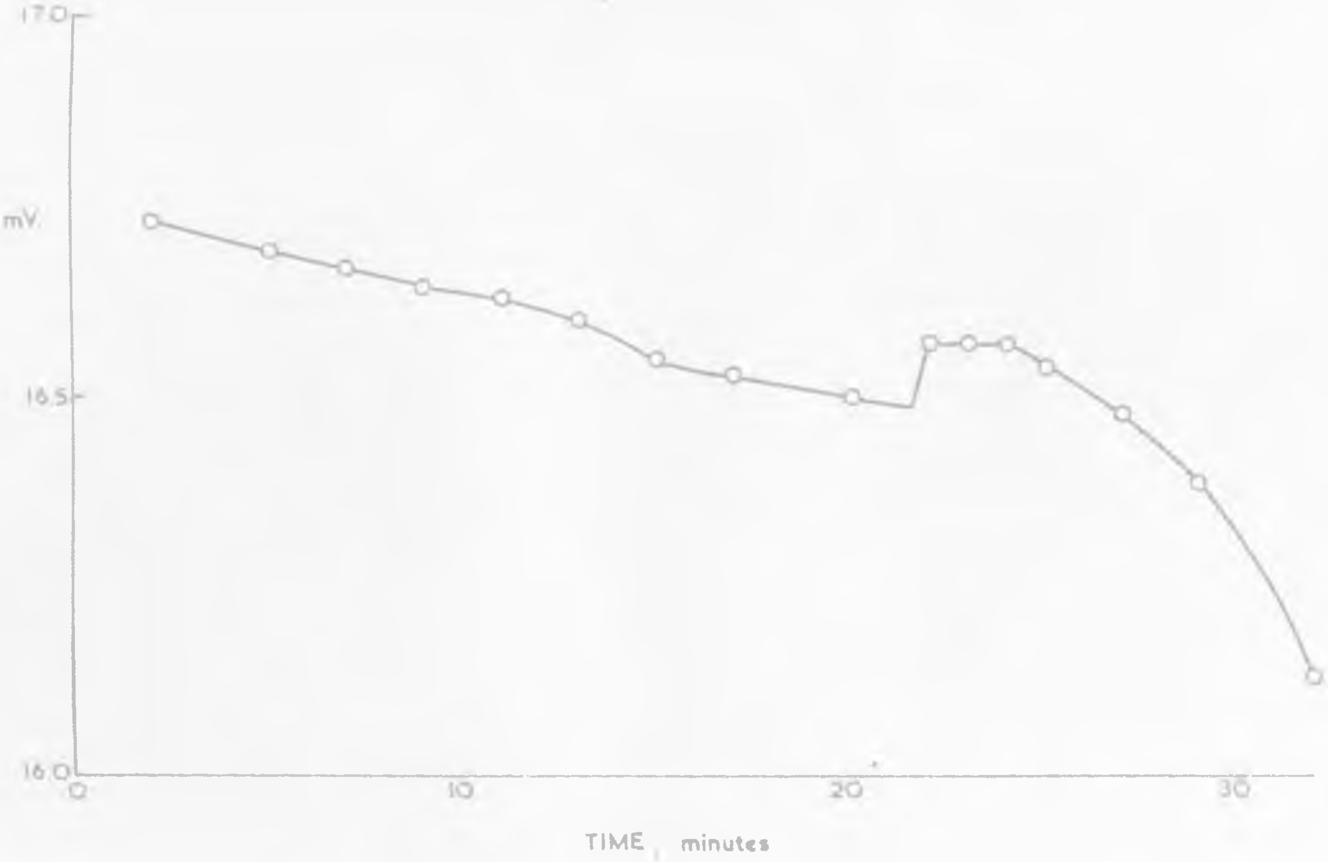
FIG. 33. CRYOSCOPE I.



APPARATUS: CRYOSCOPIC EXPERIMENT (I). FIG. 34.



CRYOSCOPIC RUN ①. FIG. 35.



TYPICAL MELTING CURVE. FIG. 36.

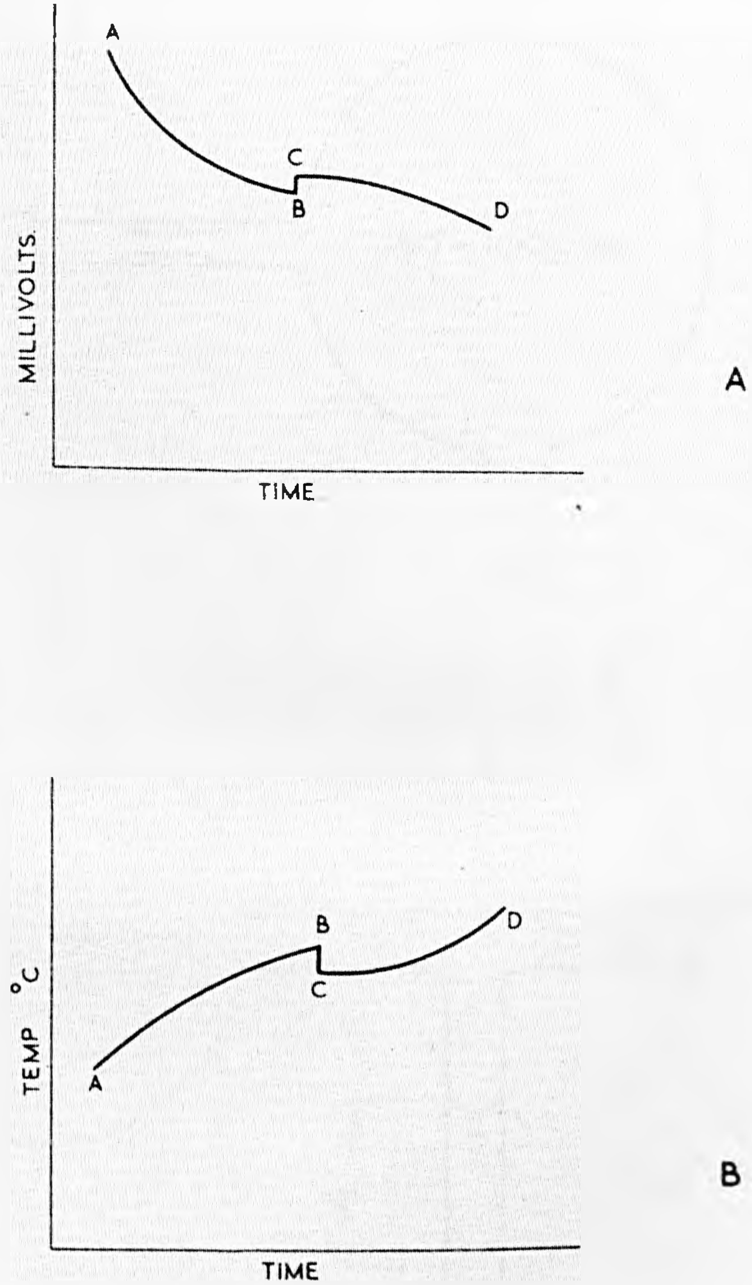


FIG. 37.

IDEALISED MELTING CURVES.

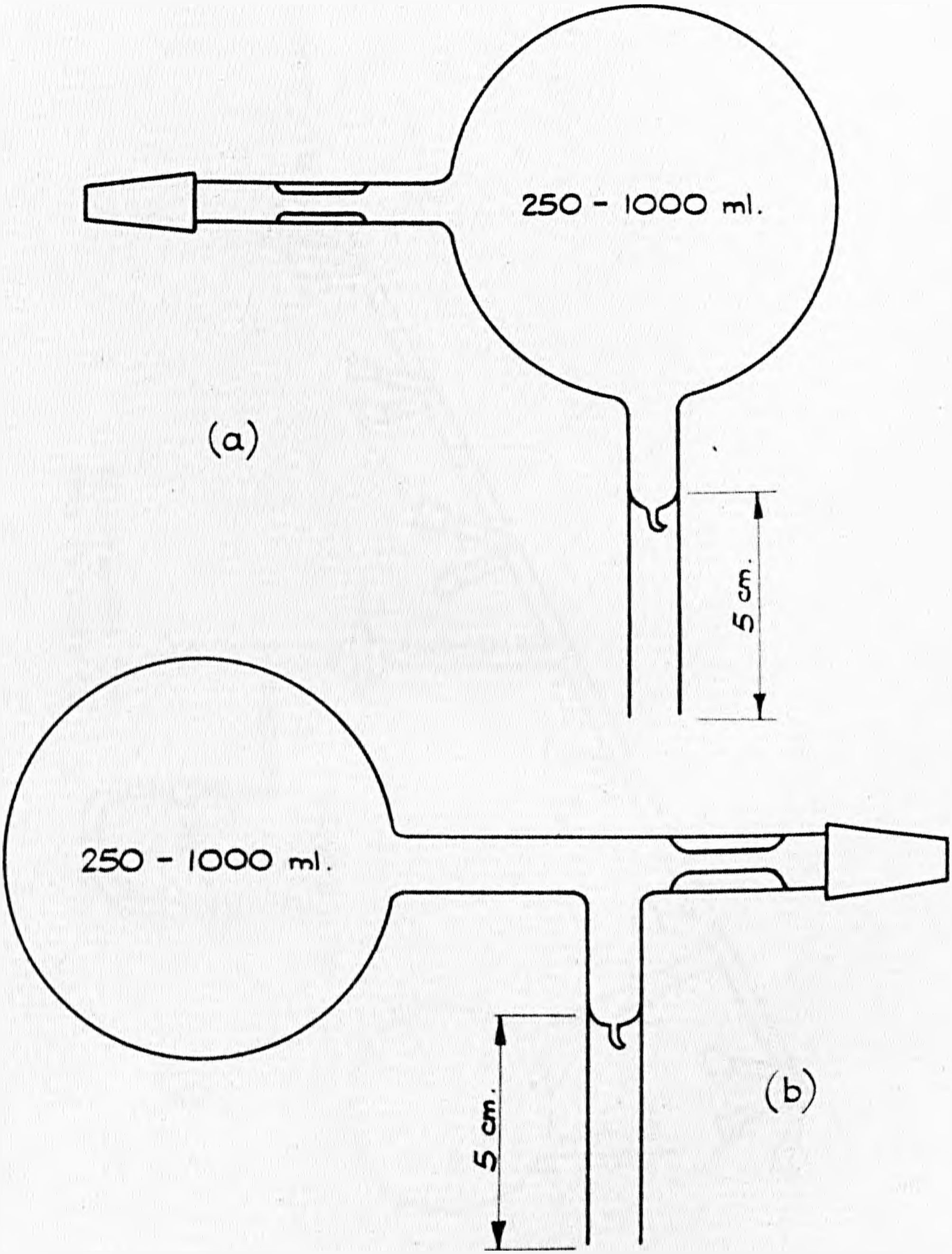


FIG. 38. NITRIC OXIDE BULBS.

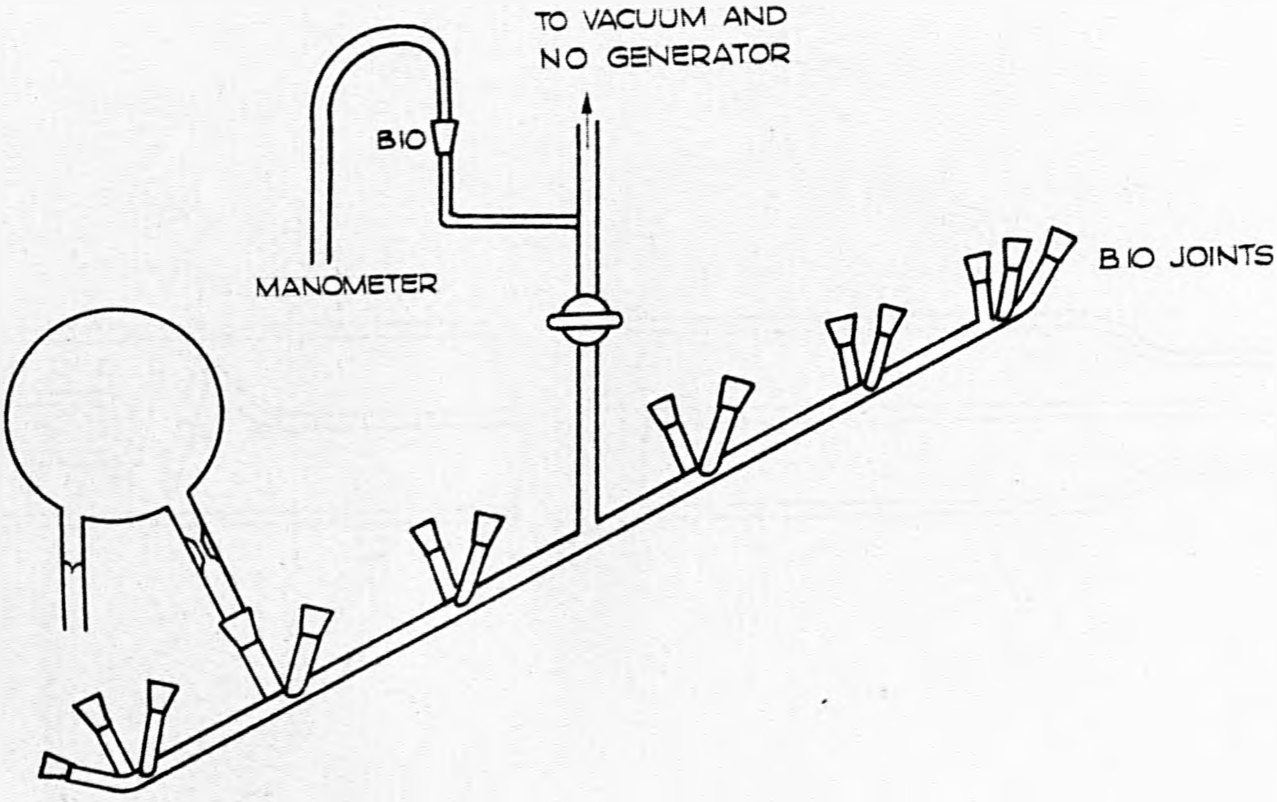
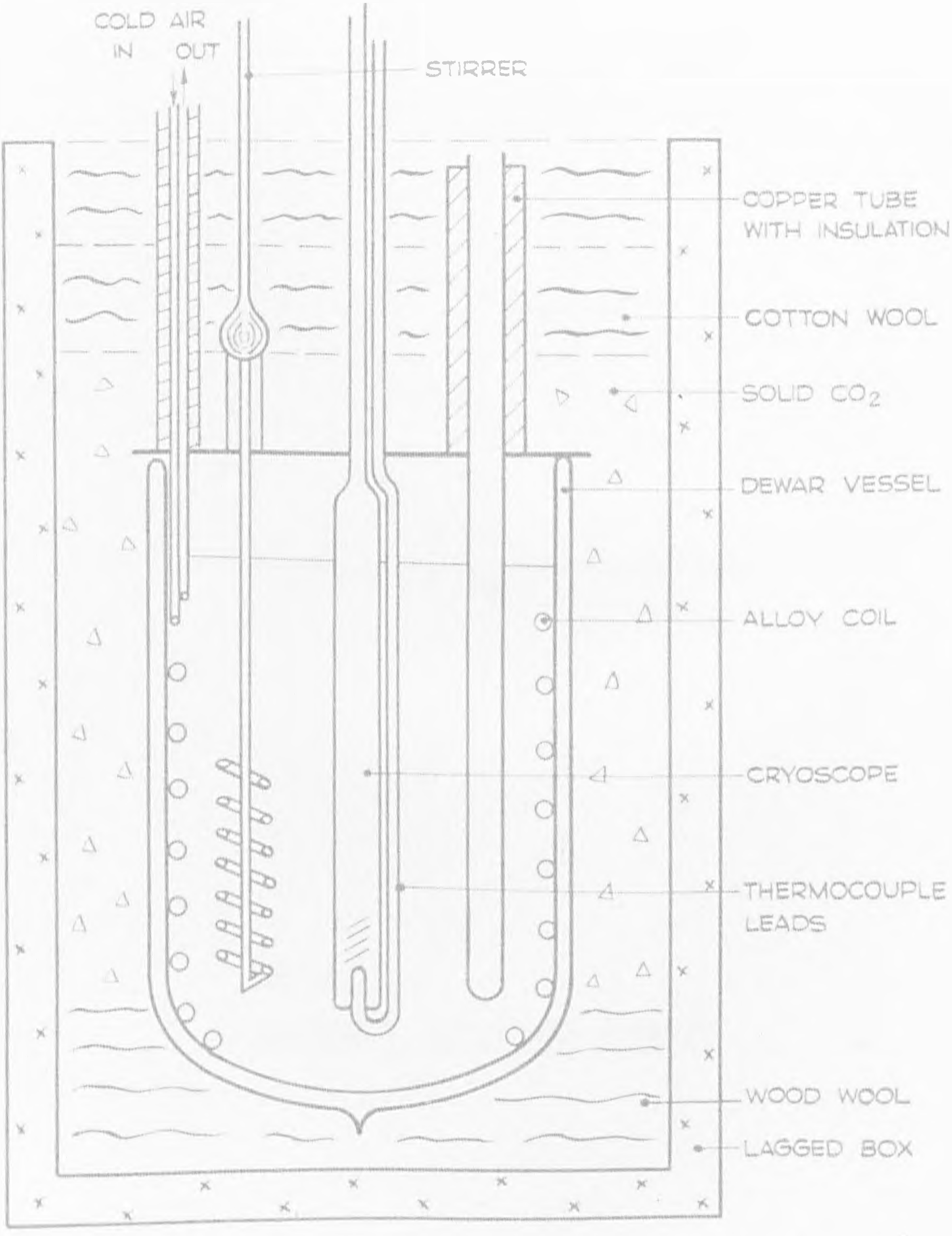


FIG. 39. APPARATUS FOR FILLING NITRIC OXIDE BULBS.

CRYOSCOPE 2. FIG. 40.



APPARATUS: CRYOSCOPIC EXPERIMENT ②. FIG. 41.

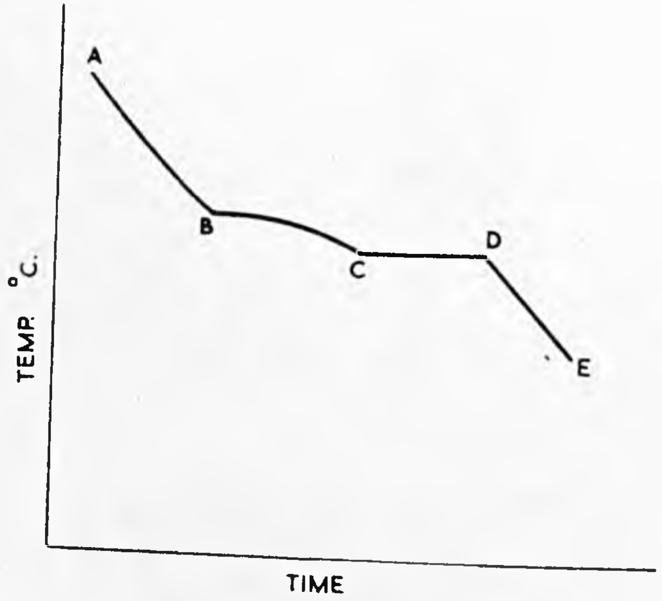
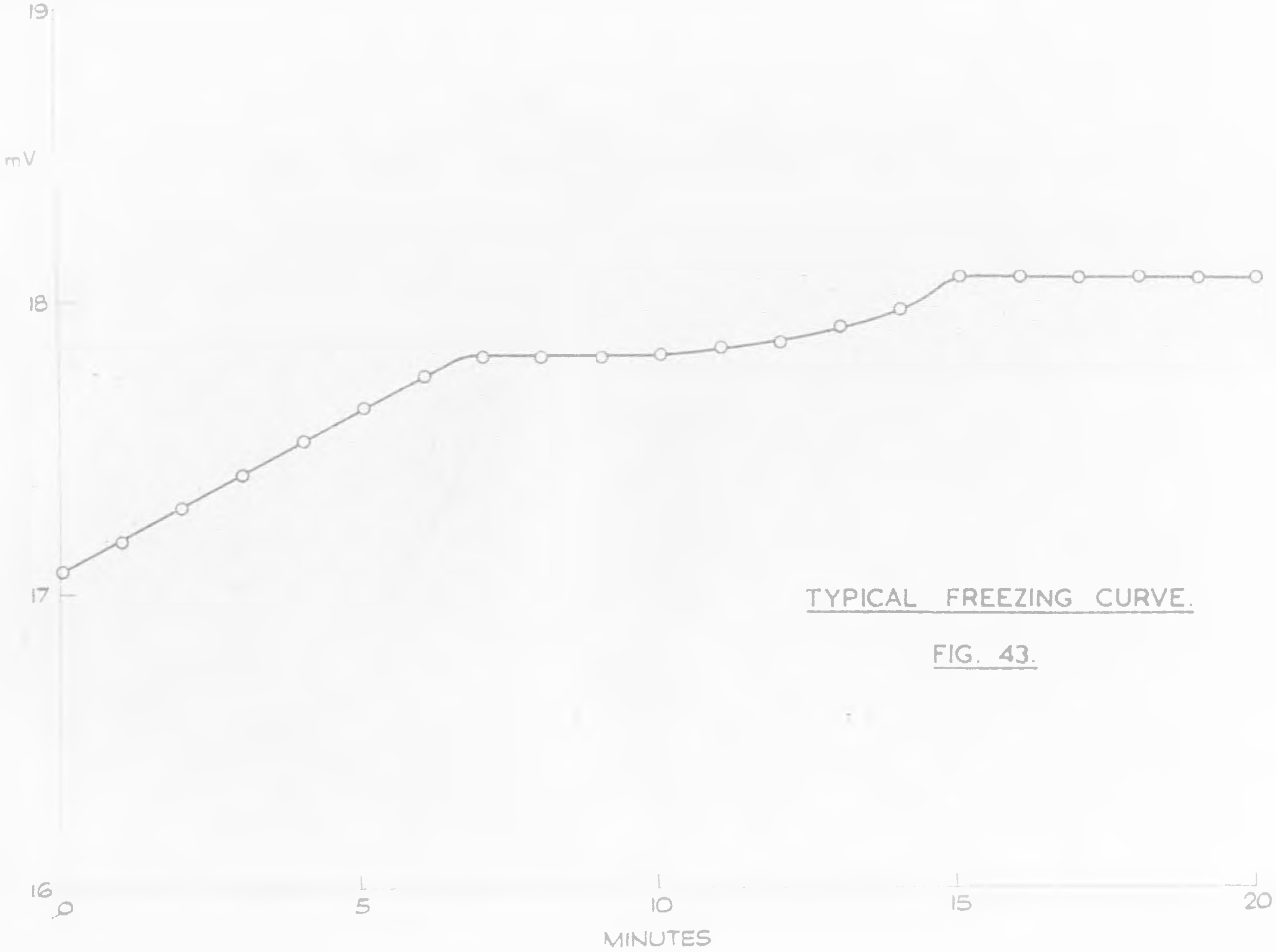


FIG. 42.

IDEALISED FREEZING CURVE.



TYPICAL FREEZING CURVE.

FIG. 43.

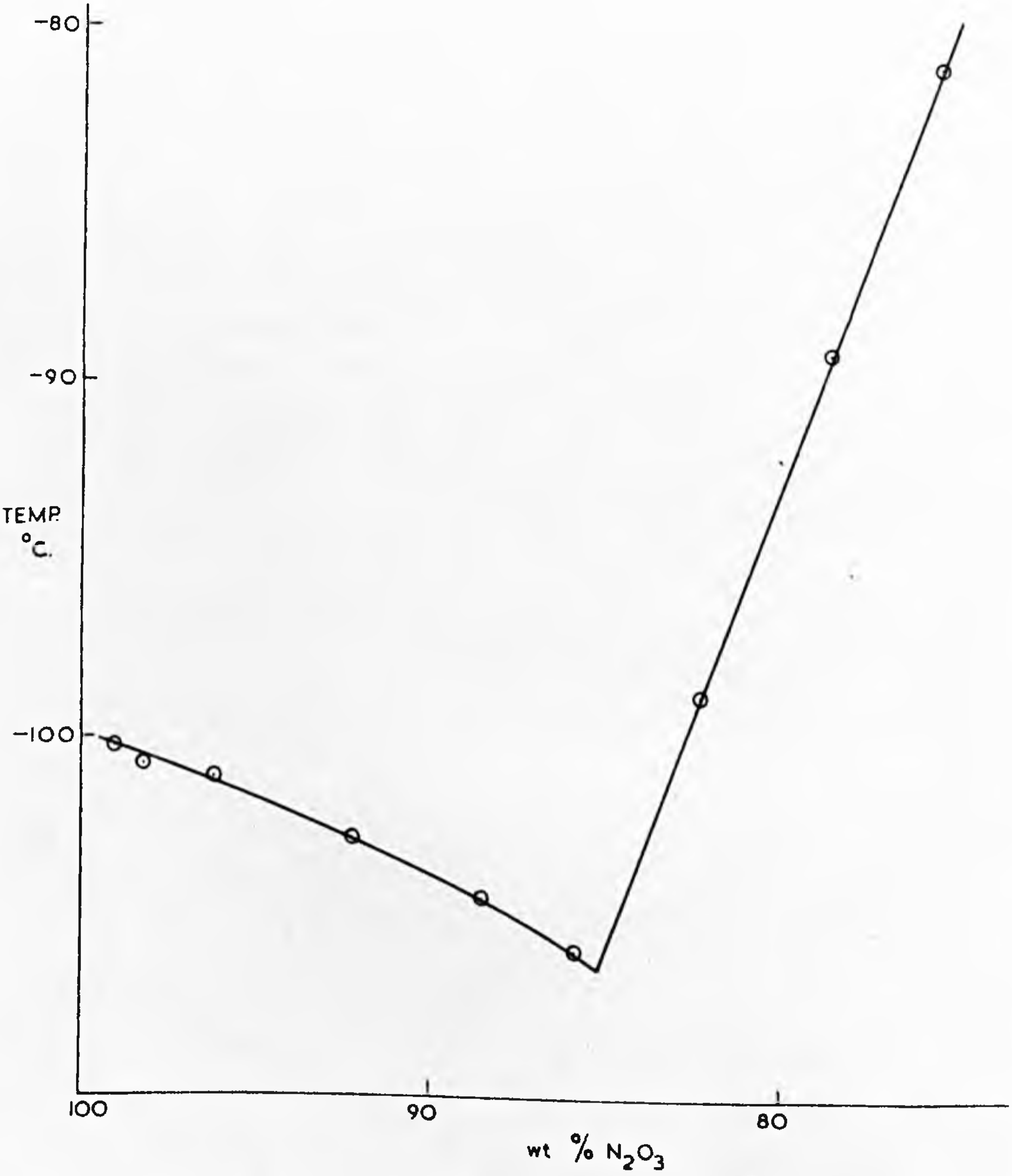


FIG. 44.

CRYOSCOPY : EXPERIMENT 2

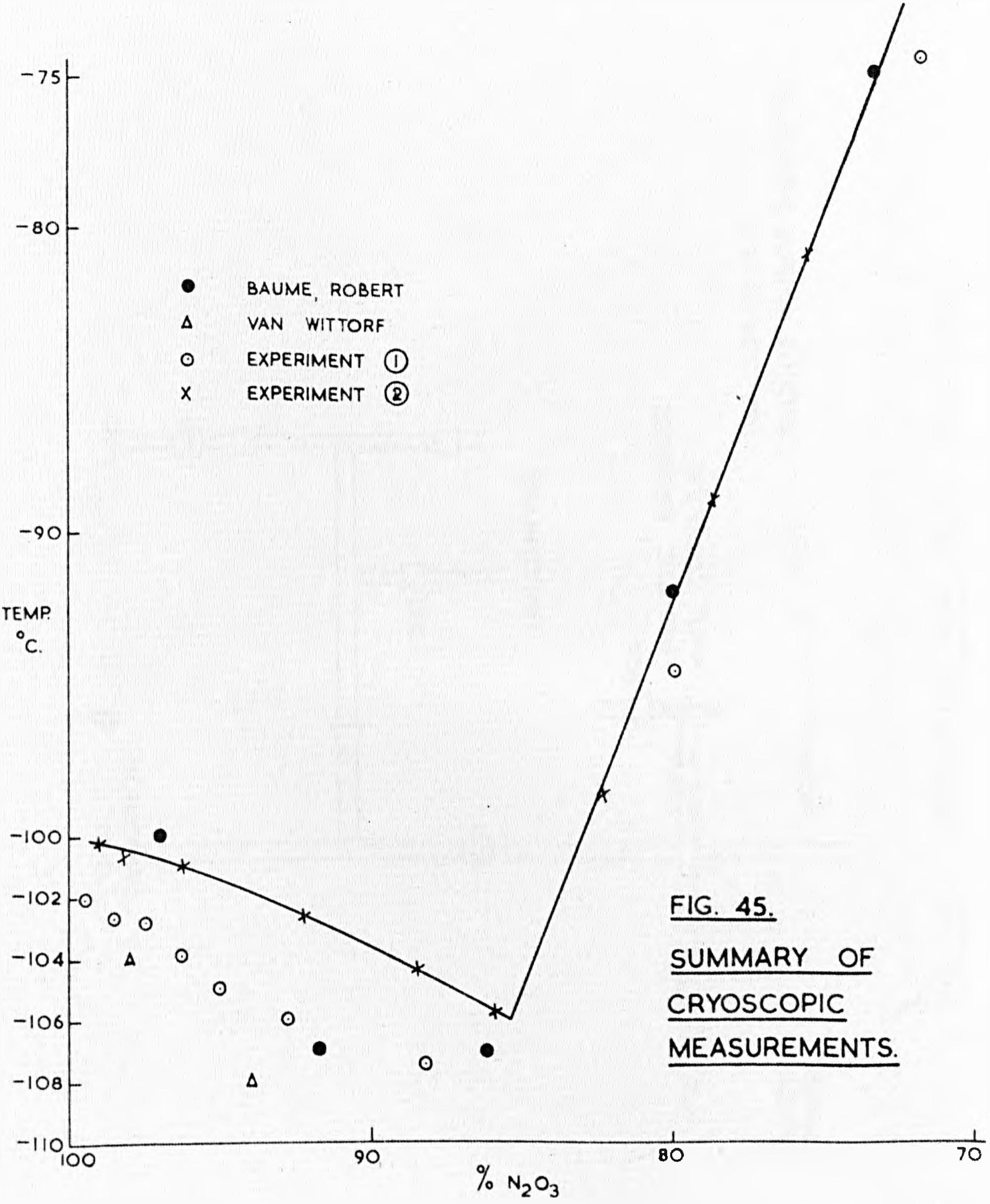


FIG. 45.

SUMMARY OF CRYOSCOPIC MEASUREMENTS.

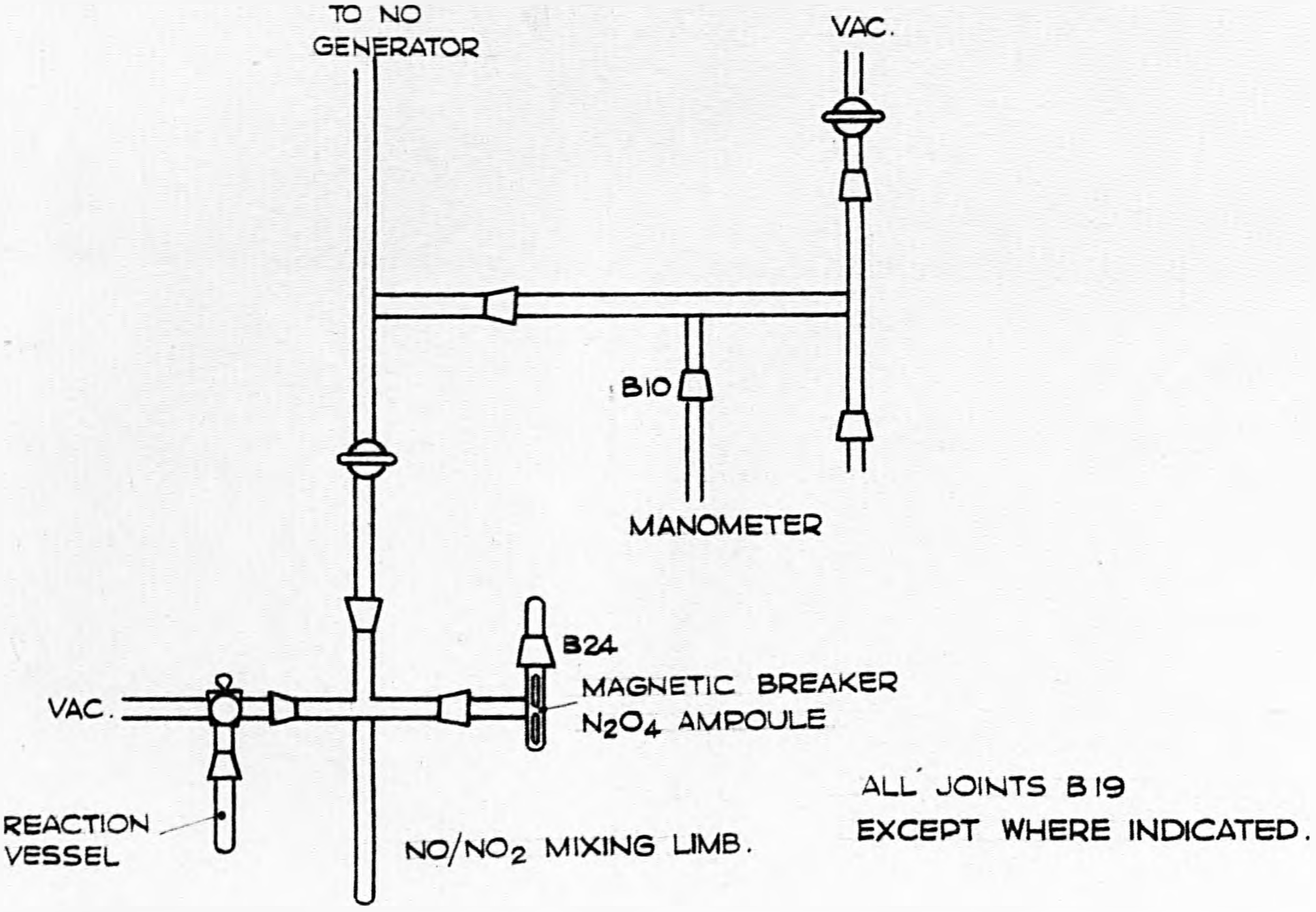
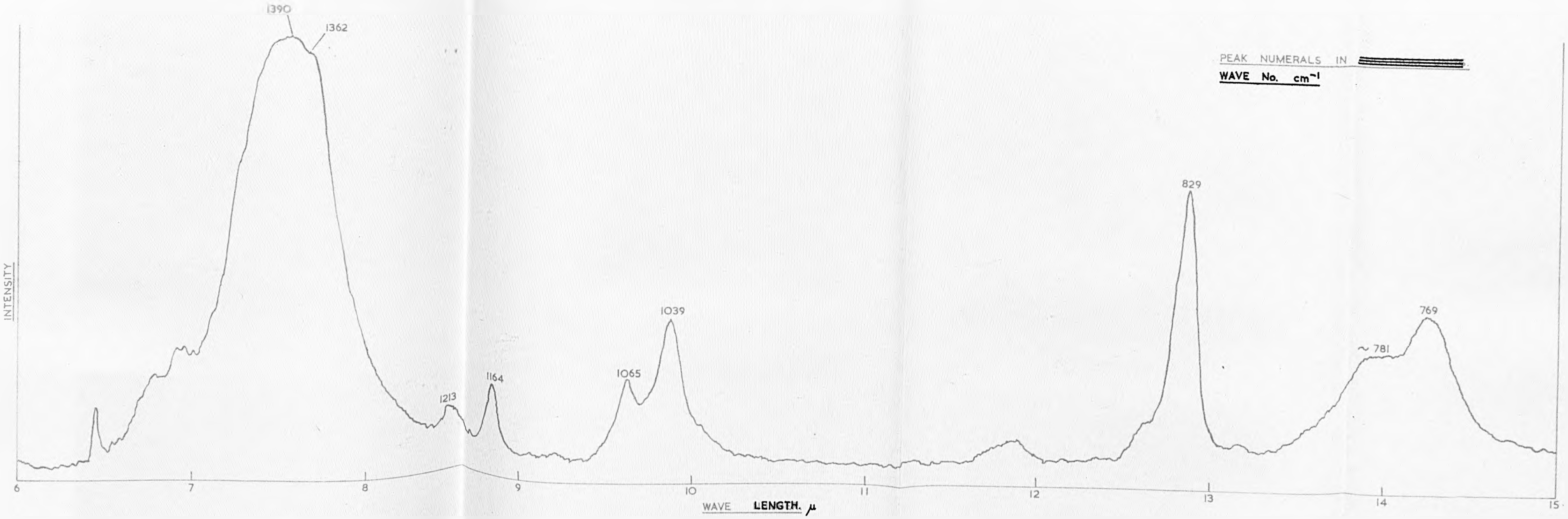
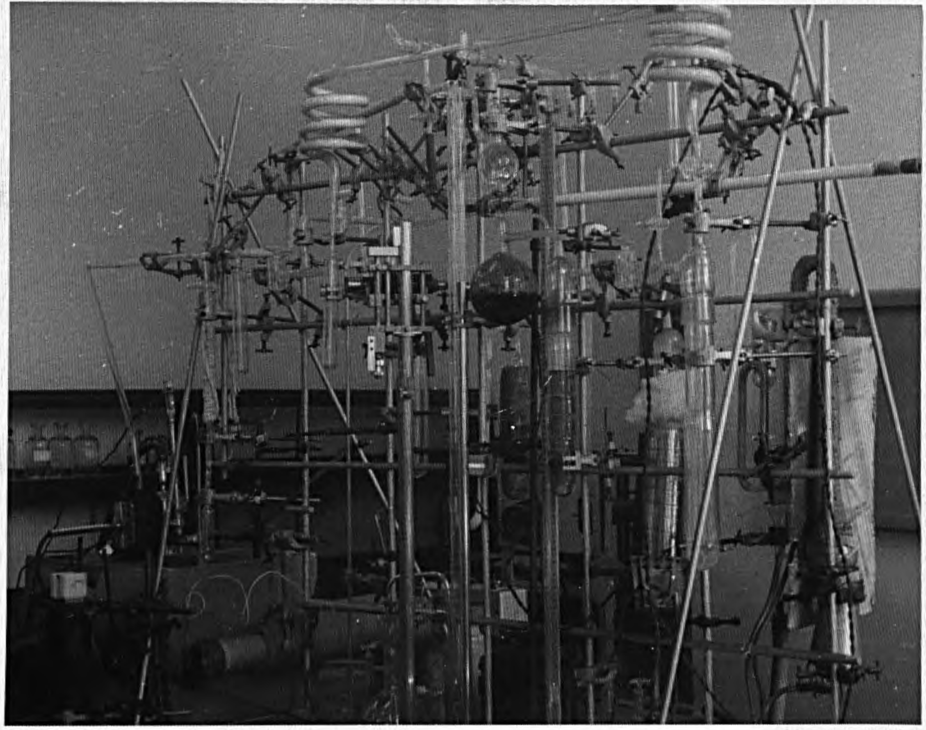


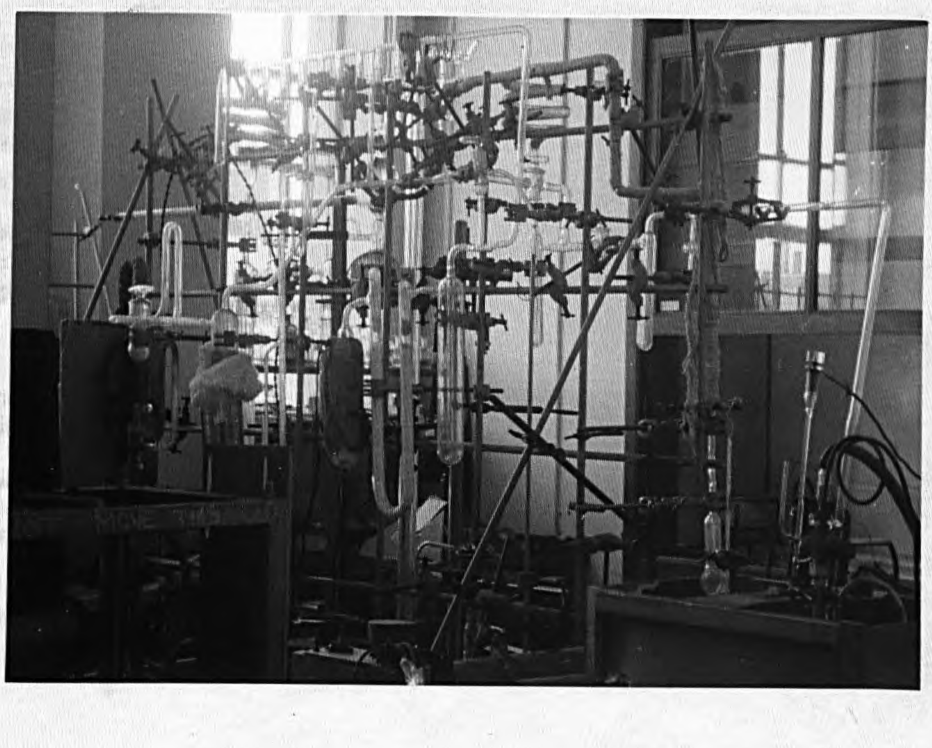
FIG. 46. APPARATUS FOR N_2O_3 REACTIONS.



INFRA-RED TRACE REACTION PRODUCT SWB 19.

FIG. 47.





Preprinted from the Journal of the Chemical Society,
April, 1957, (319), pages 1681—1686.

319. *Dinitrogen Trioxide. Part I. Stability in the Gaseous Phase.*

By I. R. Beattie and S. W. Bell.