A THESIS

entitled

STUDIES OF THE GASEOUS OXIDATION OF SULPHUR DIOXIDE

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ABSTRACT

This thesis describes an investigation into the kinetics and mechanism of the gaseous oxidation of sulphur dioxide both in the absence and presence of added gaseous catalysts and at temperatures between 500 and 1000°C.

In the Introduction a survey is made of previous studies of the oxidation of sulphur dioxide, particularly in the gas phase. Special reference is made to the NO-catalysed reaction because oxides of nitrogen are known promoters of the oxidation and they occur in conjunction with sulphur dioxide in flue gases.

The Experimental section describes the techniques and apparatus employed. A conventional vacuum system was used and the reactions were studied in silica reaction vessels. In general the reactions were followed by pressure change measurements but these were supplemented by colorimetric analysis of the residual sulphur dioxide.

The Results section gives details of the kinetic and analytical results obtained. The kinetics of the reaction in the absence of added catalysts have been determined only over a rather narrow temperature range (900-1050°C). In the presence of nitric oxide, reaction takes place at an appreciable rate at temperatures as low as 400°C. The catalysed reaction is essentially homogeneous and its rate is unaffected by nitrogen and water vapour. Experiments are also described in which

sulphur dioxide + oxygen mixtures have been added to decomposing hydrogen peroxide vapour, and to oxidising carbon monoxide and organic fuels.

The experimental findings are critically examined in the Discussion. On the basis of the dependence of the rate of the uncatalysed reaction on the concentration of the reactants and of the value of the activation energy, a tentative reaction mechanism is proposed which involves initially the collisional activation of sulphur dioxide. The observed kinetic relationships of the NO-catalysed reaction can be satisfactorily explained in terms of a mechanism involving the interaction of sulphur dioxide with the species NO_2 and NO_3.

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R.M.H.

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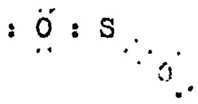
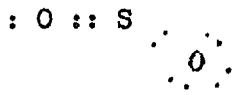
INTRODUCTION

A The physical and chemical properties of sulphur dioxide and sulphur trioxide and their importance in corrosion and air pollution

1. Physical and chemical properties

Altogether some six oxides of sulphur have been characterised[1]. Of these only sulphur dioxide and sulphur trioxide are stable both under normal atmospheric conditions and at higher temperatures, although sulphur monoxide has a transient existence in some reactions in shock-heated gases[2]. The physical properties of the two principal oxides of sulphur are summarized in Table 1. For both compounds the S – O bond length indicates some double bond character and the structures probably involve resonance forms such as :





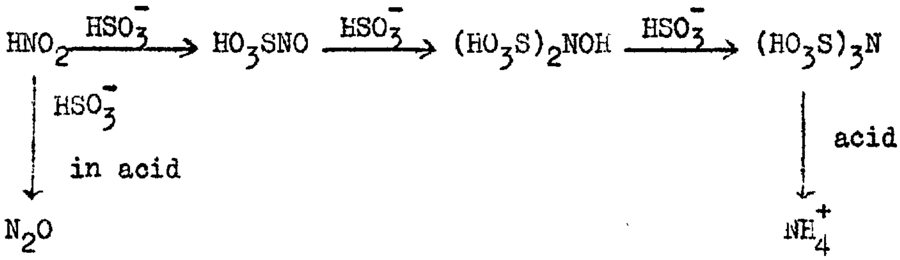
Sulphur dioxide acts both as an oxidising agent (e.g. towards hydrogen sulphide) and as a reducing agent (e.g. towards oxygen). The reducing properties are the more important, particularly in aqueous solution. Sulphur dioxide dissolves readily in water (ca. 10% by weight at 20°C and 760 mm. Hg) giving solutions of sulphurous acid. These solutions contain largely bisulphite (HSO_3^-) ions, with smaller concentrations of sulphite ($SO_3^=$) ions. The acid is unknown in the free state, although a hydrate, $SO_2.7H_2O$ can be crystallized from

Table 1

The physical properties of sulphur trioxide and sulphur dioxide[1].

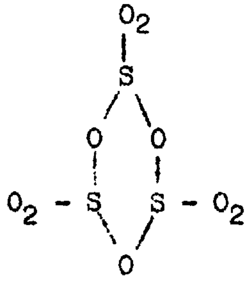
PROPERTY	SULPHUR TRIOXIDE				SULPHUR DIOXIDE
	Liquid	Alpha form	Beta form	Gamma form	
Equilibrium melting point, °C		62.3	32.5	16.8	-75.46
Heat of fusion, kcal mole^{-1}		6.2(62.3°C)	2.9(32.5°C)	1.8(16.8°C)	1.796
Heat of sublimation, kcal mole^{-1}		16.3(62.3°C)	13.0(32.5°C)	11.9(16.8°C)	
Heat of vaporization, kcal mole^{-1}	10.2	10.1(62.3°C)	10.1(32.5°C)	10.0(16.8°C)	5.96
Vapour pressure, mm. Hg at 0°C		5.8	32	45	
25°C		73	344	433	
50°C		650	950	950	
75°C		3000	3000	3000	
Heat of formation, kcal mole^{-1}			105.2	106	
Density, grams ml.$^{-1}$	1.904				1.46(-10°C)
Boiling point, °C	44.5				10.02
O-S-O bond angle	120				129
S-O bond length, A	1.43				1.46

concentrated solutions at low temperatures. Typical of the reducing properties of sulphur dioxide are its reactions with nitrous acid[3]

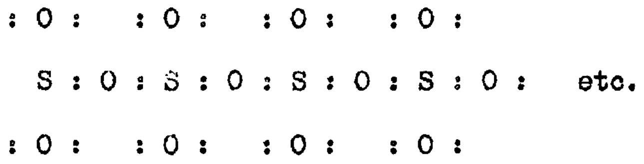


Sulphur trioxide is a strong acid converting basic oxides to sulphates and it is also an oxidising agent giving free halogens (except fluorine) with many halides. In the solid state sulphur trioxide exists in three distinct forms:

γ - SO_3 - an ice-like solid with a structure



β - SO_3 - an asbestos-like solid with a chain structure



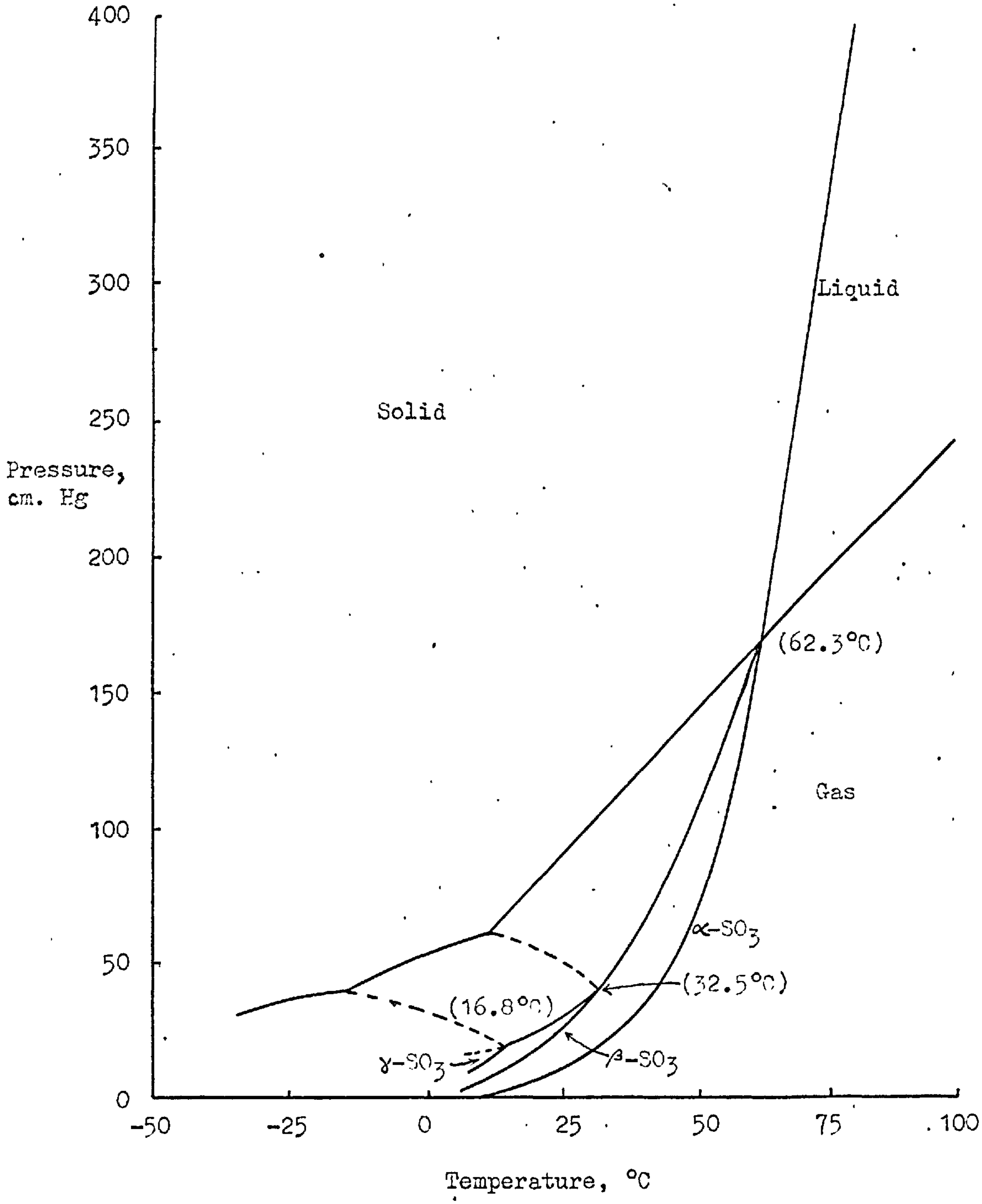
$$\begin{array}{l} :O: \quad :O: \quad :O: \quad :O: \\ S:O:S:O:S:O:S:O: \quad \text{etc.} \\ :O: \quad :O: \quad :O: \quad :O: \end{array}$$

α - SO_3 - similar to β - SO_3 but with the chains joined in a layer arrangement.

Figure 1 shows the vapour pressure relations among the forms of

Figure 1

Vapour pressure relations for modifications of sulphur trioxide[1].



sulphur trioxide[4]. All the forms enter into the same chemical reactions but the order of reactivity of the solid forms is usually

$$\gamma - SO_3 > \beta - SO_3 > \alpha - SO_3$$

The reaction with water to yield sulphuric acid is highly exothermic (21.3 kcal/mole) and results in the formation of many hydrates (Figure 2). Sulphuric acid is one of the most important basic materials of the chemical industry and is usually prepared by burning sulphur or sulphide minerals to produce sulphur dioxide (containing ca. $3\frac{1}{2}\%$ sulphur trioxide) which is then oxidised catalytically to sulphur trioxide.

2. Corrosion and air pollution by sulphur dioxide and sulphur trioxide

Conventional fuels contain carbon and hydrogen plus small amounts of other elements; these elements may be non-combustible and form ash or they may burn with the fuels. The normal oxidation products of carbon and hydrogen are carbon dioxide and water which are comparatively inert, causing neither corrosion in boiler plants nor unpleasant air pollution. Sulphur, which occurs as an impurity in almost all fuels, leads on combustion to the formation of a mixture of sulphur dioxide and sulphur trioxide, which is responsible for both corrosion and air pollution. Sulphur trioxide is the more harmful of these two oxides as it forms sulphate deposits on metals which cause the protective metal oxide coating to be fluxed off and also produces acid mists with a very high dew point. For example a flue gas

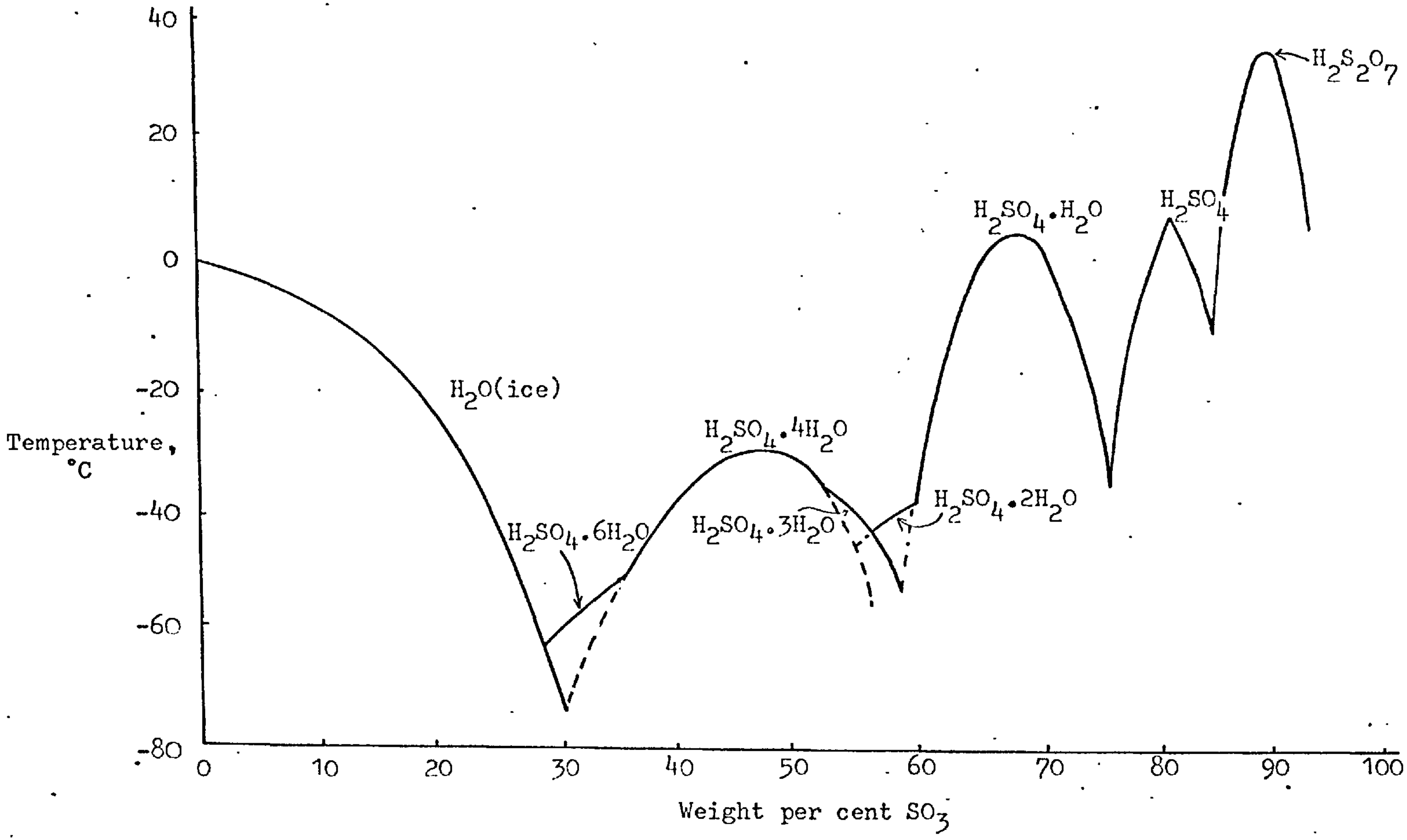


Figure 2

Phase relations in the system sulphur trioxide - water[1].

containing 10% water would normally have a dew point of 56°C but in the presence of 50 p.p.m. of sulphur trioxide this rises to ca. 150°C. This means that, if the heat-exchange surfaces are not kept above this temperature, sulphuric acid will be deposited. In practice, therefore, thermal efficiency is sacrificed to prevent corrosion.

The formation of sulphur trioxide in flames is well known[5,6,7], but there is some increase in the sulphur trioxide content of flue gases after they leave the superheaters (ca. 1000°C) and as they reach the air heater stage (ca. 400°C)[8]. This reaction may be catalysed heterogeneously and studies have therefore been made of the catalytic effects of metals (e.g. clean and rusty mild steel) that are used in heat exchange systems[9,10]. The possibility of course arises that under certain conditions the reaction may occur in the gas phase but this aspect has hitherto received little attention.

B The gaseous oxidation of sulphur dioxide to sulphur trioxide

1. The equilibrium between sulphur dioxide and sulphur trioxide

The most comprehensive and detailed work on the equilibrium between sulphur dioxide, oxygen and sulphur trioxide over platinum catalysts is that of Bodenstein[11], whose results may be expressed in the form:

$$\log_{10} K = -10373/T - 2.222 \log_{10} T + 14.585$$

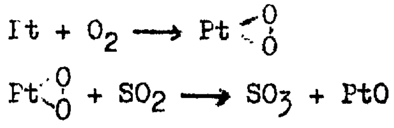
where $K = [SO_2]^2 [O_2] / [SO_3]^2$ and all concentrations are expressed in moles/litre.

Later workers[12,13] have confirmed Bodenstein's values of the equilibrium constant and Lovejoy et al.[14] have calculated theoretical equilibrium constants based on data from the infra-red spectrum of sulphur trioxide. In view of the consistency of the different sets of results and the widely different experimental methods employed, the accuracy of these results, which are shown in able 2, must be accepted.

2. The oxidation of sulphur dioxide over heterogeneous catalysts

Much work has been carried out on the catalysed oxidation of sulphur dioxide to sulphur trioxide over heterogeneous catalysts, the chief catalysts used being platinum, palladium, vanadium pentoxide, ferric oxide, iron/copper oxides and chromium/tin oxides. Most of the studies have been confined to the determination of the formal kinetic relationships and little attempt has been made to deduce the mechanisms involved. Table 3 summarises the kinetic results observed by various workers.

It has been shown for platinum catalysts that the active complex contains one molecule of sulphur dioxide per molecule of platinum[15] and that the rate of adsorption of sulphur dioxide is the rate-determining step. However later workers[24], while agreeing that the active complex contains only one metallic atom, suggest the following mechanism:



$$\mathrm{Pt} + \mathrm{O_2} \longrightarrow \mathrm{Pt}\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}$$

$$\mathrm{Pt}\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix} + \mathrm{SO_2} \longrightarrow \mathrm{SO_3} + \mathrm{PtO}$$

Table 2

Observed values for the equilibrium constant at various temperatures.

Ref. No.	T (°K)	ln K_p (observed)	ln K_p (calculated)	$\triangle$ ln K_p
11	801	3.44	3.49	+ 0.05
	852	2.62	2.64	+ 0.03
	900	1.88	1.88	0.00
	953	1.17	1.17	0.00
	1000	0.62	0.60	- 0.02
	1062	- 0.05	- 0.05	0.00
	1105	- 0.47	- 0.52	- 0.05
	1170	- 1.03	- 1.11	- 0.08
12	933	1.45	1.44	- 0.01
	936	1.38	1.39	+ 0.01
	943	1.27	1.30	+ 0.03
	945	1.25	1.27	+ 0.02
13	850	2.57	2.66	+ 0.09
	852	2.50	2.64	+ 0.14
	876	2.31	2.25	- 0.06
	876	2.24	2.25	+ 0.01
	902	1.88	1.88	0.00
	919	1.53	1.62	+ 0.09
	941	1.37	1.33	- 0.04
	954	1.21	1.16	- 0.05
	965	0.98	1.00	+ 0.02
	1001	0.63	0.60	- 0.03
	1001	0.64	0.60	- 0.04

Table 3

Kinetic results of studies of the catalysed oxidation of sulphur dioxide.

Ref.	Catalyst	Activation energy (kcal/mole)	Observed kinetics
11	Pt	ca. 10	$k[SO_2]/[SO_3]^{0.5}$
15	7% Pt on asbestos	-	$k[SO_2]$ or $k[SO_2] \ln \frac{[SO_2]}{[SO_3]}_{eq.} - \ln \frac{[SO_2]}{[SO_3]}$
13	Pt (hot wire)	-	$\frac{k(\text{distance from equilibrium})}{[SO_3]^{0.5}}$
16 17	Pt (massive) or Pt on SiO_2	23.3 ± 0.6	-
18	Commercial Pt	25.6	-
19	Pure V_2O_5	38	-
20	Pure V_2O_5	34	$\frac{k_1[SO_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}}{[SO_3]} - \frac{k_2[SO_3]^{\frac{1}{2}}}{[SO_2]^{\frac{1}{2}}}$
21	V_2O_5, K_2SO_4, SiO_2	27	-
21	Commercial V_2O_5	23	$\frac{k[SO_2]^{0.8}[O_2]}{[SO_3]^{0.8}}$
22	Commercial V_2O_5	29-31	$k[SO_2]^{0.4}[O_2]^{0.8}$
20	Commercial V_2O_5	-	$k[SO_2]^{0.5}[O_2]^{0.5}$
23	V_2O_5 on alundum	21-9.5 depending on the carrier gas	$k[SO_2]$

$$PtO + SO_2 \longrightarrow SO_3 + Pt$$

Over vanadium pentoxide and ferric oxide catalysts the rate of adsorption of oxygen is found to be the rate-determining step[16]; this is confirmed by Calderbank[22], who has suggested a mechanism of the form:

$SO_2 + 2e = SO_2^{=}$ (fast chemisorption, $\Delta H = -23.8$ kcal/mole) (1)

$SO_2^{=} + O_2 \longrightarrow SO_3 + O^{=}$ (slow) (2)

$O^{=} = \frac{1}{2}O_2 + 2e$ (fast desorption, $\Delta H = +6.4$ kcal/mole) (3)

It is proposed[26] that the oxygen in (2) requires first to be adsorbed in an active position on the vanadium pentoxide. A similar scheme could apply equally well to the platinum-catalysed system if the relative rates of (1) and (2) were reversed.

Both Frazer and Kirkpatrick[27] and Neumann[28] have considered possible mechanisms for the oxidation of sulphur dioxide over commercial catalysts consisting of V_2O_5-K_2SO_4-SiO_2. Neumann's mechanism assumes that the vanadium (V) oxide is reduced to the vanadium (IV) oxide by the sulphur dioxide, the silica acting as an inert support. However Frazer et al.[27] point out that under the reaction conditions used the pyrosulphate ($K_2S_2O_7$) formed is liquid and can act as a solvent for the vanadium pentoxide; it is suggested that on reaction with sulphur dioxide the vanadium (V) is reduced to vanadium (III) by the reaction

$$K_2S_2O_7 + V_2O_5 + 2SO_2 \longrightarrow 2KV(SO_4)_2$$

and that sulphur trioxide is then formed by the reaction

$$2KV(SO_4)_2 + 2SiO_2 \longrightarrow V_2Si_2O_7 + K_2S_2O_7 + 2SO_3 \;;$$

the vanadium is finally restored to the pentavalent state by the oxidation of the vanadium silicate according to the equation

$$V_2Si_2O_7 + O_2 \longrightarrow V_2O_5 + 2SiO_2 \;.$$

Some equilibrium measurements (e.g. those of Bodenstein[29] and Kapustinsky[12]) have been made approaching from the sulphur trioxide side. Bodenstein in his work relied on the catalytic effect of silica on the decomposition of sulphur trioxide; such catalysis has been reported for the forward reaction[30] but this finding has not been confirmed in more recent work[31].

3. The oxidation of sulphur dioxide in flames

There have been extensive studies of the oxidation of sulphur dioxide in flames[5,6,7] and it has been found that the equilibrium constants obtained for systems containing molecular oxygen and solid catalysts do not necessarily apply to flames and other systems where atomic oxygen may be present. For example it has been found that in Bunsen flames [6] the extent of conversion of sulphur dioxide to sulphur trioxide depends on

(a) the nature of the flame

(b) the position in the flame where measurements are made

(c) the concentration of sulphur dioxide in the gases

(d) the presence of flame inhibitors such as nitric oxide.

No sulphur trioxide is found in smoky flames[7] and the maximum sulphur trioxide concentration occurs just above the visible limit of the flame. This agrees with the position of maximum oxygen atom concentration as found by Gaydon[5]. Hedley[7], using a flat flame, observed that the final conversion of sulphur dioxide to sulphur trioxide corresponds to that expected for temperatures associated with the outer edges of the flame (ca. 1200°C). In oxygen-rich flames, sulphur trioxide was found in concentrations well above those predicted by Bodenstein's data, but no sulphur trioxide was found in fuel-rich flames.

It has also been observed[31] that, when mixtures of sulphur dioxide and oxygen are passed through a quartz tube in furnaces at above 1000°C, no conversion to sulphur trioxide takes place but that, if a little benzene is added so that a flame is produced, sulphur trioxide is immediately formed.

4. The oxidation of sulphur dioxide to sulphur trioxide catalysed by oxides of nitrogen

(a) The principal oxides of nitrogen

Of the seven oxides of nitrogen - N_2O, NO, N_2O_3, $(NO_2)_x$, N_2O_5, NO_3 and N_2O_6 - only N_2O, NO and $(NO_2)_x$ are stable at room temperatures and upwards, although NO_3 is thought by some workers[34,35] to have a transient existence during the decomposition of the more stable oxides at high temperatures and is well characterised in shock tube spectra. Of the unstable oxides, N_2O_3 is only stable as a solid; the liquid decomposes to give NO and NO_2 in the gas phase. The decomposition of N_2O_5 is a classic example of a first order reaction, the rate of which is appreciable at room temperature, and involves the distinct steps:

$$N_2O_5 \longrightarrow NO_2 + NO_3$$

$$\text{and} \quad NO_3 \longrightarrow NO_2 + \tfrac{1}{2}O_2 .$$

N_2O_6 (not the dimer of NO_3)[1] breaks down rapidly as soon as it is formed.

(b) Nitrous oxide decomposition

This compound decomposes rapidly above 560°C to give nitrogen and oxygen, and the kinetics of this reaction have been extensively studied both in the pure gas and in the presence of additives. Sulphur dioxide and other compounds[36] have been added to decomposing nitrous oxide at temperatures between 650 and 750°C. The main reaction has been found to consist of the two stages:

$$N_2O + N_2O \;=\; N_2O^{*} + N_2O$$

$$N_2O^{*} \longrightarrow N_2 + O^{\cdot} .$$

The rate decreased slightly when the concentration of sulphur dioxide was greater than that of nitrous oxide, and at a given temperature the rate of disappearance of nitrous oxide was a little greater when sulphur dioxide was present. The results can be expressed in terms of the empirical equation:

$$\frac{d[N_2O]}{dt} = k' \, [N_2O]^{1.45} + k'' \, [N_2O]^{0.58} \, [SO_2] .$$

It was observed that the volume of nitrogen formed was equal to the volumes of nitrous oxide and sulphur dioxide that had been consumed, provided that less than half the sulphur dioxide had reacted. In the later stages of the reaction a little oxygen was produced but no nitric oxide was detected. The following mechanism was suggested:

$$N_2O + N_2O = N_2O^* + N_2O \qquad (1)$$

$$N_2O + SO_2 = N_2O^* + SO_2 \qquad (2)$$

$$N_2O^* \longrightarrow N_2 + O^{\bullet} \qquad (3)$$

$$O^{\bullet} + SO_2 \longrightarrow SO_3 \qquad (4)$$

$$O^{\bullet} + O^{\bullet} + M \longrightarrow O_2 + M \qquad (5)$$

$$O^{\bullet} + N_2O \longrightarrow N_2 + O_2 \qquad (6)$$

$$O^{\bullet} + N_2O \longrightarrow 2NO \qquad (7)$$

When sulphur dioxide constituted a large proportion of the reaction mixture, it was postulated that reactions (5), (6) and (7) could be neglected in comparison with reaction (4). The rate expression then became:

$$\frac{d[N_2O]}{dt} = \frac{k_1\ [N_2O]^2}{1 + k_{-1}[N_2O]/k_3} + \frac{k_2\ [N_2O][SO_2]}{1 + k_{-1}[N_2O]/k_3}$$

which agrees with the observed rate equation over limited ranges of reactant concentrations.

Kaufman[37], who studied the decomposition of nitrous oxide at 772°C, noticed that a small pressure of sulphur dioxide (13mm.) reduced the glow from nitrous oxide (at 600 m.) by 40% showing that, even under these conditions, reaction (4) competes effectively with reaction (7). More recently Linnett et al.[38] used the decomposition of nitrous oxide as a source of oxygen atoms but observed that small quantities of nitric oxide were formed which affected the reaction with sulphur dioxide. A limiting value was observed for the ratio, initial sulphur dioxide/sulphur dioxide consumed. This is explained by a balance between the reactions:

$$O^{\cdot} + SO_2 \longrightarrow SO_3 \qquad (4)$$

$$\text{and} \quad O^{\cdot} + SO_3 \longrightarrow SO_2 + O_2 \qquad (8)$$

or by the occurence of a pair of reactions such as

$$NO_2 + SO_2 \longrightarrow SO_3 + NO \qquad (9)$$

$$\text{and} \quad NO_2 + SO_3 \longrightarrow SO_2 + NO + O_2 . \qquad (10)$$

In the presence of large quantities of inert gases which inhibit the formation of nitric oxide and nitrogen dioxide, the ratio, $k_8:k_4$, was 0.16 at 688°C but in the absence of inert gases and when additional nitric oxide was added, the ratio of initial sulphur dioxide/sulphur dioxide consumed (i.e. $k_{10}:k_9$) became 2.6 at the same temperature.

(c) The interconversion of nitrogen dioxide and nitric oxide

The thermal decomposition of nitrogen dioxide has been studied by several workers, all of whom interpreted their results in terms of a simple bimolecular reaction

$$2NO_2 \longrightarrow 2NO + O_2 \tag{11}$$

which was governed by a rate law of the form:

$$-\frac{d[NO_2]}{dt} = k[NO_2]^2 \tag{12}$$

Values for the equilibrium constant

$$K = \frac{[NO][O_2]^{\frac{1}{2}}}{[NO_2]}$$

were determined by Bodenstein and Lindner[39] and are shown in Table 4.

Bodenstein and Ramstetter[40] determined the values of the bimolecular rate constant, k, over the temperature range 320 - 380°C. Measurements were extended to 750°C by Rosser and Wise[41] who concluded that the reaction is a simple homogeneous bimolecular reaction; the activation energy obtained was in good agreement with the value found by Bodenstein and Ramstetter [40].

Shock tube measurements have been used to follow the reaction at temperatures between 1187 and 2027°C [43]. The results obtained give an activation energy close to that found at lower temperatures, but yield a value for k that is ca. 10 times larger than that predicted by the earlier results. Ashmore and Levitt[44] studied the reaction photometrically at ca. 400°C and found an anomalously high rate (roughly twice that expected) in the early

Table 4

Values of the equilibrium constant of the interconversion of nitrogen dioxide and nitric oxide[42].

T°K	$K = \frac{[NO][O_2]}{[NO_2]}$
300	8.385×10^{-7}
350	2.172×10^{-5}
400	2.534×10^{-4}
450	1.384×10^{-3}
500	8.006×10^{-3}
550	2.824×10^{-2}
600	8.082×10^{-2}
650	1.986×10^{-1}
700	4.220×10^{-1}
750	8.181×10^{-1}
800	1.469
850	2.455
900	3.870

stages. After about 10% of decomposition had occurred, however, the rates agreed with other determinations in the temperature range 370 - 435°C. The anomalously high early rate was not altered by the addition of large pressures of nitrogen, nor by other tests designed to show whether nitrogen dioxide was being adsorbed on the tap grease or diffusion was taking place between the vessel and the connecting dead space. However the initial high rate was eliminated by the addition of a pressure of nitric oxide about equal to that of the nitrogen dioxide, and it was suggested that, besides reaction (11), several additional reactions were taking place, e.g.

$$NO_2 + NO_2 \longrightarrow NO + NO_3 \qquad (13)$$

$$NO_3 + NO_2 \longrightarrow NO + NO_2 + O_2 \qquad (14)$$

During the normal overall reaction these steps are eliminated as the concentration of nitric oxide builds up owing to the occurrence of the process:

$$NO_3 + NO \longrightarrow NO_2 + NO_2 \qquad (15)$$

The recombination of nitric oxide with oxygen is well known as one of the few simple examples of a third order reaction. It was first studied by Bodenstein[45] and Kornfeld et al.[46] As with many third order reactions the apparent activation energy is small and negative[47] (0.5 – 1.1 kcal/mole) and this finding can be explained in terms of a pre-equilibrium:

$$NO + O_2 \rightleftharpoons NO_3$$

followed by $NO_3 + NO \longrightarrow 2NO_2$.

Treacy and Daniels[48] studied this reaction spectroscopically at room temperatures (0 - 65°C) and low pressures (1 - 20 mm. Hg) and found a third order rate expression. However at the lowest pressures used the order with respect to nitric oxide was slightly greater than 2 and that with respect to oxygen slightly less than 1, but at higher pressures the orders approached 2 and 1 respectively. They explain their results in terms of the mechanism:

$$NO + O_2 \rightleftharpoons NO_3 \qquad (16)$$

$$NO_3 + NO \rightleftharpoons NO_3.NO \qquad (17)$$

$$NO_3.NO + NO_2 \rightarrow 2NO + O_2 + NO_2 \qquad (18)$$

$$NO_3 + NO_2 \rightleftharpoons N_2O_5 \qquad (19)$$

$$NO_3 + NO \rightarrow 2NO_2 \qquad (15)$$

$$NO_3.NO + NO \rightarrow 2NO_2 + NO \qquad (20)$$

Reaction (18) explains the slight reduction in rate caused by the presence of nitrogen dioxide.

Recently the oxidation of nitric oxide has received much further attention. Tipper[34] has reported that the rate of oxidation of nitric oxide is decreased by the addition of nitrogen; for example, 100mm. nitrogen added to a mixture containing 100mm. nitric oxide and 50mm. oxygen halved the rate; the effect was observed over the whole temperature range investigated (20 - 570°C).

This result contrasts however with earlier work[41] and with the even more recent measurements by Ashmore[35] who studied the three component system ($NO_2 + NO + O_2$) in detail at 360°C and less extensively at other temperatures. In the course of this investigation values were determined for the rate constant for the overall reaction

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

over the temperature range 100 - 506°C. The temperatures involved were higher than those attained in any previous accurate work. Using the results of other workers concerning nitrogen trioxide, Ashmore discussed the role of this intermediate in the oxidation of nitric oxide. It was concluded that mechanisms involving nitrogen trioxide cannot be used to explain the results of Tipper and that an inert additive should cause a slight increase in the rate of formation of nitrogen dioxide by the reaction

$$2NO + O_2 + M \longrightarrow NO_3.NO + M .$$

Tipper and Williams[34] added sulphur dioxide to an ($NO + NO_2 + O_2$) system in the temperature range 20 - 570°C and found that sulphur dioxide had the same retarding effect as was observed with nitrogen. Since however their results involving nitrogen have been rejected by later workers[35], their measurements involving sulphur dioxide must also be viewed with caution. The amount of oxygen lost was greater than that required to convert the sulphur dioxide to sulphur trioxide and it was concluded that this is due to the formation of N_2O_3 which condensed out with the sulphur trioxide in the cool parts of the apparatus where a white solid was observed to form. However it does appear that there is a rapid reaction of the form:

$$N_xO_y + SO_2 \longrightarrow SO_3 + N_xO_{y-1}$$

where N_xO_y is NO_2, NO_3 or some other product of the nitric oxide - oxygen reaction.

The oxidation of sulphur dioxide by nitrogen dioxide is well known to take place in the presence of water and is indeed the basis of the lead chamber process. Kuz'-minykh[49] has suggested that the individual steps in the lead chamber process are:

$$NO_2 + SO_2 = NO + SO_3 \quad (1)$$

$$NO + \tfrac{1}{2}O_2 = NO_2 \quad (2)$$

$$SO_3 + H_2O = H_2SO_4 \quad (3)$$

all of which may take place in the gas phase. It is believed however that the first and rate-determining step (1) takes place faster on droplets of concentrated sulphuric acid than in the gas phase. It is suggested that an increase in the reaction temperature from the usual 50°C to ca. 120°C would give a higher yield but that the lead lining of the reaction chamber would not withstand this increased temperature. This constructional problem has discouraged work at higher temperatures. Other indications of a gas phase reaction are available from such observations as the reduction of the bleaching powers of nitrogen oxides by the addition of sulphur dioxide[50].

Tipper's study[34] of the reaction between dry sulphur dioxide and nitrogen dioxide at temperatures up to 208°C showed that the rate of pressure change was directly proportional to the concentration of both sulphur dioxide and nitrogen dioxide

$$\text{i.e.} \quad \frac{dp}{dt} \propto [SO_2][NO_2] .$$

A solid of formula $(SO_3)_2N_2O_3$ was deposited during the reaction, however, making it difficult to relate the rate of pressure change to the rate of oxidation of sulphur dioxide. Above 208°C the kinetics became complicated and it was assumed that this was due to the increasing importance of the dissociation of nitrogen dioxide to nitric oxide and oxygen.

5. <u>The oxidation of sulphur dioxide by atoms and free radicals</u>

As was mentioned earlier, large quantities of sulphur trioxide are formed when sulphur dioxide is added to oxygen-rich flames. In methane-air flames, many products, both charged and uncharged, have been identified (e.g. CO_2, $CH_3^{:}$, CH^*, free electrons) and of special interest are $O^{\bullet}$, $OH^{\bullet}$, $HO^{\bullet}$ and NO^* since these are oxidising species which are common to all hydrocarbon-(or hydrogen-)air flames.

It has been shown above that oxides of nitrogen can cause rapid oxidation of sulphur dioxide, so that NO^* and its products may play some part in the oxidation of sulphur dioxide in flames.

The order of efficiency of fuels for the oxidation of sulphur dioxide in flames is:

methane > hydrogen > carbon monoxide

which is the same order as that for the concentration of oxygen atoms in the respective flames as measured by Gaydon[5].

At lower temperatures the formation of sulphur trioxide by the reaction of sulphur dioxide with oxygen atoms was observed by Geib and Harteck[51]. The fact that 8% of the sulphur dioxide was converted at liquid oxygen temperatures indicates that the activation energy of the reaction is low. Quantitative data are scarce, but Kaufman[52] quotes a value, of about 3×10^{16} cm.^{6} mole^{-2} sec.$^{-1}$ for the rate constant of the termolecular reaction:

$$O^{\cdot} + SO_2 + O_2 \longrightarrow SO_3 + O_2$$

at 295°K. The production of atomic species by an electrical discharge is difficult at pressures above a few mm. Hg but the thermal decomposition of nitrous oxide has been used to produce oxygen atoms at higher temperatures and pressures. It has been confirmed that a rapid reaction between sulphur dioxide and oxygen atoms takes place under these conditions[36].

It is possible however that $OH^{\cdot}$ and $HO_2^{\cdot}$ also play some part in the oxidation of sulphur dioxide. The homogeneous decomposition of hydrogen peroxide is a possible source of OH radicals. This reaction has been studied extensively[53] but there is no report of the decomposition having been carried out in the presence of sulphur dioxide.

C The present work.

It has been shown that oxygen atoms readily oxidise sulphur dioxide and are probably the main oxidising species in oxygen-rich flames. Other studies at low temperatures have shown that oxides of nitrogen may play an important part in the oxidation of sulphur dioxide, but there does appear to be a significant temperature region where no studies have been made of the oxidation of sulphur dioxide, either in the presence or absence of nitrogen oxides.

The present work was designed to study the homogeneous oxidation of sulphur dioxide between 400 and 1000°C. It was intended that the reaction between sulphur dioxide and oxygen should be studied alone and in the presence of oxides of nitrogen, hydroxyl radicals and various organic compounds. These additives were chosen for their interest from both an academic and an industrial point of view, as their use should give information about the mechanism of the homogeneous oxidation of sulphur dioxide and also have some relevance to the oxidation of sulphur dioxide under industrial conditions.

EXPERIMENTAL

EXPERIMENTAL

CONTENTS

A. Apparatus

B. Materials

C. Procedure

1. Gas handling

2. Analysis

EXPERIMENTAL

A Apparatus

1. General construction of the vacuum system

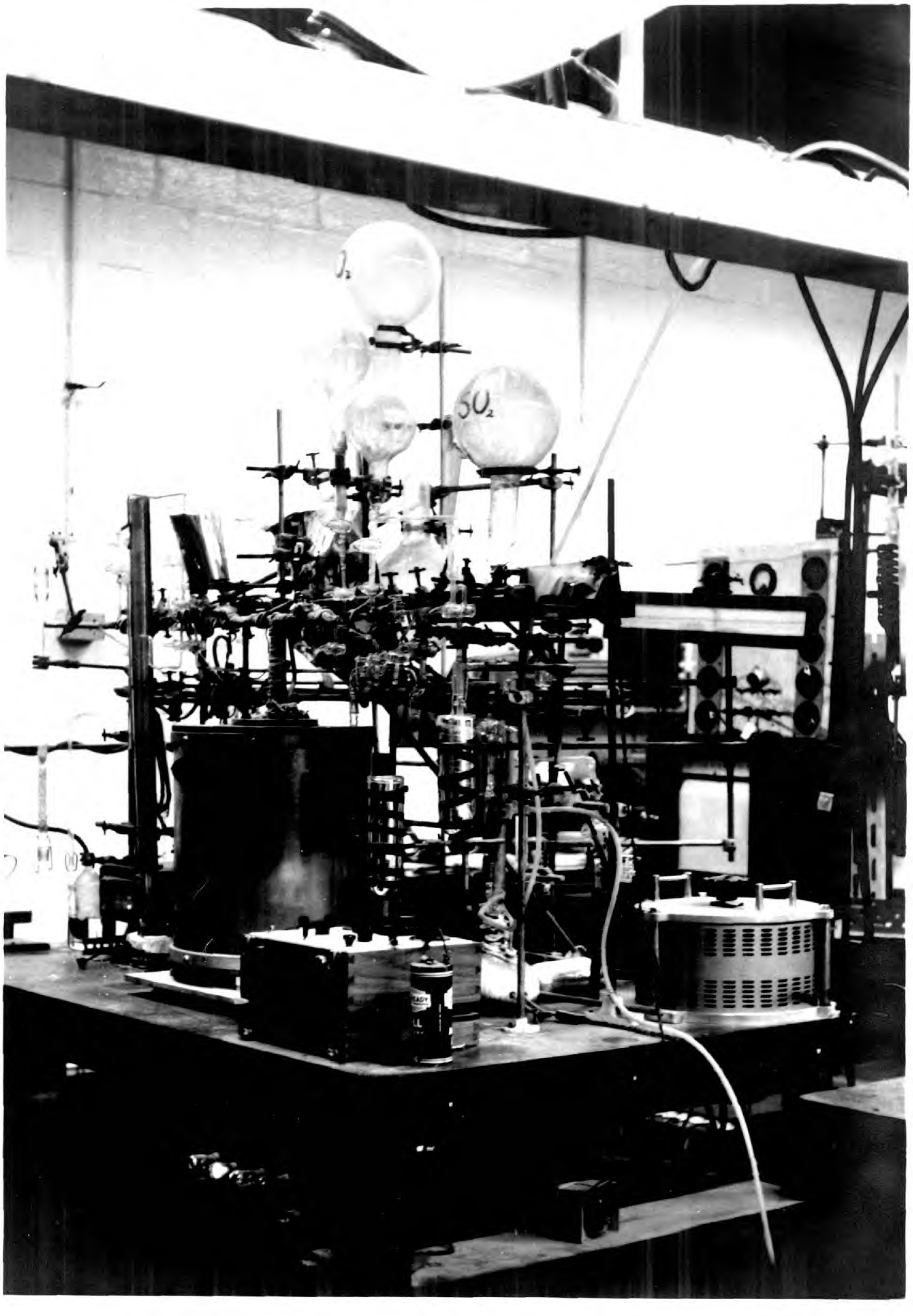
The vacuum system was constructed of pyrex glass with the exception of the reaction vessel which was of silica; it is illustrated in Plate 1 and shown diagrammatically in Figure 3. The section between taps A_1 and A_2 was made of 2mm. capillary tubing, the remainder being of larger (5-10mm.) bore. Sulphur dioxide, oxygen and nitrogen were introduced via the columns C_1 or C_2, to the cold traps T_1 and T_2. Final purification, by distillation, was completed prior to storage in the 5-litre vessels G_1, G_2 and G_3. Nitric oxide was prepared and stored on the other side of the reaction vessel. The gas was prepared and purified in vessels fitting into sockets S_1 and S_2 and stored in the 1-litre globe G_4. The vessel G_5 was a calibrated volume (313.50 $cm.^3$) which was also used for mixing nitric oxide and sulphur dioxide at room temperature. A 1-litre globe, G_6, containing copper sulphate crystals ($CuSO_4.5H_2O$), fitted at cone K_1, could be used for the addition of controlled quantities of water vapour to gaseous mixtures. The system was evacuated by a two-stage mercury diffusion pump P_1 backed by a rotary oil pump P_2.

2. Pressure measurements

An ordinary open manometer, M_1, was used for normal

Plate 1

The apparatus



Key to Figure 3

$A_1 - A_9$ = Taps

$C_1 - C_2$ = Drying columns

F = Furnace

$G_1 - G_4$ = Storage vessels

G_5 = Calibrated volume and pre-mix vessel

G_6 = Vessel for water addition

K_1 = Cone

$M_1 - M_3$ = Manometers

P_1 = Mercury diffusion pump

P_2 = Rotary oil pump

R = Reaction vessel

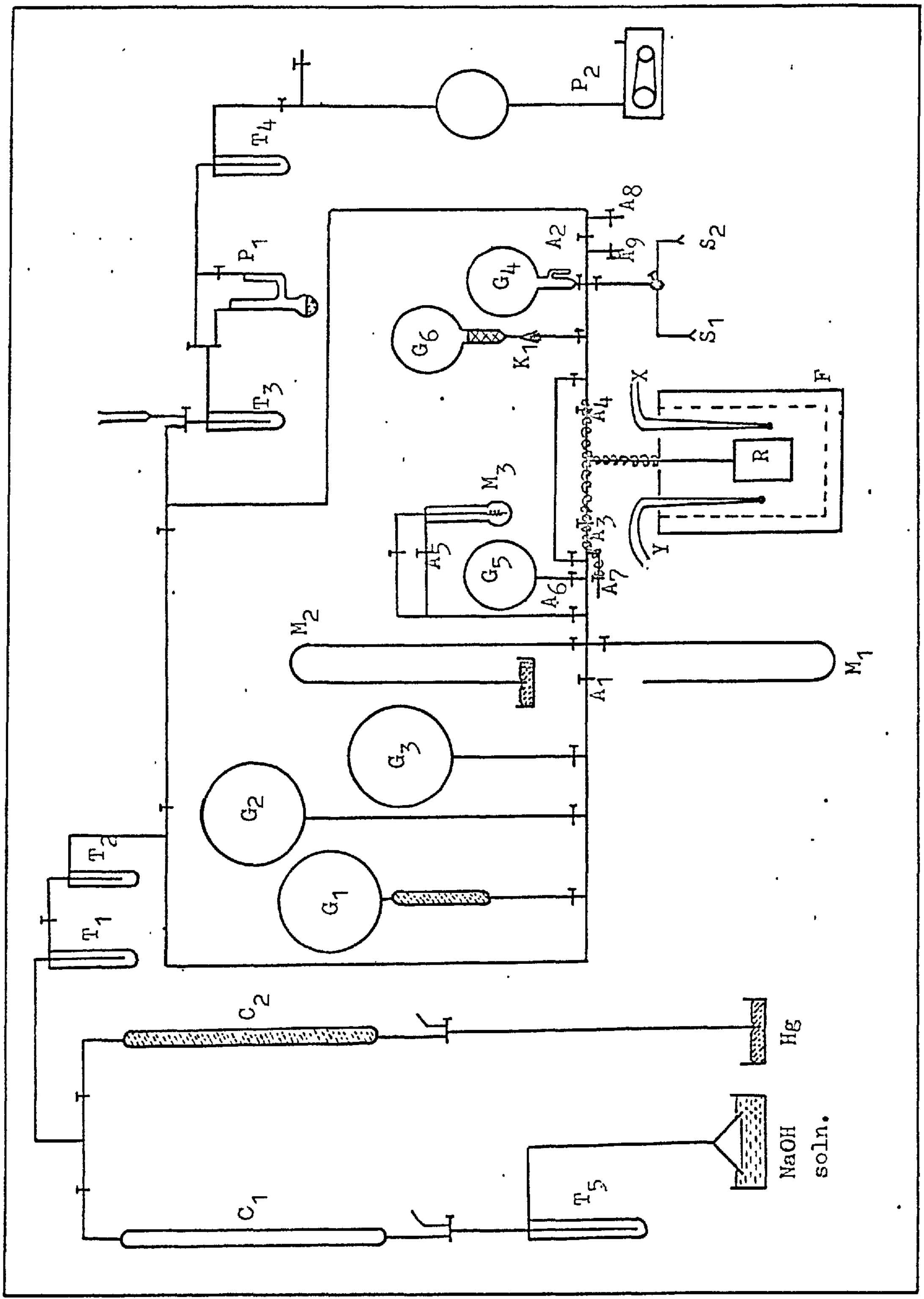
$S_1 - S_2$ = Sockets

$T_1 - T_5$ = Cold traps

X and Y = Platinum/Platinum (87%)-Rhodium (13%) thermocouples

Figure 3

The apparatus



measurements of "large" (> 25mm.) pressures of oxygen, sulphur dioxide and nitrogen. A U-tube barometer, M_2, attached to a mirrored scale was used for measuring such pressure changes over a long period as it is independent of atmospheric pressure changes. A Springham's glass spiral gauge, M_3, was used in conjunction with a lamp and scale (Figure 4) for measuring small pressures and small pressure changes. A calibration curve (deflection of light versus pressure in cm. Hg) was used to convert the actual readings to known pressure units. This was checked periodically.

3. Reaction vessels

All the reaction vessels used were made of transparent silica. The two identical unpacked vessels were cylindrical with a length of 8.5 cm. and a diameter of 6 cm. (resulting volume ca. 250 cm.^{3}, surface area 220 cm.^{2}); it was closed at one end and had a narrow neck attached to the other end. This neck protruded from the furnace and was connected to the pyrex vacuum line by means of a graded seal. The packed vessels were 7.5 cm. in length and 7 cm. in diameter and contained ten tubes of 1.5 cm. internal diameter and 1 mm. wall thickness. This left a volume of ca. 250 cm.^{3} and a surface area of 820 cm.^{2}. The surface : volume ratio was thus approximately four times that of the unpacked vessels.

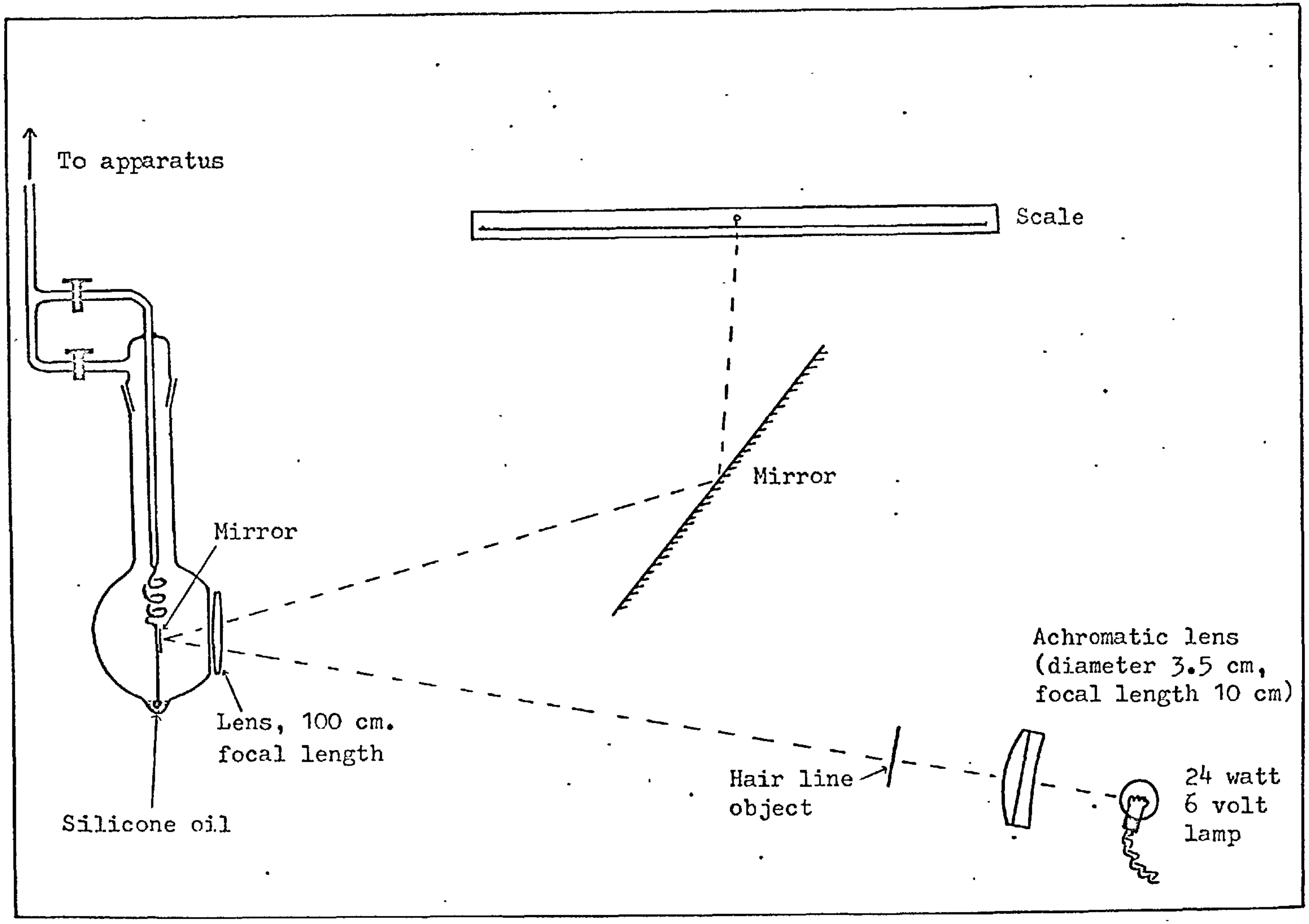


Figure 4

Optical arrangement for spiral gauge.

4. Lubricants

The taps and joints which were in regular use and came into contact with oxides of sulphur were lubricated with Kel-F 90 Grease as this was found to be the only grease that was resistant to sulphur trioxide (both dry and moist). Other joints and taps in the inlet system were lubricated with a silicone high vacuum grease. Permanent joints at pumps were sealed with Picein wax.

5. Greaseless stopcocks

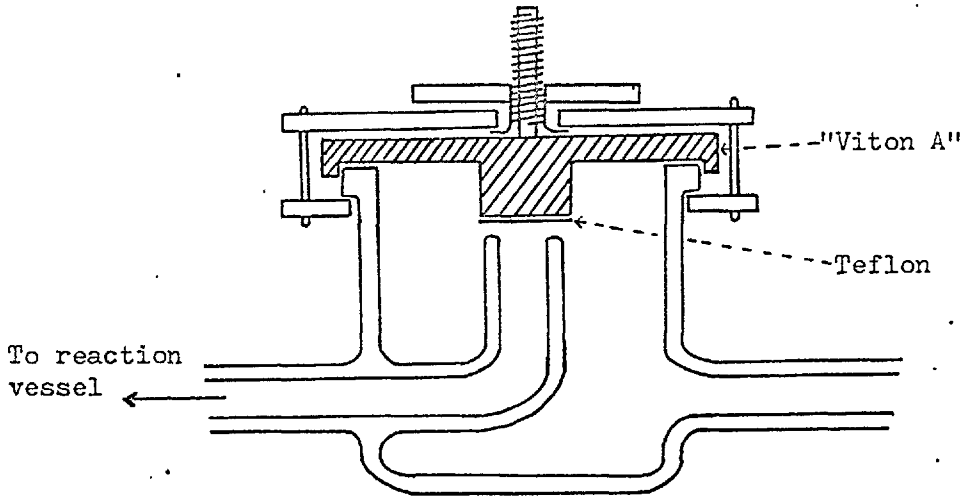
Stopcocks, A_3 and A_4, were of the Springham greaseless type and were fitted with "Viton A" fluorocarbon rubber diaphragms, which were modified slightly by having a thin sheet (0.005 in.) of teflon glued to the centre of the diaphragm in such a way that no rubber came into contact with the reacting gases. (Figure 5).

6. The heating of the vacuum line

The section of the vacuum line immediately above the reaction vessel and the furnace and between the two greaseless stopcocks was electrically heated to ca. 180°C. The line was first wrapped in asbestos paper and nichrome wire (12-14 ohms/yd.) was then wound on to this. This was followed by a further binding of asbestos paper, and a layer of asbestos string. The windings were connected to the 240V. D.C. mains and the current passing was controlled by a potential dividing resistance of 200 ohms.

Figure 5

Modified Springham greaseless stopcock.



7. Furnace

This was a vertical electric furnace consisting of an inner fireclay tube, 12.5 cm. in diameter and 40 cm. in length, wound with kanthal wire to a total resistance of ca. 10 ohms at room temperature. A typical example of the temperature gradient along the furnace tube, at an elevated temperature, is shown in Figure 6. The reaction vessel was placed between 18 and 26 cm. from the top of the furnace, since this position gave the minimum temperature variation over the length of the vessel (2°C at 700°C).

8. Temperature measurement

A platinum/platinum (87%)-rhodium (13%) thermocouple, X, supported in a twin-bore mullite tube, was inserted into the furnace in such a way that the hot junction was at the same depth, and close to, the mid-point of the side of the reaction vessel. The cold junction was maintained at the temperature of melting ice and the resulting e.m.f. was measured on a potentiometer; the corresponding temperature was calculated by means of standard tables. The temperature of the heated portion of the line was measured with a chromel-alumel thermocouple with the hot junction sealed in glass, which in turn was sealed to the line. The cold junction was maintained at the temperature of melting ice and the e.m.f. was measured potentiometrically. After the hot junction of the thermocouple had been sealed into glass, the values of the

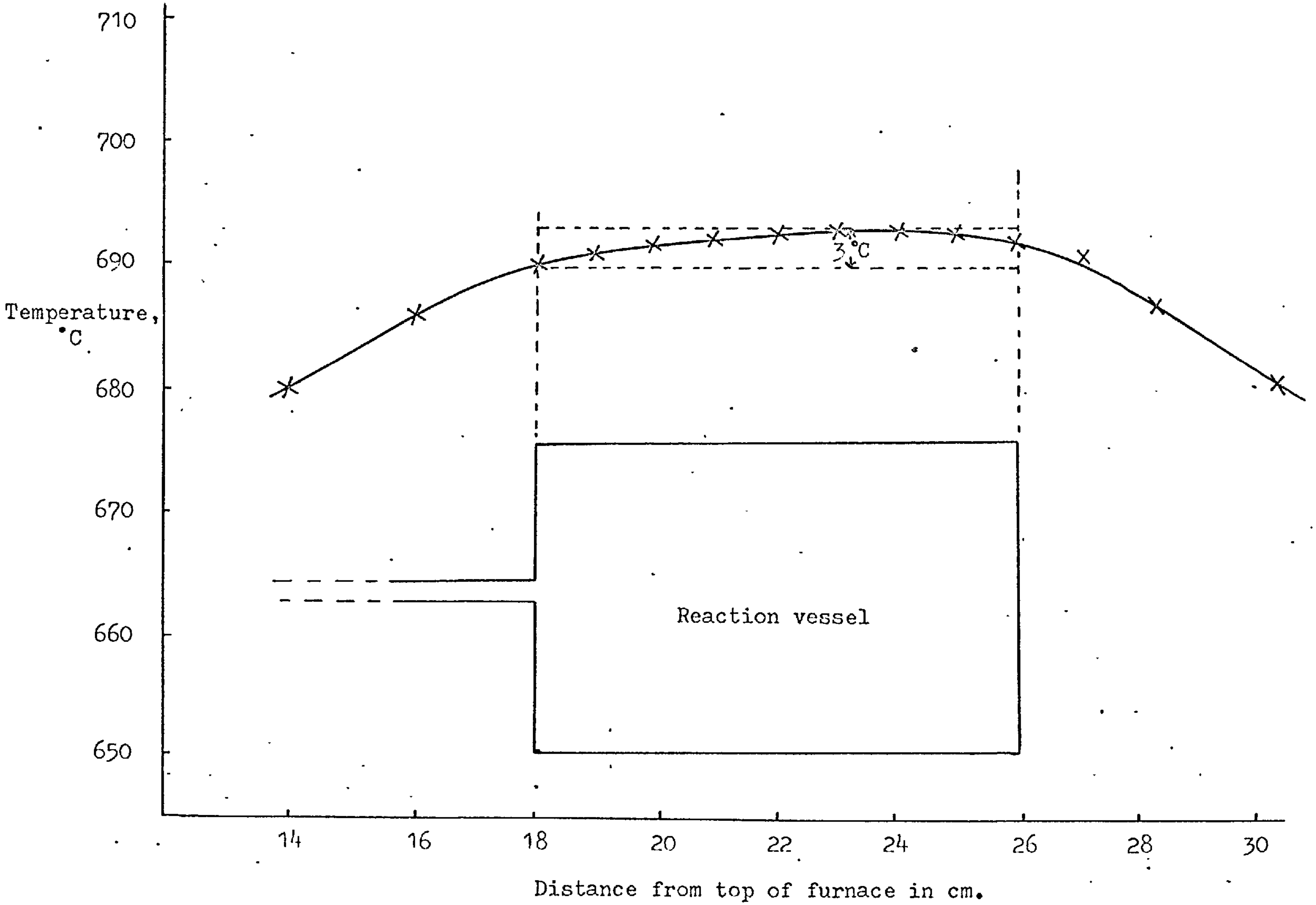


Figure 6

The temperature gradient along the furnace tube at 690°C.

e.m.f. developed at standard temperatures were compared with those given in the Handbook of Chemistry and Physics[54], and found to be in close agreement.

9. Temperature control

The furnace temperature was controlled by an electromagnetically operated on-off switch in conjunction with a potentiometer. The electromagnetic switch was triggered by a signal from a platinum/platinum-rhodium thermocouple (Figure 7).

The voltage of the input current was adjusted with the potentiometer, so that the furnace temperature maintained itself ca. 10°C above the required value. The required temperature was set on the controller scale and the on-off switch then maintained the temperature automatically within ± 1°C of the expected value.

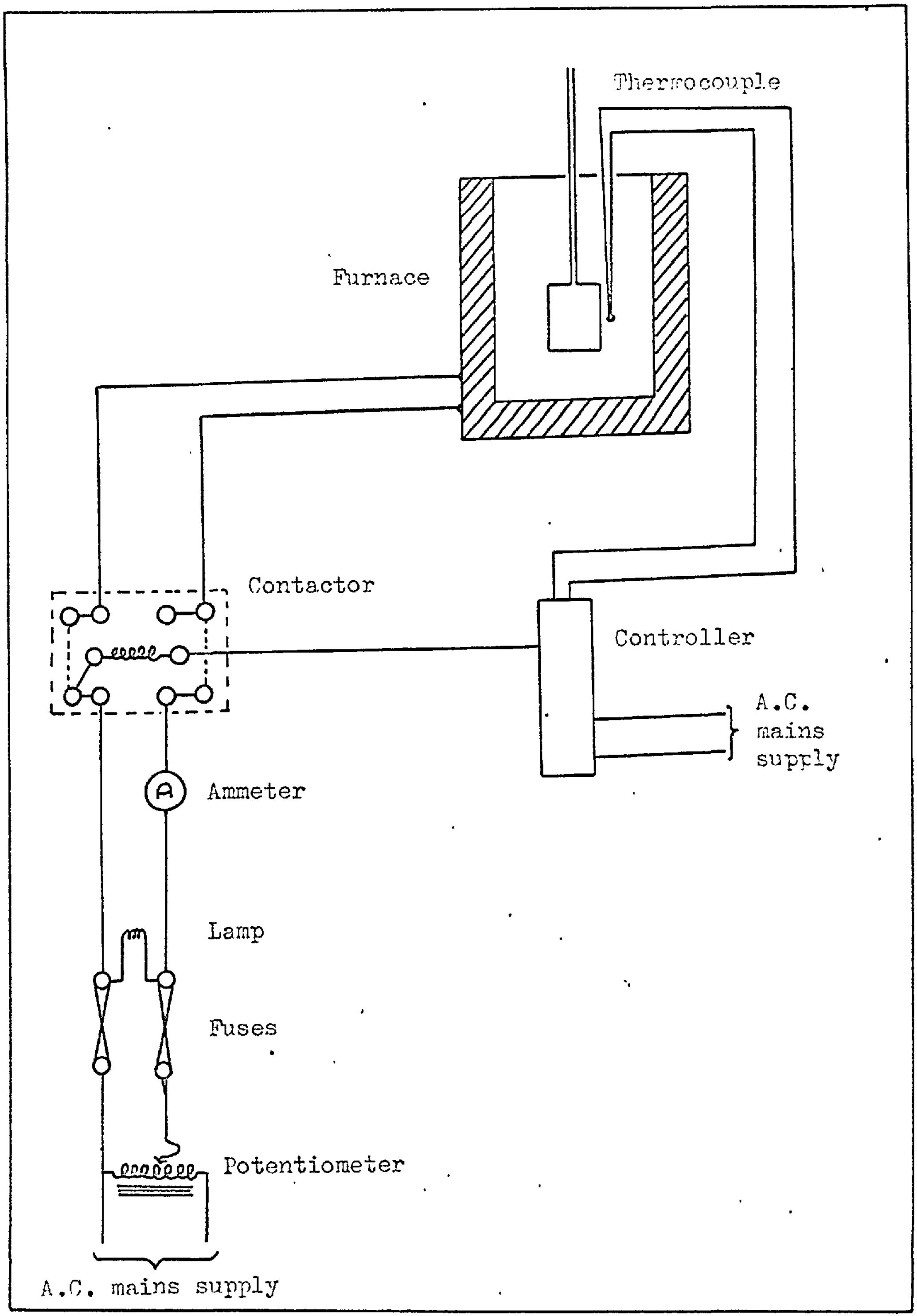
B Materials

1. Oxygen from cylinders was dried by passage through a column of anyhdrous magnesium perchlorate (anhydrone). It was then condensed in a trap cooled in liquid nitrogen and distilled, the middle fraction being used to fill a 5-litre globe fitted with an anhydrone-filled side arm.

2. Sulphur dioxide from a siphon was further purified by distillation. The gas was condensed in a solid carbon dioxide/alcohol trap, the middle fraction was collected and the distillation

Figure 7

Wiring diagram for furnace temperature controller.



was repeated. In some early experiments, further drying was attempted by the use of phosphorus pentoxide, but this appeared to contaminate the gases and was found to produce effects which could not be overcome by the addition of water vapour.

3. Nitrogen was usually obtained from "oxygen-free" cylinders of the compressed gas and was dried by passage through a column of anhydrone prior to storage. In some later experiments, liquid nitrogen was poured into trap T_2 and, after about a third had boiled off, the remainder was cooled by placing a Dewar of liquid nitrogen around it, any excess nitrogen being allowed to escape to the atmosphere through the mercury blow-off. Nitrogen from both these sources behaved identically.

4. Carbon dioxide was obtained from a cylinder of the compressed gas or by the evaporation of solid carbon dioxide.

5. Carbon monoxide was obtained from a cylinder of the compressed gas.

6. Nitric oxide was prepared by the reaction between moist sodium nitrite and ferrous sulphate. The resulting gases were collected in a cold finger at liquid nitrogen temperature. After being evacuated, the finger was heated to -78°C in a solid carbon dioxide/alcohol bath. The liberated gas was recondensed and the distillation was repeated; the final product was colourless.

7. Hydrogen peroxide vapour was obtained from a sample of 99.8% high test peroxide kindly supplied by Laporte Chemicals Limited. 1 - 2 cm.^{3} of the liquid were stored in a small glass globe (ca. 10 cm.^{3} capacity) which had been washed in permanganic acid followed by hydrogen peroxide. After the liquid had been degassed, hydrogen peroxide vapour was admitted to a pre-mix vessel (ca. 350 cm.^{3} capacity) via a greaseless stopcock. The storage vessel and pre-mix vessel were maintained at 50 ± 0.2°C in a water-bath (Figure 8) and the connections to the reaction vessel were maintained above this temperature by electrical heating.

8. Ethane was obtained from cylinders of the compressed gas of purity greater than 99.8%.

9. Ethylene was obtained from cylinders of the compressed gas of purity greater than 99.7%.

10. Acetylene from commercial cylinders was purified by passage through bubblers containing respectively: 30% sodium bisulphite; 30% sodium hydrosulphite and 2% indigo carmine in 10% potassium hydroxide; and finally water. The gas was dried over calcium chloride and degassed silica gel[58].

11. Acetone, benzene, ethanol, n-hexane and cyclohexane AnalaR grade liquids were degassed by repeated freezing and pumping. The vapours were then obtained as required by slight warming of the liquid.

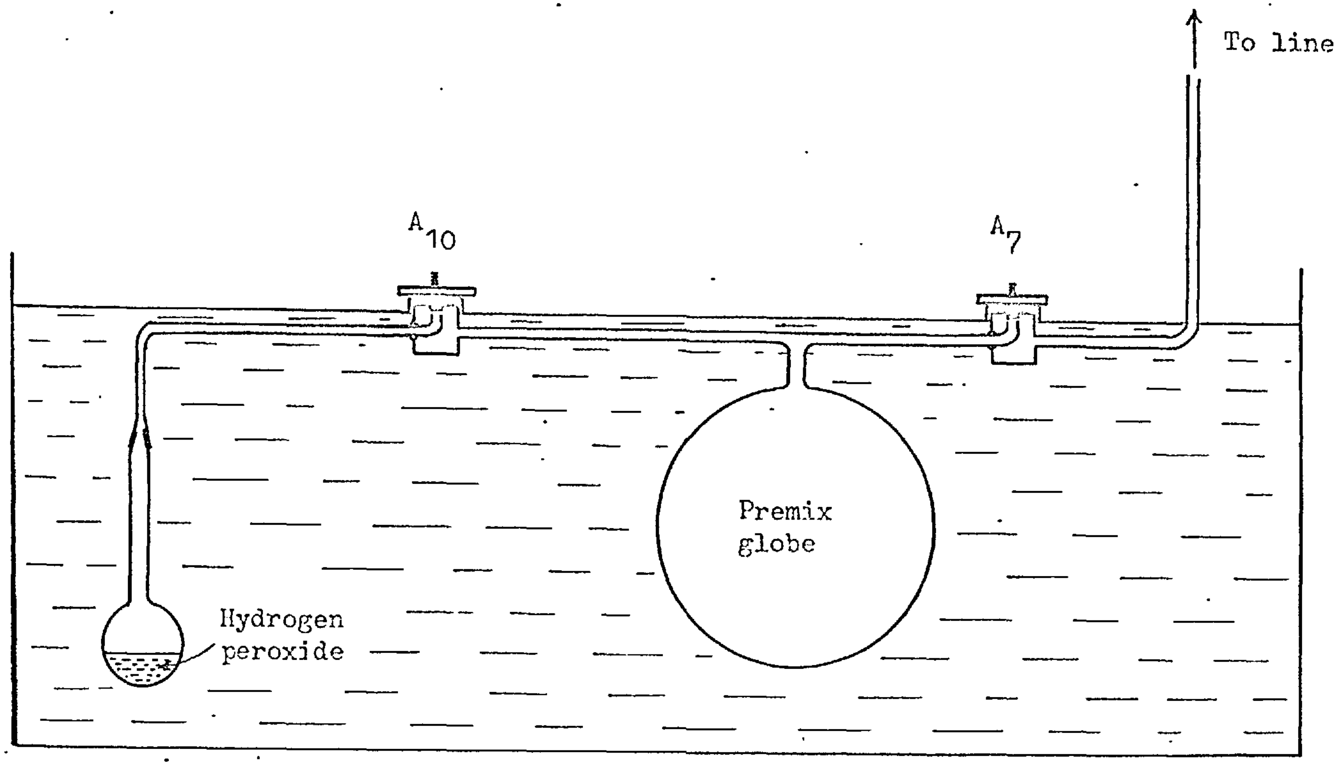


Figure 6

Apparatus for admission of hydrogen peroxide vapour.

12. Water. The addition of water vapour to the reaction mixture was accomplished by the use of moist oxygen. This oxygen was allowed to pick up a known quantity of water vapour by storing it over a bed of crystals of copper sulphate pentahydrate. The water vapour pressure in equilibrium with the copper sulphate crystals was then determined from tables[55].

C Procedure

1. Gas handling

(a) Rate measurements

The gases were admitted to the reaction vessel in the order: nitric oxide, sulphur dioxide, oxygen or nitrogen. The final gas admitted was used in the outer case of the spiral gauge to prevent the adsorption of nitric oxide and sulphur dioxide in the silicone damping oil of the spiral gauge. For pressures of nitric oxide less than 2mm. a mixture of nitric oxide and sulphur dioxide was first prepared in the standard volume, G_5. It was found that this procedure gave the same results as experiments in which the nitric oxide and sulphur dioxide were admitted separately.

A known pressure of a nitric oxide + sulphur dioxide mixture was admitted to the reaction vessel. Tap A_3 was then closed and the line was evacuated. The sulphur dioxide was then added to the reaction vessel, its pressure being measured on the dipping mercury manometer, M_2. Tap A_3 was again closed, the line was evacuated and that part of the line between taps A_1 and A_2 and the spiral gauge was then filled with oxygen to a pressure such that, when tap A_3 was opened, the oxygen entered the reaction vessel to the required pressure. The reaction mixture was isolated by closing taps A_3, A_4 and A_5. In order to observe the total pressure of the mixture, taps A_3 and A_6 were opened. The change in pressure in the reaction vessel was followed using the observed deflection of the light spot from the spiral gauge.

(b) Reactions in the presence of hydrogen peroxide.

The hydrogen peroxide pre-mix vessel (Figure 8) was connected to the line via tap A_7. The pre-mix vessel was evacuated, tap A_7 was closed and tap A_{10} was opened for a few seconds; this procedure was repeated several times to remove air or oxygen. Finally the pre-mix vessel was evacuated, tap A_7 was closed and tap A_{10} was opened for a minute. After tap A_{10} had been closed, sulphur dioxide or a sulphur dioxide + oxygen mixture was admitted from the line via tap A_7, which was immediately closed. The line was then evacuated for half a minute before the mixture was allowed to expand into the hot reaction vessel via greaseless taps A_7 and A_3. The gases were not admitted to a manometer unless this had first been filled with oxygen to a pressure slightly higher than the final pressure. The reaction vessel and pre-mix vessel were washed with hydrofluoric acid before use in order to reduce surface-catalysed decomposition of the hydrogen peroxide.

(c) Reactions of sulphur dioxide with oxidising organic gases

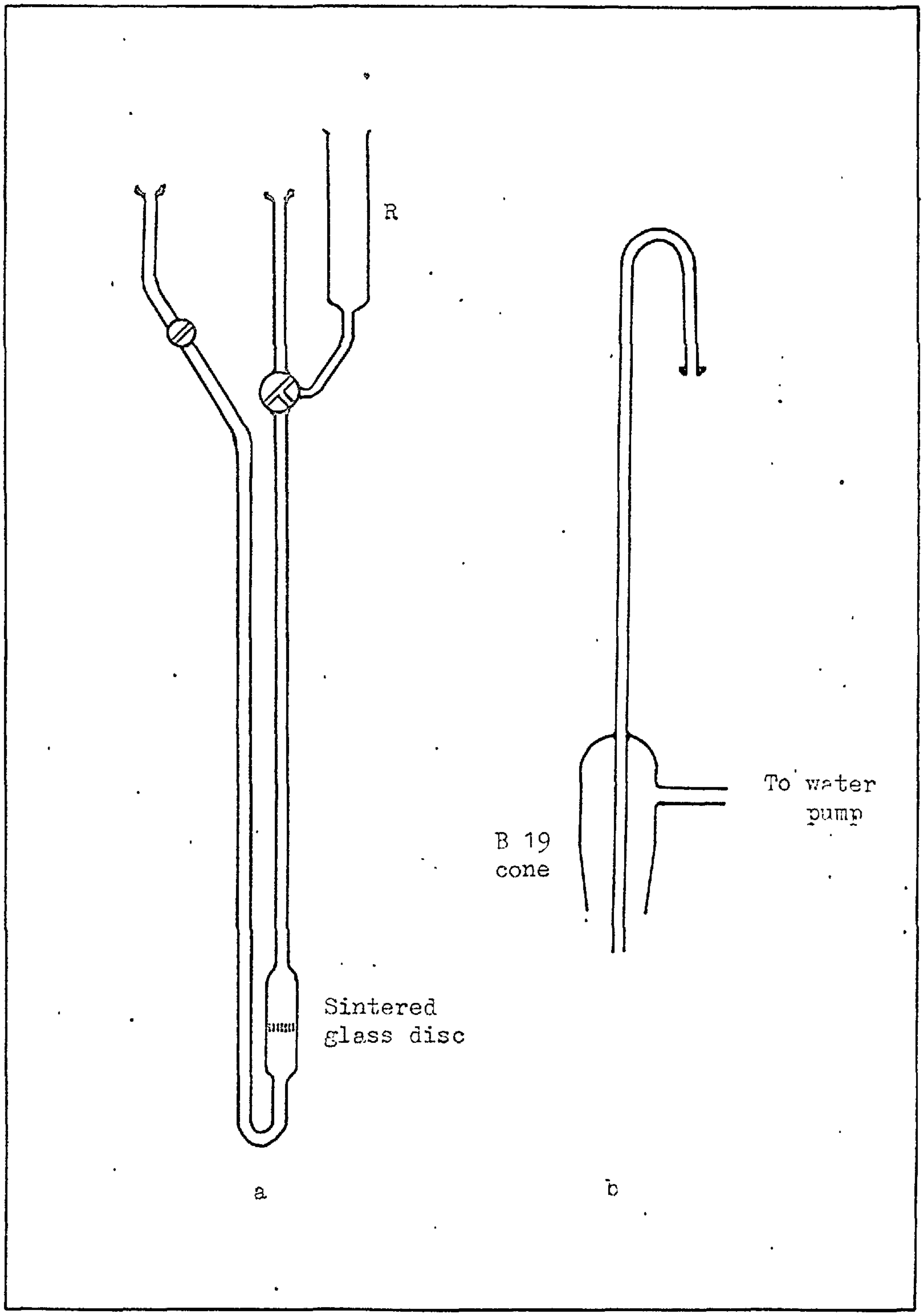
Additive gases were stored in globe G_3 and the liquids were kept in a tube connected to socket S_1. These were then mixed with oxygen or an oxygen + sulphur dioxide mixture in the pre-mix vessel G_5. An ignition was considered to occur when admission of the gases to the furnace was followed by an audible "click" and a flash of light. An ignition of this type always caused a flash-back to the pre-mix vessel.

(d) Removal of gases for analysis

The gases were removed from the vessel by pumping them out via tap A_4. In early experiments, trap T_3 was fitted with a three-arm tap so that solutions could be admitted to dissolve the contents. It was, however, found to be more accurate and convenient to use a U-tube of the form shown in Figure 9a between taps A_8 and A_9. The sintered glass disc was included, as it was observed that frozen sulphur dioxide could be blown through the U-tube under certain conditions. The trapped gases were dissolved by admission of 25 $cm.^3$ of 67% aqueous ethanol via the three-way tap from the reservoir R. When all the gases had been dissolved, i.e. when the tube was completely filled with liquid, the solution was transferred to a 250 $cm.^3$ conical flask by means of the suction device shown in Figure 9b. The contents of the U-tube were carefully rinsed into

Figure 9

Apparatus for the extraction of gases for analysis.



the 250 cm.^{3} flask with three further 25 cm.^{3} aliquots of aqueous ethanol.

2. Analysis

(a) Summary of methods of analysis of sulphur oxides

Individually, sulphur dioxide and sulphur trioxide can be determined accurately. Three of the established physical methods of gas analysis which are highly specific and which might reasonably be expected to be suitable for the estimation of a mixture of the oxides of sulphur are gas chromatography, mass spectrometry and infra-red spectrometry.

The application of chromatography to gas analysis has received much attention over the past few years, but there is no published account of a successful attempt to separate sulphur trioxide and sulphur dioxide in this way either by gas-liquid or gas-solid partition chromatography. The choice of suitable materials for this purpose is severely limited by the highly reactive nature of sulphur trioxide but a combined chemical and chromatographic technique might yet prove practicable.

The usefulness of mass spectrometry for the determination of sulphur trioxide in the presence of sulphur dioxide depends upon the intensity of the peak corresponding to the formation of the sulphur trioxide positive ion, mass number 80. However it has been found that this peak is very weak in comparison with those corresponding to sulphur dioxide, sulphur monoxide and oxygen; this indicates that extensive decomposition of sulphur trioxide takes place in the ionising process[31] and no accurate estimation of sulphur trioxide by mass spectrometry is thus possible.

Owing to the high chemical reactivity of sulphur trioxide, the complete infra-red spectrum has only recently been determined[32]. Nevertheless infra-red spectrometry has proved to be a reliable method for the analysis of both sulphur dioxide and sulphur trioxide in the absence of water vapour. Unfortunately, however, the absorption peaks for the two gases are very close to each other (SO_2 1377, 1360, 1350 $cm.^{-1}$; SO_3 1399, 1383 $cm.^{-1}$) and, when a mixture of the gases contains a ten-fold excess of either constituent the absorption peaks of the gas in low concentration vanish into the shoulders of the larger peaks.

Chemical analysis of sulphur dioxide and sulphur trioxide is normally dependent on their absorption in water to form sulphate and sulphite. Sulphate is usually estimated by the precipitation of barium sulphate, a notoriously poor gravimetric method, or by direct titration with barium chloride using "thorin" as indicator, while sulphite is generally determined by a redox titration of sulphite to sulphate. This titration often gives low values for the sulphite concentration due to the oxidation of part of the sulphite by air and, to reduce this effect, inhibitors such as glycerol or isopropyl alcohol are often used. Mixtures are usually analysed by titration of the sulphite followed by determination of the total resulting sulphate. If, however, the sulphate is present only in low concentration, then it can be determined separately first.

Air pollution and flue gas studies have necessitated the development of more sensitive methods of determining low concentrations of sulphur oxides. A colorimetric method using barium chloranilate has recently found favour; this relies on the double decomposition of barium chloranilate in buffered (pH = 4) alcoholic solution when sulphate is added. The freed chloranilic acid is determined spectro-photometrically against a blank. There are two convenient peaks, one at 530 millimicrons and another at 330 millimicrons and only certain heavy metals interfere with this method. Total sulphur oxides may also be determined by absorption of the sulphur oxides in aqueous hydrogen peroxide. The precipitation of barium sulphate under carefully controlled conditions can then be used as a basis for a turbidimetric method for the determination of sulphate.

The estimation of sulphur trioxide is often hindered by the formation of a sulphuric acid "mist" which is difficult to condense. This tendency to form droplets has also been found to offer a sensitive method for the detection of sulphur trioxide. However, attempts to make this the basis of a quantitative method by measurement of the acid dew point have not produced accurate results on a practical scale, although changes in dew point as measured by any particular method in any one place do reflect changes in sulphur trioxide concentration.

(b) Summary of methods of analysing nitrogen (II and IV) oxides

The classical chemical method for the determination of nitrogen oxides involves their oxidation to nitrogen dioxide followed by absorption in dilute alkali solution, the resulting nitrous acid being determined by back titration with permanganate. This method is not very convenient for determining the ratio of nitric oxide to nitrogen dioxide and at low concentrations the oxidation of nitric oxide is very slow under normal conditions. At low concentrations, nitrogen dioxide can be determined colorimetrically by the production of the azo-dye from a mixture of benzidene hydrochloride and 2-naphthol. This latter determination can be carried out with the reagents supported on a solid in a transparent tube; the gas sample is drawn along the tube and the nitrogen dioxide is estimated by comparison of the colour produced with that of a series of calibrated tubes.

Hersch[56] has described a galvanic method for the estimation of low concentrations of nitrogen dioxide, or of nitrogen dioxide + nitric oxide (if the air stream is first passed through a tube containing heated chromium trioxide). This uses a cell system represented by

Air + NO_2	Pt (emerging)	Neutral buffered chloride solution	Ag or active carbon .

This system soon becomes "aged" so that only about 35% of the nitrogen dioxide is reduced electrochemically to nitric oxide. But once "ageing" is complete, the efficiency stays constant and the cell can be calibrated against a standard source of nitrogen dioxide.

The usual standard source of nitrogen dioxide has been the thermal decomposition of AnalaR lead nitrate, but recently for determination in flow systems use has been made of the carefully controlled electrolysis of nitroso-sulphuric acid to give nitric oxide followed by oxidation of the nitric oxide over heated chromium trioxide.

The development of simple portable methods of analysing nitrogen (II and IV) oxides in the presence of other acidic or reducible gases is of great importance for studies of air pollution caused by flue and exhaust gases. A low temperature gas-solid chromatographic method[57] has produced some useful results for simple mixtures but is lengthy and requires tedious calibration for complex mixtures.

Although spectrophotometric methods are the most reliable for the determination of nitrogen oxides under laboratory conditions, other strongly absorbing gases can interfere with the method.

(c) Analytical methods used in the present work

It was found that the only conveniently determined quantity was the sulphur dioxide present in the reaction vessel. It was not found practicable to measure directly the sulphur trioxide produced due to the losses caused by the strong adsorption of this compound on glass apparatus.

The gases from the reaction vessel were dissolved in 100 cm.^{3} of 67% aqueous ethanol as described in section C1(d) of this chapter. Three aliquots of 10 cm.^{3} were taken from each solution, and approximately 50 mg. of barium chloranilate were added to each sample and 10 drops of 20-volume hydrogen peroxide was added to two of them. The samples were allowed to stand overnight with occasional shaking, before measurement of the absorption peak at 530 millimicrons. It was found that the peak height varied directly with the sulphur dioxide concentration. However, agreement from day to day was not very good (variations of ca. 10% being recorded), the time of standing, extent of shaking and room temperature all affecting the results. Standard solutions of sulphur dioxide were therefore always prepared with each batch of analyses. These solutions were prepared from known pressures of sulphur dioxide and oxygen in the reaction vessel.

Absorption spectra were measured on a Unicam SP 800 spectrophotometer and the optical density of the samples was usually kept between 1 and 2 by dilution with an appropriate amount of aqueous alcohol.

RESULTS

RESULTS

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RESULTS

A Investigation of the suitability of the apparatus

Since no appreciable reaction was observed between pure sulphur dioxide and oxygen below 1000°C, it was decided to introduce a heterogeneous catalyst in the first instance in order to check that the formation of sulphur trioxide was accompanied by the pressure changes that would be expected from Bodenstein's equilibrium data[11].

1. The vanadium pentoxide-catalysed reaction

The most convenient catalyst was vanadium pentoxide supported on pumice (surface area $\simeq 10^4$ cm.^{2} g.$^{-1}$). At a reaction temperature of 700°C a conveniently large conversion of sulphur dioxide to sulphur trioxide should occur at a reasonable rate. However it was observed that with ca. 2g. of catalyst, 200 mm. Hg. SO_2 and 200 mm. Hg. O_2 the pressure change was ca. 120 mm. Hg. i.e. much greater than that predicted (Figure 10). This is probably due to adsorption of the sulphur trioxide on the pumice support and a second catalyst was therefore selected.

2. The platinum-catalysed reaction

After the reaction vessel had been thoroughly cleaned with 40% hydrofluoric acid and distilled water, a 20 cm. length of platinum wire (17 s.w.g.) was placed in the reaction vessel. With a reaction mixture containing 200 mm. Hg. SO_2 and 200 mm.

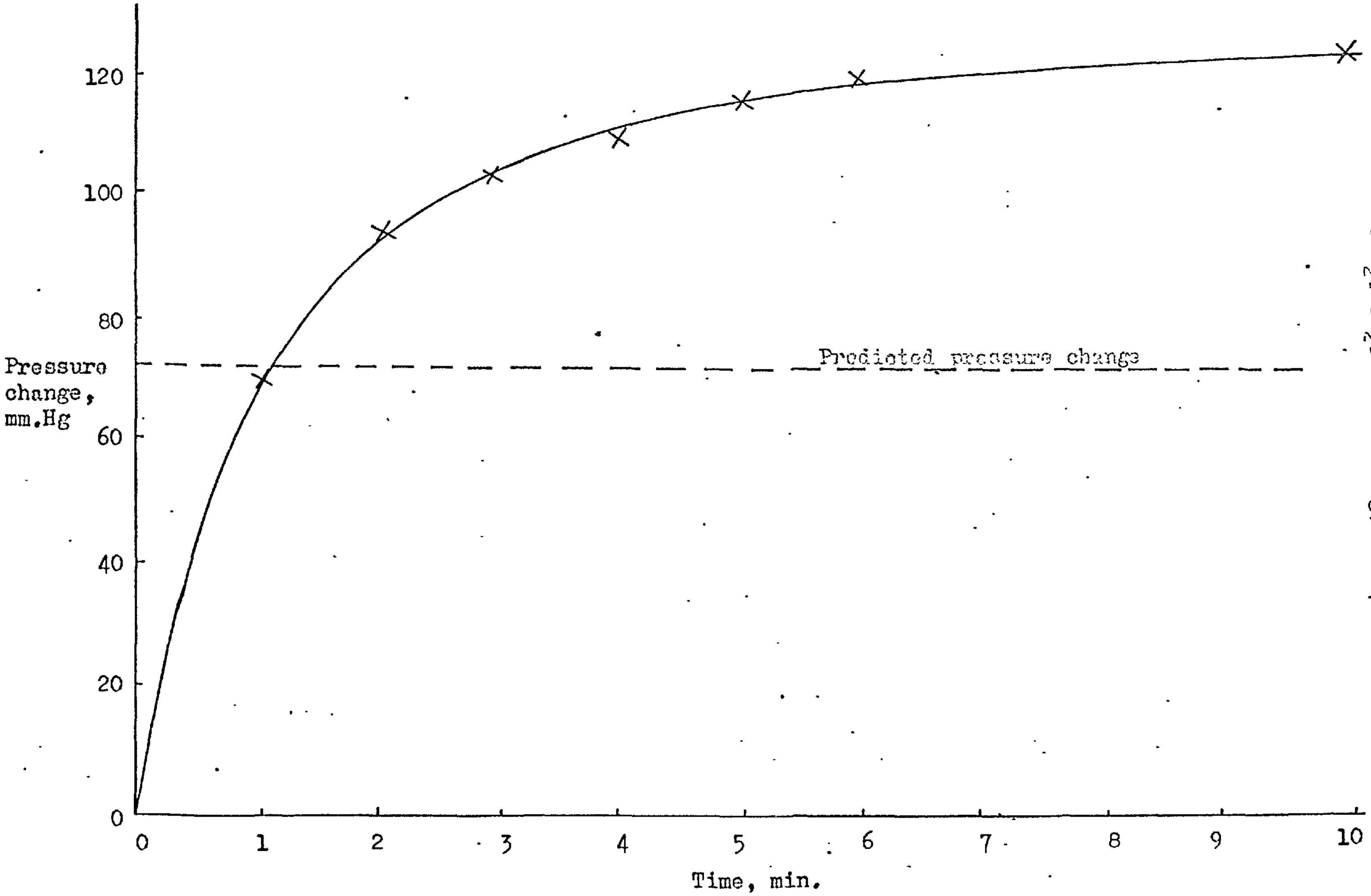


Figure 10

Pressure/time curve for the oxidation of sulphur dioxide in the presence of a vanadium pentoxide catalyst at 700°C. ($[SO_2]=[O_2]=$ 200 mm. Hg)

Hg. O_2 at 700°C it was observed that, after the pressure decrease predicted for equilibrium, there was a continued, but slower, decrease in pressure (Figure 11). This is probably caused by condensation of the sulphur trioxide in the vacuum line between taps A_3 and A_4 (Figure 3), which at this stage were normal silicone-greased taps. This region of the apparatus was heated to ca. 100°C but, although under these conditions the rate of pressure decrease beyond the predicted value was lower, the initial rate also decreased. In subsequent runs the initial rate was found to decrease progressively until, after four runs, no reaction was observed (Figure 11). On removal from the reaction vessel, the platinum wire was found to have a white coating. Taps A_3 and A_4 had required regreasing after each run as the reaction products had reacted with the silicone grease to produce a white brittle substance. The hypothesis that the white coating on the platinum wire arose from the action of sulphur oxides on the silicone grease was checked by replacing taps A_3 and A_4 with modified greaseless taps (Figure 5). A fresh length of platinum wire was inserted and reproducible kinetics were then obtained for a mixture containing 300 mm. Hg. SO_2 and 300 mm. Hg. O_2. When the line temperature was increased to 200°C, the final rate of pressure decrease (3 mm. Hg. per day) was insignificantly small (Figure 12). Unfortunately the diaphragms of the greaseless taps were found to be seriously

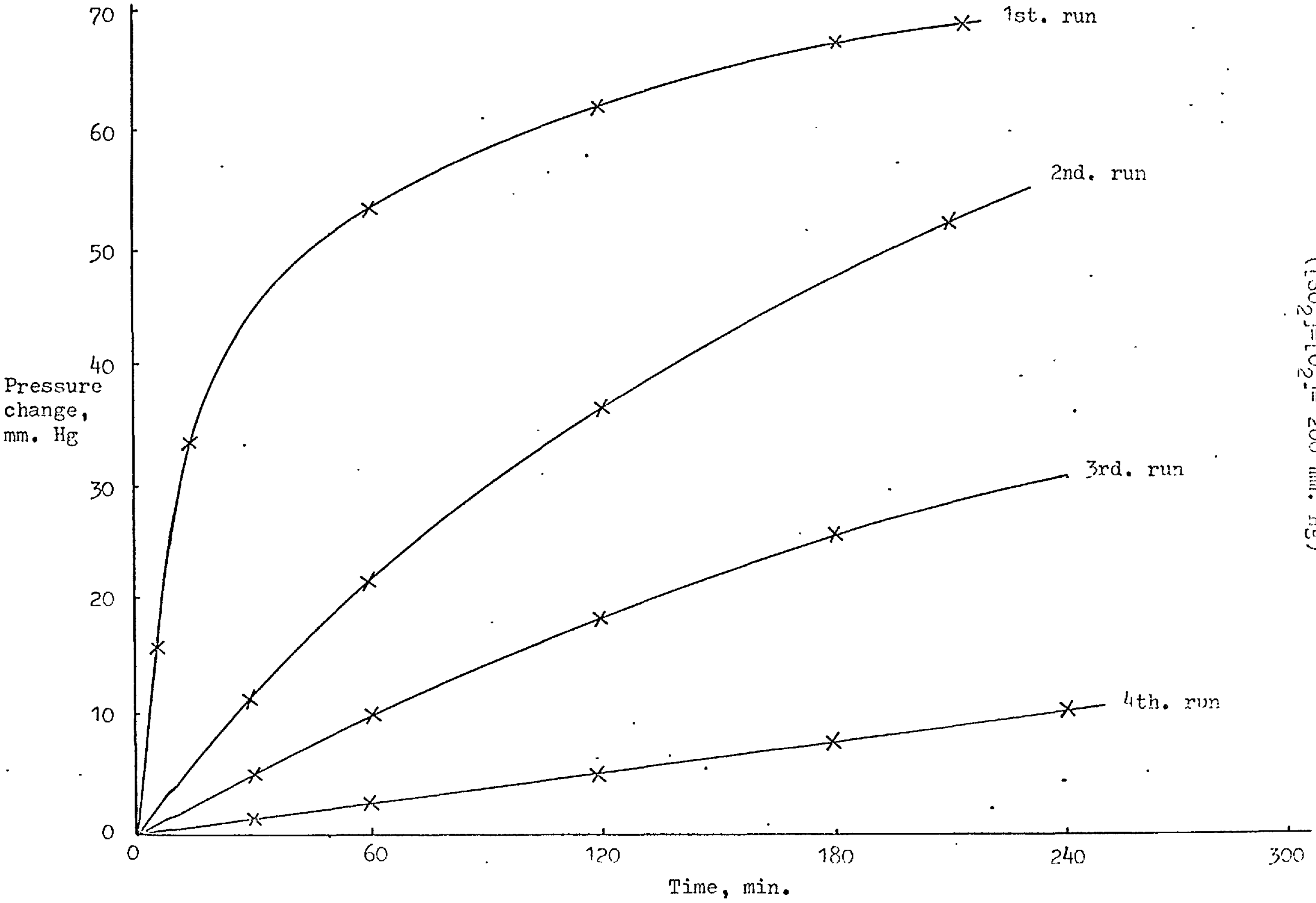


Figure 11

Pressure/time curves for the oxidation of sulphur dioxide showing the poisoning of a platinum catalyst at 700°C. ($[SO_2]=[O_2]=$ 200 mm. Hg)

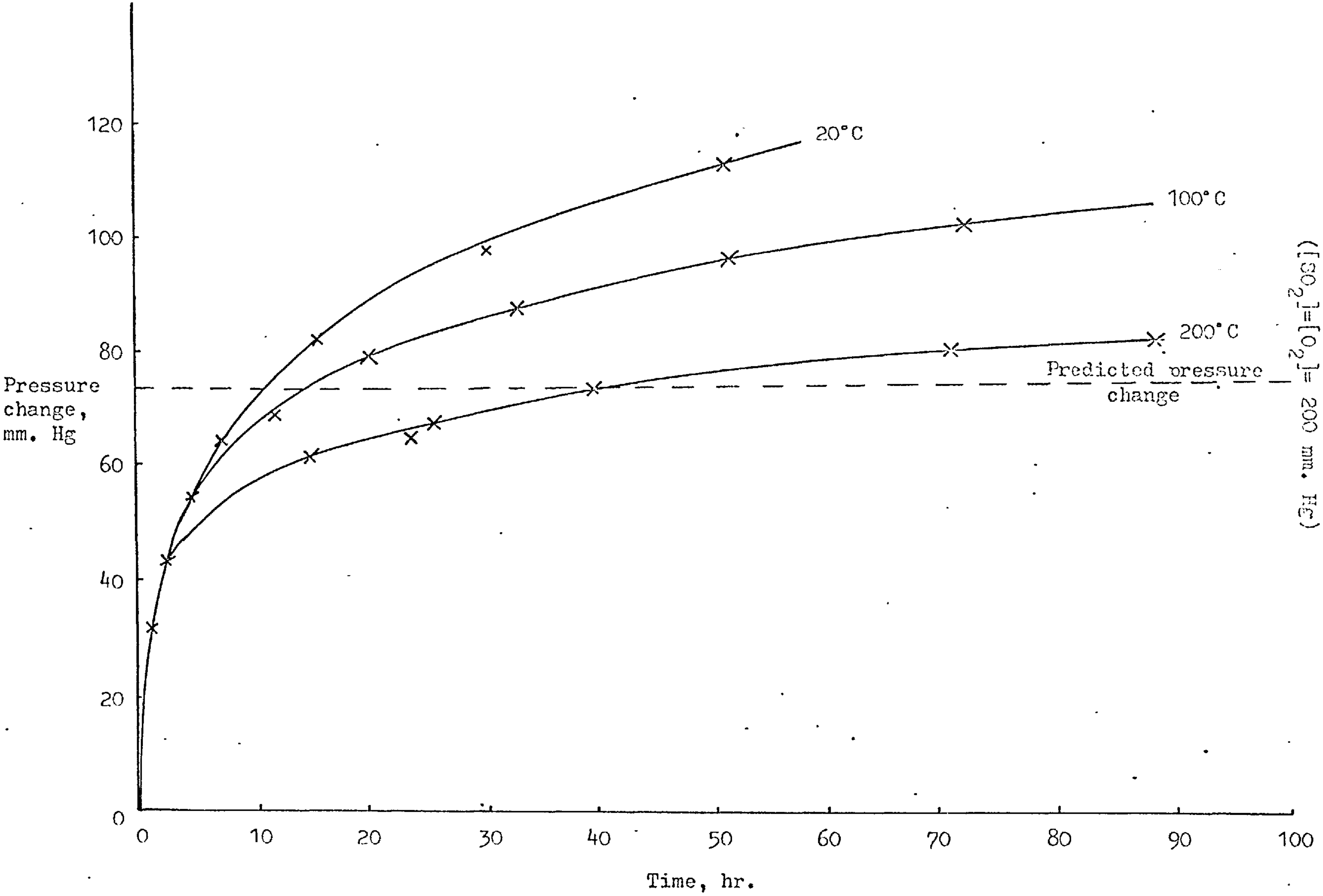


Figure 12

Pressure/time curves showing the effect of heating the apparatus around the reaction vessel at 700°C.

($[SO_2]=[O_2]=$ 200 mm. Hg)

effected by sulphur trioxide and they were therefore covered with protective layers of teflon. This reduced the attack by sulphur trioxide but did not entirely eliminate it. The apparatus, modified in this way, was used in all other experiments.

B The oxidation of sulphur dioxide in the absence of added catalysts

A new vessel, uncontaminated by catalysts, was cleaned with hydrofluoric acid and thoroughly rinsed with distilled water before being used for the experiments described below. All rates of reaction reported in this section are measured in moles of sulphur trioxide formed per litre per minute.

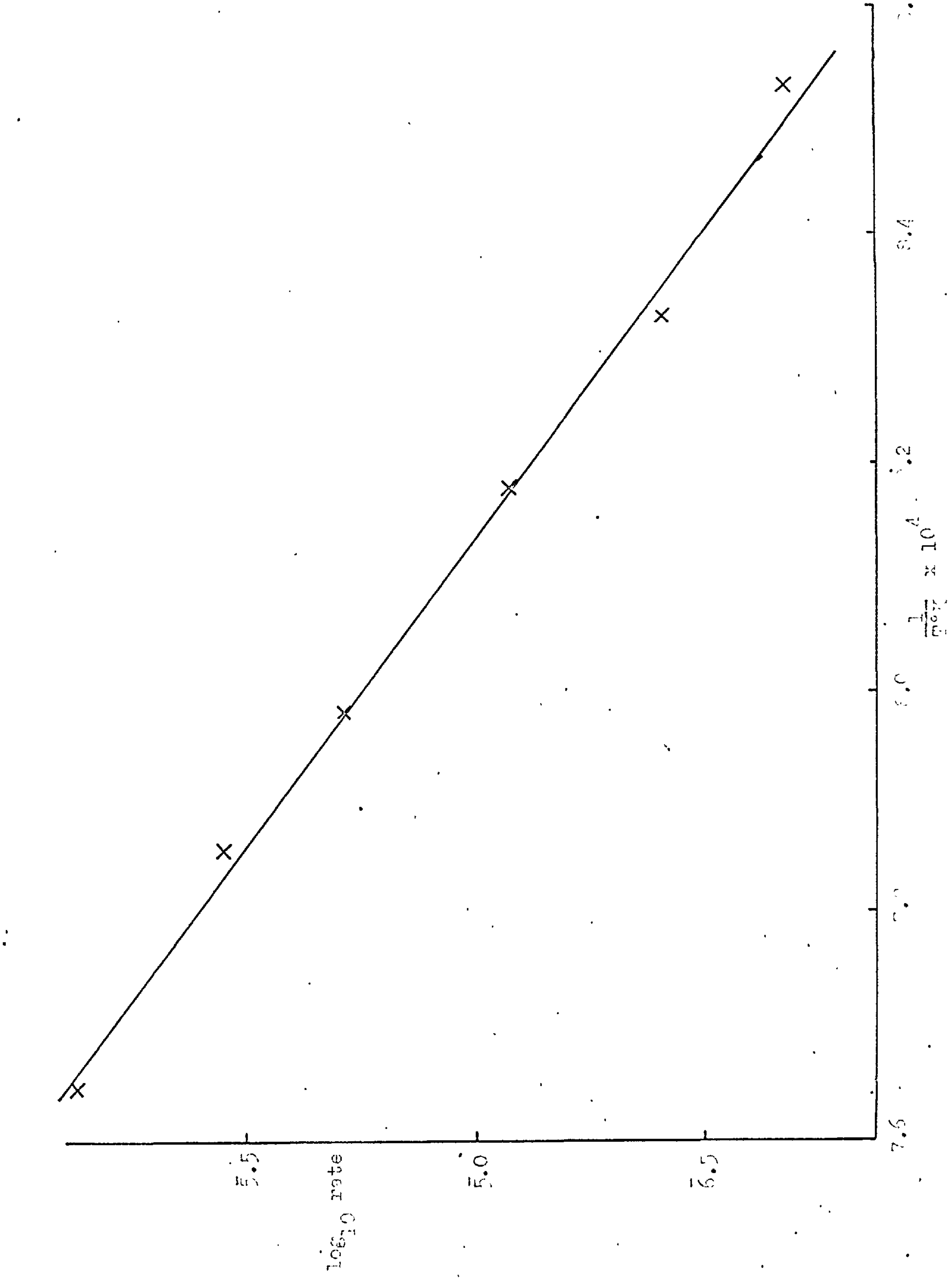
1. Variation of the initial rate with temperature

Sulphur dioxide (200 mm. Hg) and oxygen (200 mm. Hg) were admitted to the reaction vessel at 700°C but no change of pressure was observed. This was repeated at 800, 900 and 1000°C, and at the higher temperatures a slow reaction was observed. The initial rate of this reaction was measured between 900 and 1035°C using a gas mixture containing constant molar quantities of each of the two reactants; viz. $SO_2 = O_2 = 2.5 \times 10^{-3}$ mole l^{-1}.

The overall activation energy (Figure 13) appears to be ca. 80 kcal. mole^{-1}; all the results shown represent the average values for at least five runs. This value must be regarded as

Figure 13

An Arrhenius plot for the reaction between sulphur dioxide and oxygen. ($[SO_2]=[O_2]= 2.5 \times 10^{-3}$ mole l^{-1})



approximate on account of the difficulty of determining accurately the initial rate of reaction due to the very low rates involved and the small amount of chemical change which occurs at these temperatures.

2. Variation of the initial rate with the pressures of sulphur dioxide and oxygen

The influence on the initial rate of reaction of the partial pressures of sulphur dioxide and oxygen was studied at 950°C. In an attempt to measure the apparent order of reaction with respect to the two reactants, plots of $\log_{10}$ initial rate versus $\log_{10}$ concentration of the gas being varied, were constructed. The reaction appears to be first order with respect to sulphur dioxide (Figure 14) but largely independent of the oxygen pressure (Figure 15).

3. Variation of the initial rate with the pressures of added gases

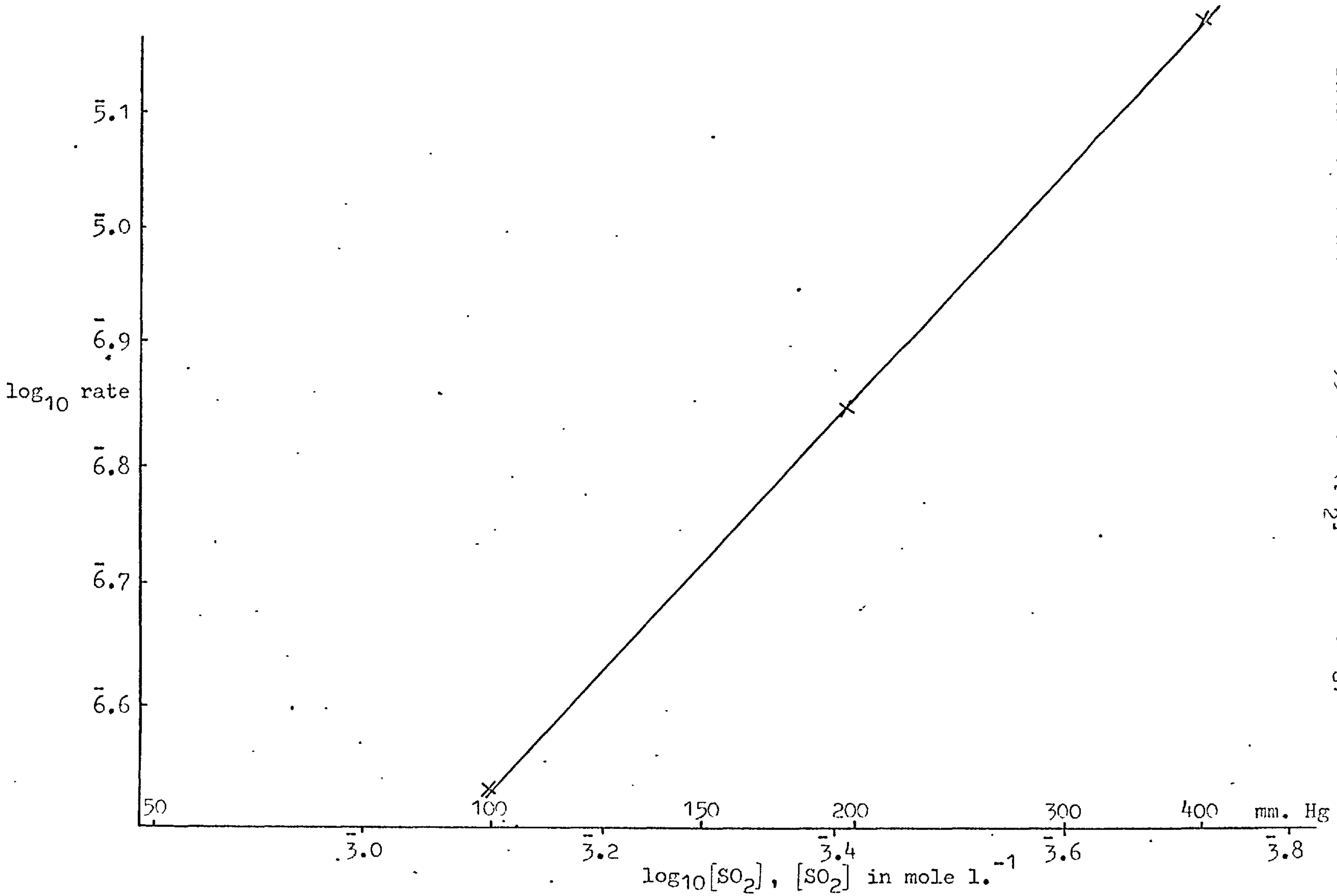
The effect of added nitrogen or water vapour on the rate of reaction, also measured at 950°C, was found to be negligible as shown in Table 5.

4. Variation of the initial rate with surface:volume ratio

The effect of varying the surface:volume ratio was investigated by repeating the experiments in a packed vessel, the

Figure 14

Plot of $\log_{10}$ initial rate of oxidation versus $\log_{10}$ sulphur dioxide concentration at 950°C. ($[O_2]$ = 200 mm. Hg)



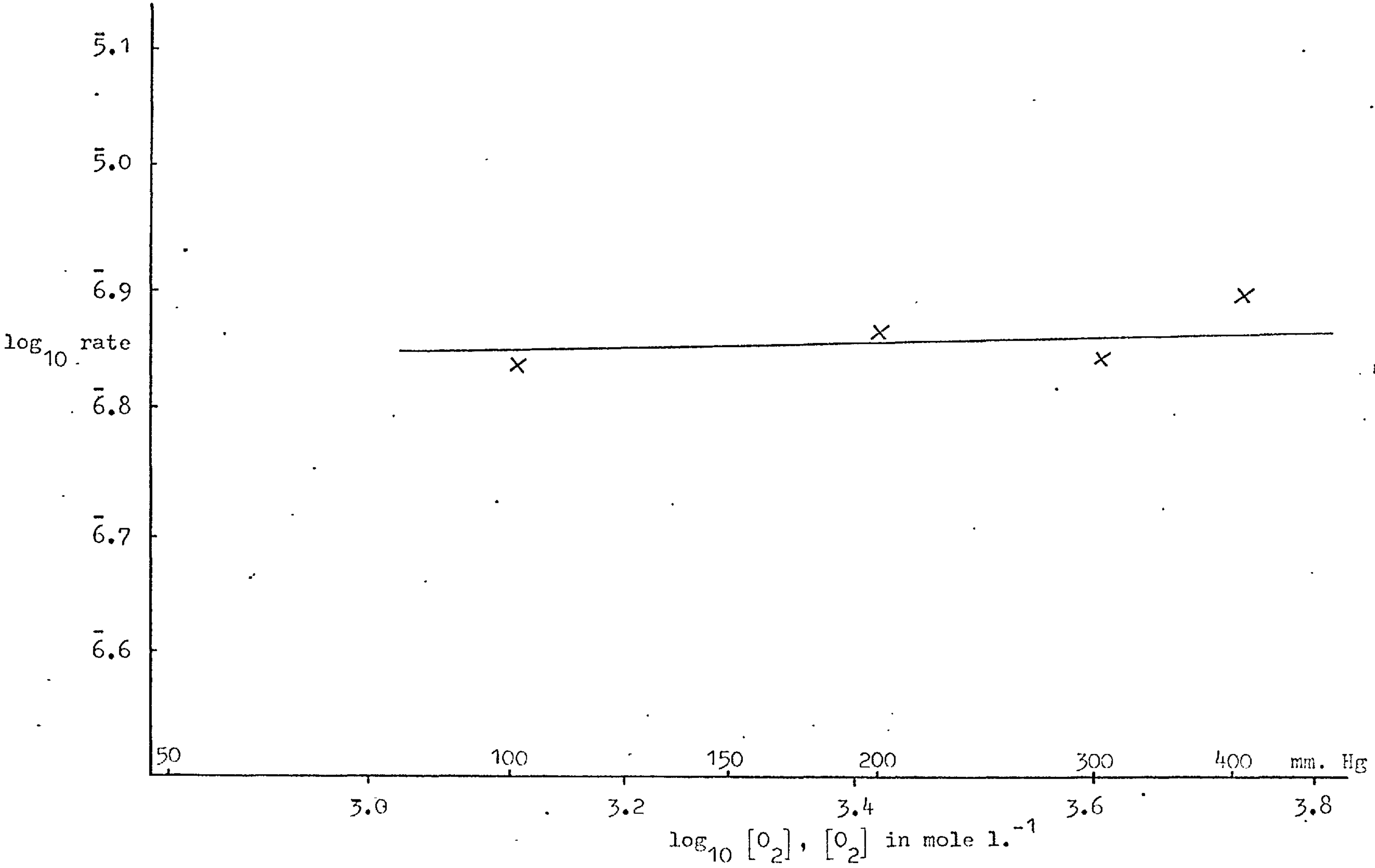


Figure 15

Plot of $\log_{10}$ initial rate of oxidation versus $\log_{10}$ oxygen concentration at 950°C. ($[SO_2]$= 200 mm. Hg)

Table 5

The influence of the surface and of inert gases on the rate of reaction in the absence of added catalysts at 950°C.

$[SO_2] = [O_2] = 2.6 \times 10^{-3}$ mole $l.^{-1}$

Reaction vessel	$[N_2]$ (mole $l.^{-1}$)	$[H_2O]$ (mole $l.^{-1}$)	Rate of formation of sulphur trioxide (mole $l.^{-1}$ $min.^{-1}$)
unpacked	-	-	7.1×10^{-6}
packed	-	-	7.0×10^{-6}
unpacked	1.3×10^{-3}	-	7.2×10^{-6}
unpacked	2.6×10^{-3}	-	7.4×10^{-6}
packed	2.6×10^{-3}	-	7.3×10^{-6}
unpacked	-	6.6×10^{-4}	7.2×10^{-6}
packed	-	6.6×10^{-4}	7.3×10^{-6}

surface:volume ratio of which was four times that of the unpacked vessel. As this change had no detectable effect on the rate (Table 5 and Figure 16), no further packing was attempted.

C The oxidation of sulphur dioxide in the presence of nitric oxide

Preliminary investigations of the reaction were carried out at 700°C. Nitric oxide (20 mm. Hg) was added to a mixture of sulphur dioxide (200 mm. Hg) and oxygen (200 mm. Hg), and a rapid pressure decrease was observed. The NO-catalysed reaction was therefore subsequently extensively investigated. All rates of reaction reported in this section are measured in moles of sulphur trioxide formed per litre per minute.

1. Variation of the initial rate with the pressure of nitric oxide

Studies were first made of the effect on the initial rate of the partial pressure of nitric oxide. Pressure-time curves were recorded and the initial rates were obtained from these. A log-log plot (Figure 17) shows two distinct sections, a straight line of slope $\simeq 2$ at high nitric oxide concentrations ($> 10^{-4}$ mole l^{-1}) and a curved portion of slope varying between 2 and ca. 0.5 at lower concentrations of the catalyst.

2. Variation of the initial rate with temperature

A given sulphur dioxide + oxygen mixture (containing

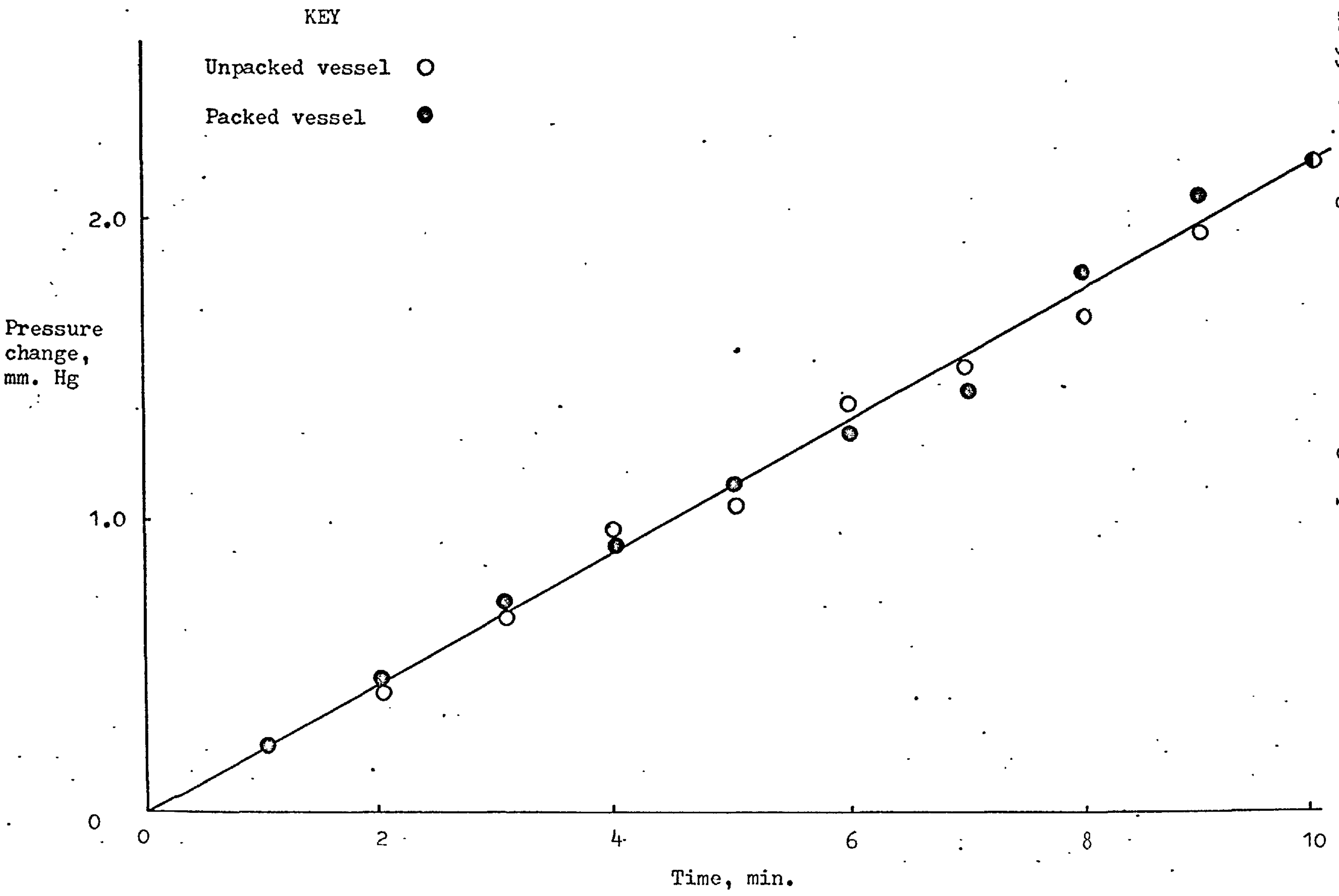
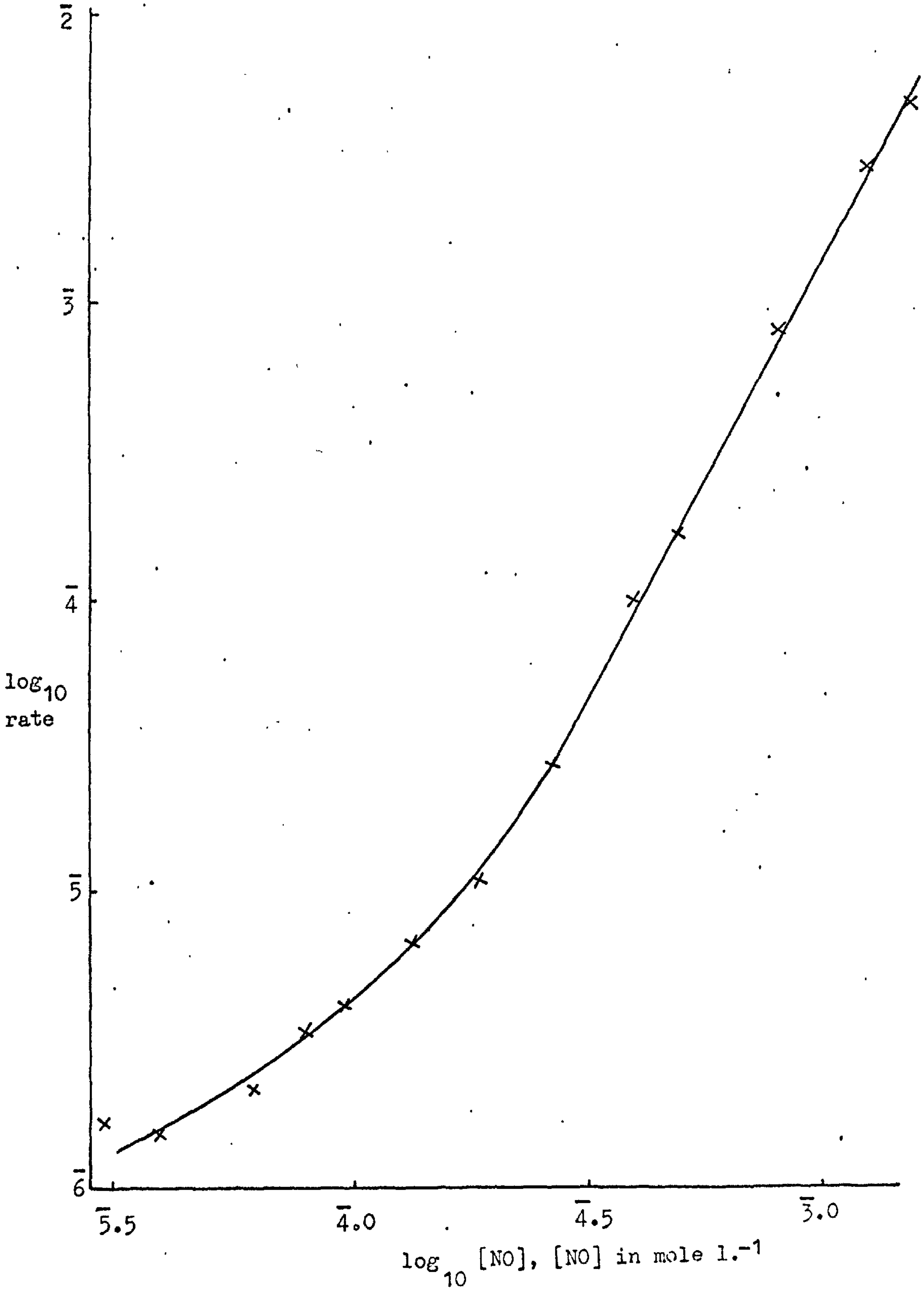


Figure 16

Typical pressure/time curves for the oxidation of sulphur dioxide at 950°C showing the effect of using a packed vessel.

Figure 17

Plot of $\log_{10}$ initial rate of oxidation versus $\log_{10}$ nitric oxide concentration at 700°C. ($[SO_2]=[O_2]=$ 200 mm. Hg)



3.3×10^{-3} mole 1^{-1} of each reactant: equivalent to 200 mm. Hg pressure at 700°C) was used throughout these experiments. Various pressures of nitric oxide (1-80 mm. Hg) were added to this mixture and the effect of temperature was studied between 400 and 900°C. The results are shown in Figure 18.

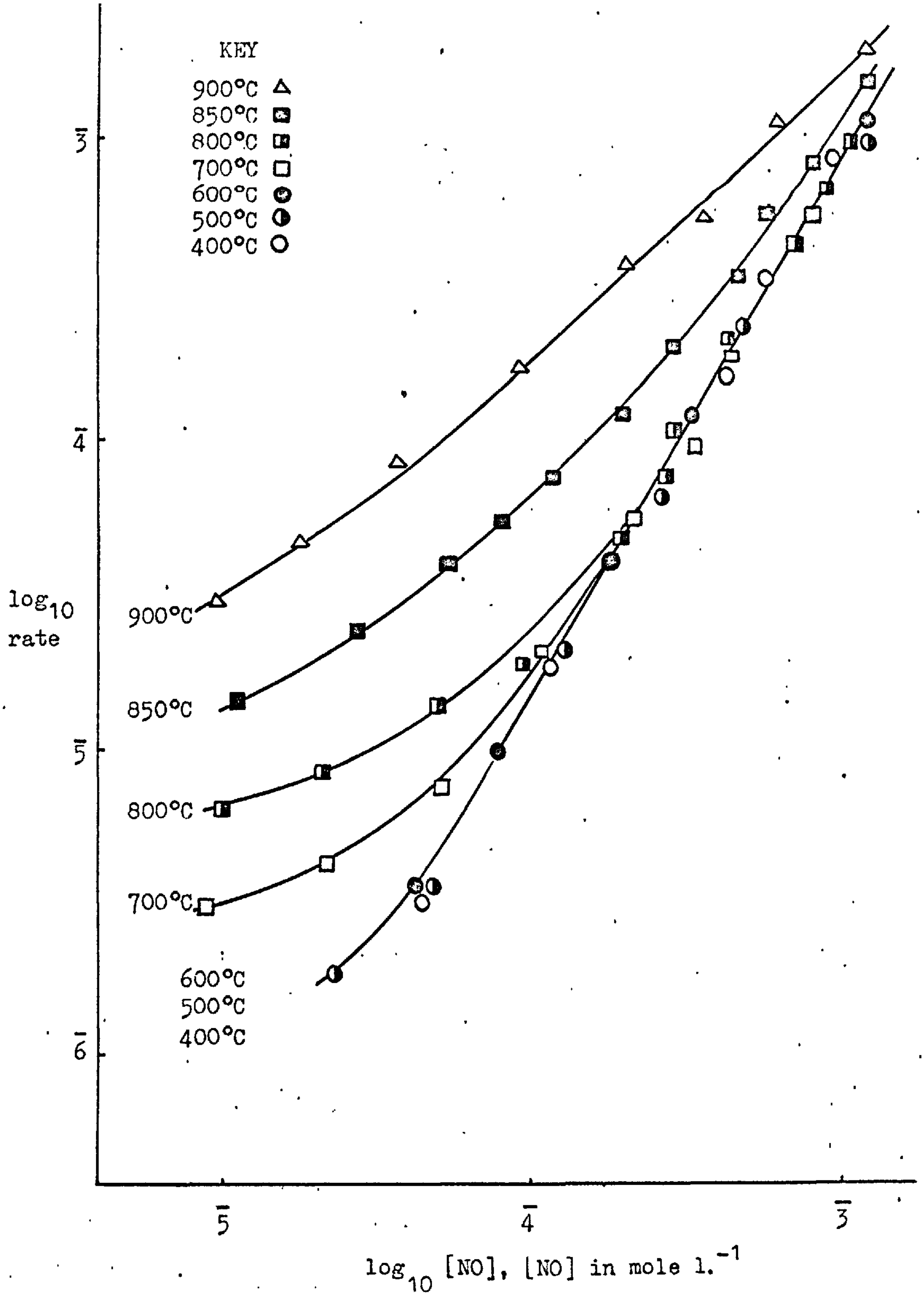
3. Variation of the initial rate with the pressures of sulphur dioxide and oxygen

From the results described in section C1 above, it was clear that different reactions were taking place at high and low concentrations of nitric oxide. The effects of the partial pressures of sulphur dioxide and oxygen were therefore studied separately in each region. At high nitric oxide concentrations ($> 10^{-4}$ mole 1^{-1}) the initial rate of reaction was found to be independent of the sulphur dioxide pressure over the range studied (Figure 19) and to be directly proportional to the pressure of oxygen as shown in Figure 20. At low nitric oxide concentrations, the rate of reaction was found to vary directly with the oxygen pressure (Figure 21) and to increase slightly with increasing sulphur dioxide pressure (Figure 22). Measurements could not be made at lower sulphur dioxide concentrations as the total pressure change became small compared with the initial rate of reaction.

Figure 18

Plot of $\log_{10}$ initial rate of oxidation versus $\log_{10}$ nitric oxide concentration at 400-900°C.

$([SO_2]=[O_2]= 3.3 \times 10^{-3}$ mole l.$^{-1})$



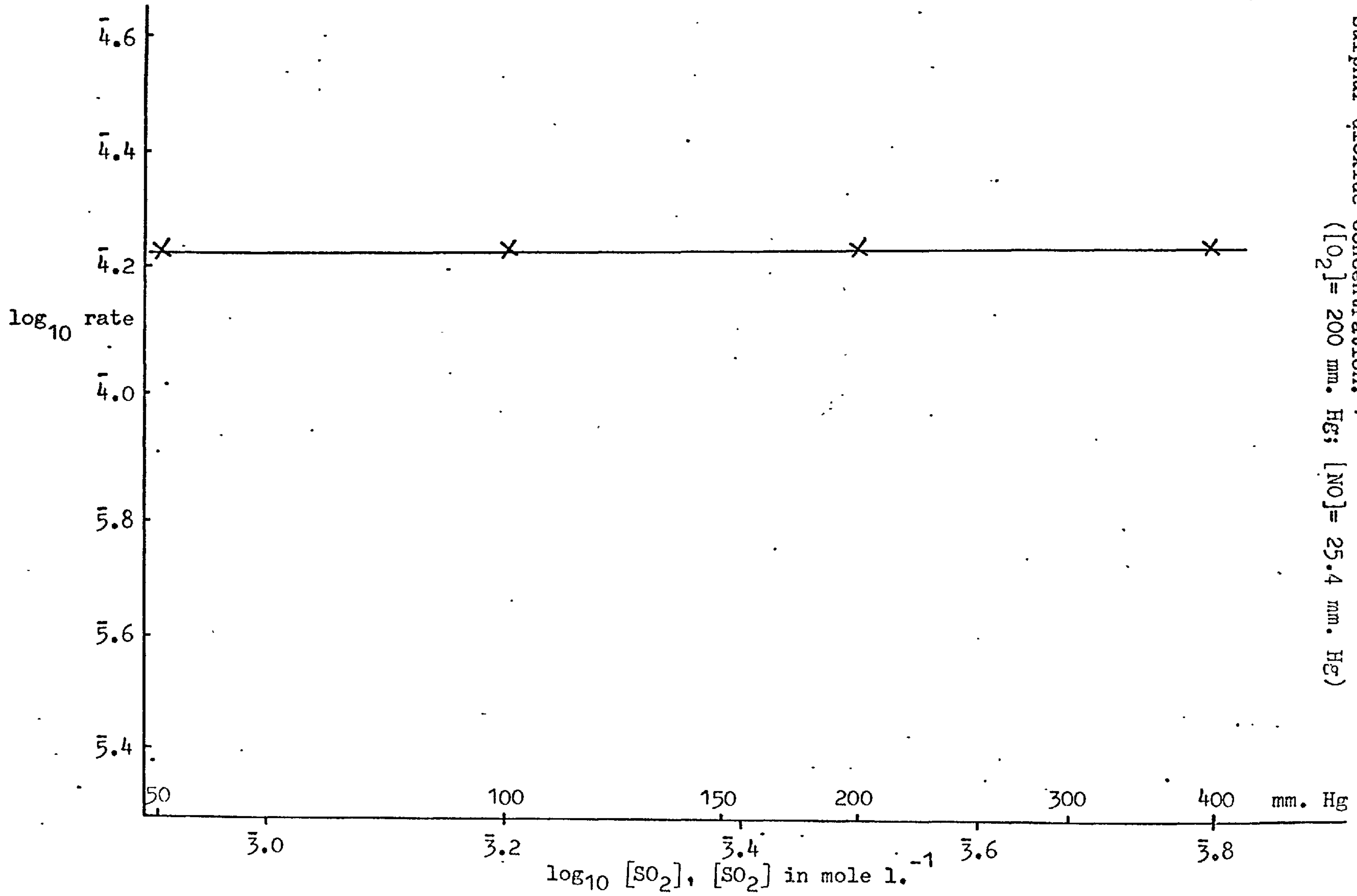


Figure 19

Plot of $\log_{10}$ initial rate of oxidation at 700°C and in the presence of a high concentration of nitric oxide versus $\log_{10}$ sulphur dioxide concentration.

($[O_2]$= 200 mm. Hg; $[NO]$= 25.4 mm. Hg)

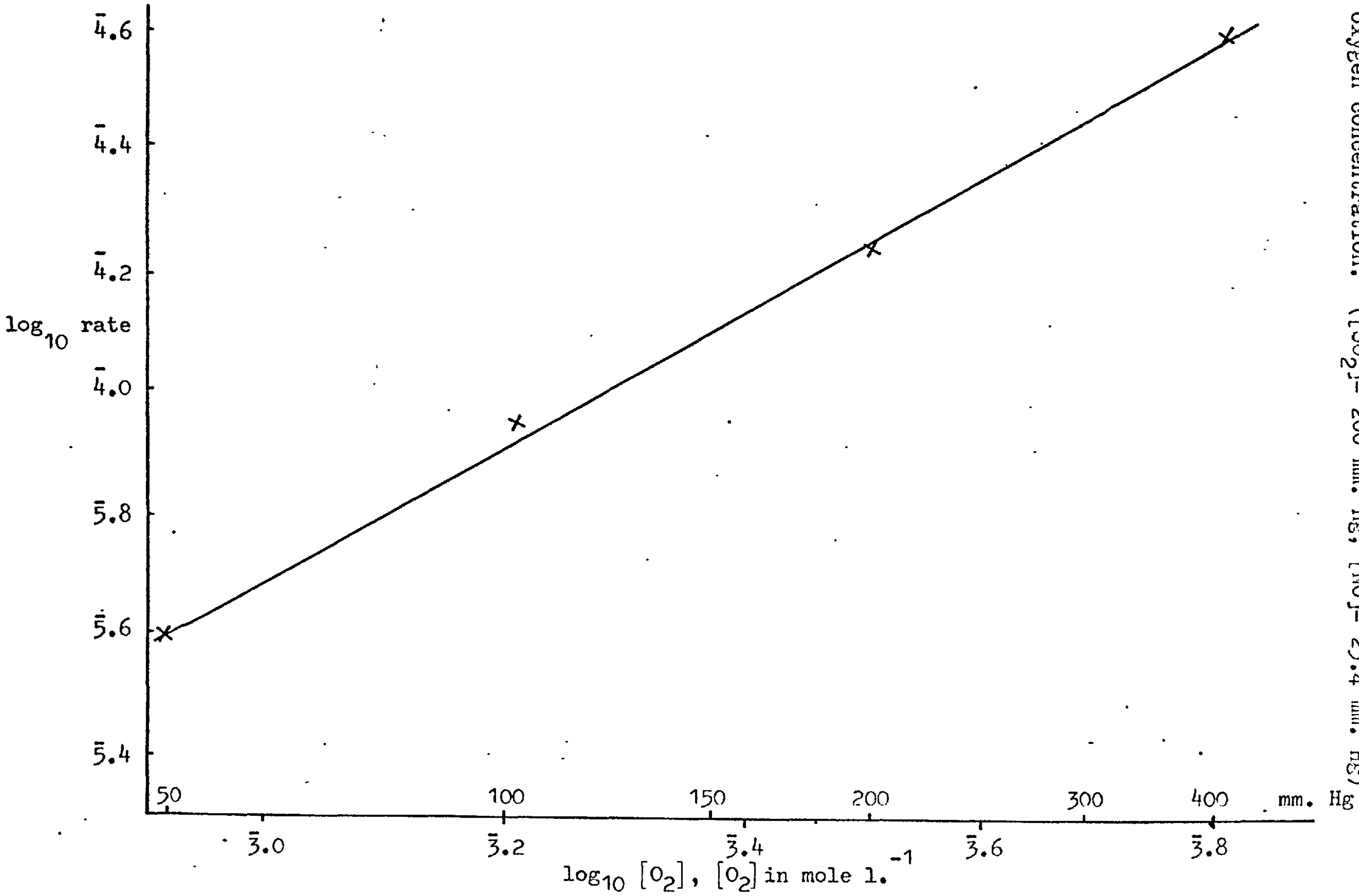


Figure 20

Plot of $\log_{10}$ initial rate of oxidation at 700°C and in the presence of a high concentration of nitric oxide versus $\log_{10}$ oxygen concentration. ($[SO_2]$= 200 mm. Hg; $[NO]$= 25.4 mm. Hg)

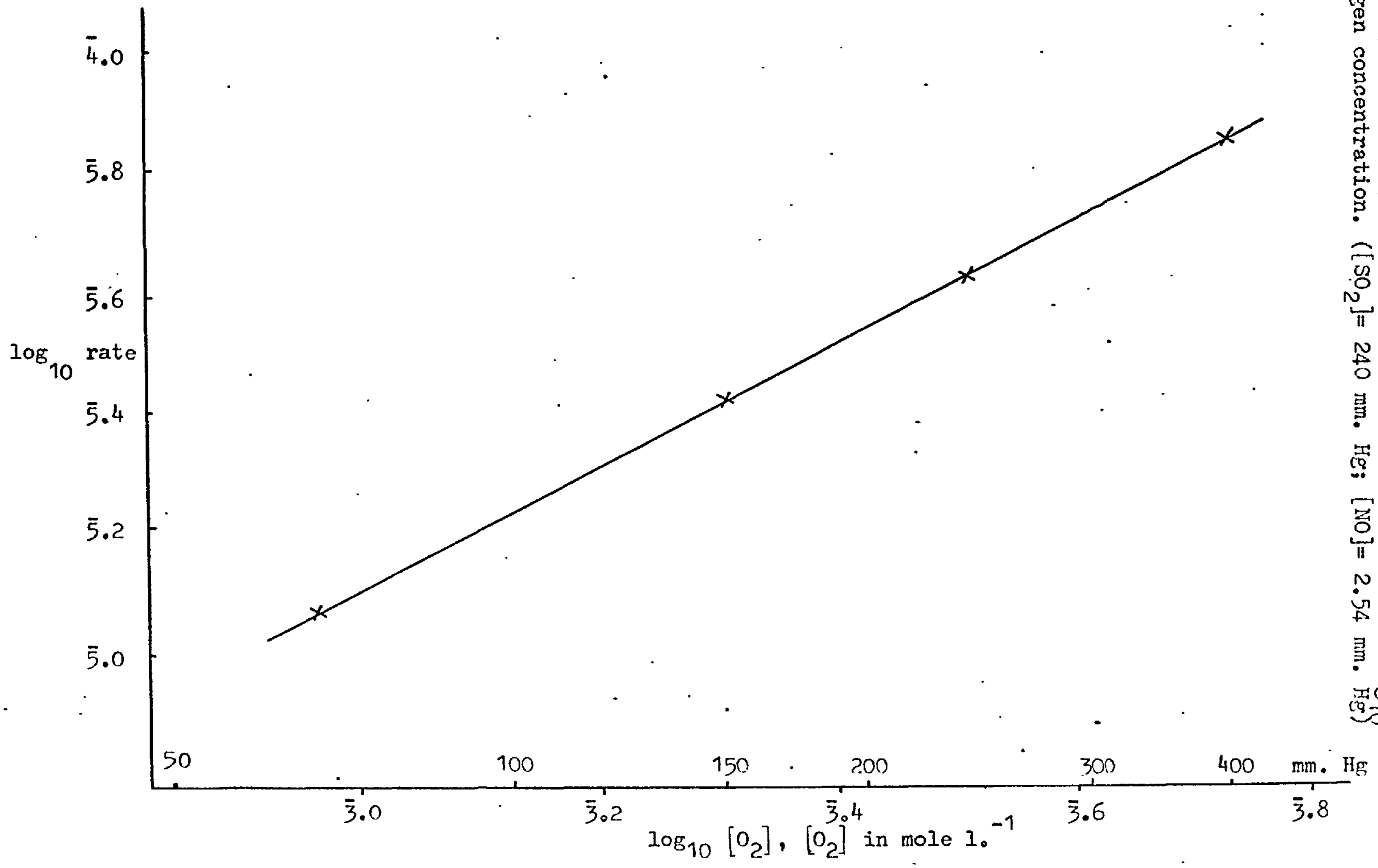


Figure 21

Plot of $\log_{10}$ initial rate of oxidation at 900°C and in the presence of a low concentration of nitric oxide versus $\log_{10}$ oxygen concentration. ($[SO_2]$= 240 mm. Hg; $[NO]$= 2.54 mm. Hg)

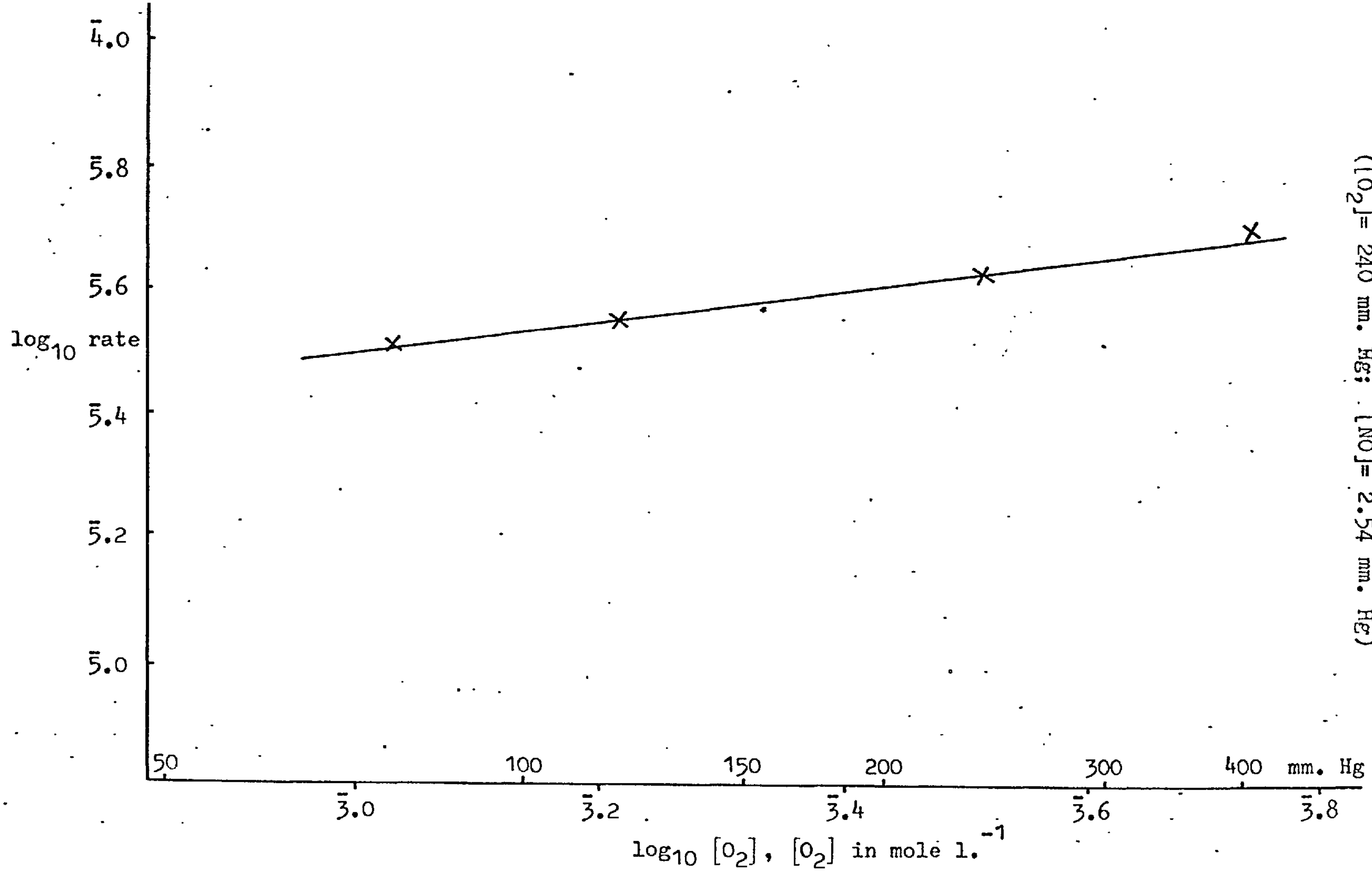


Figure 22

Plot of $\log_{10}$ initial rate of oxidation at 900°C and in the presence of a low concentration of nitric oxide versus $\log_{10}$ sulphur dioxide concentration.

($[O_2]$= 240 mm. Hg; $[NO]$= 2.54 mm. Hg)

4. Variation of the initial rate with the addition of nitrogen, water vapour and carbon dioxide

The effect of added nitrogen, water vapour and carbon dioxide was found to be negligible in the presence of both high and low concentrations of nitric oxide. These results and those of similar experiments at 900°C are shown in Table 6.

5. Variation of the initial rate with the surface:volume ratio

The effect of surface:volume ratio was studied at both high and low nitric oxide concentrations by replacing the unpacked reaction vessel by the packed one. No significant variation in rates was observed (Figure 23) and no further packing was carried out.

6. Consumption of nitric oxide during the reaction

A reaction mixture containing nitric oxide (25 mm. Hg), sulphur dioxide (100 mm. Hg) and oxygen (100 mm. Hg) was allowed to react for 20 minutes by which time the rate of pressure change had become negligibly small (less than 0.02 mm. Hg min.$^{-1}$). A further 100 mm. Hg sulphur dioxide and 100 mm. Hg oxygen were then added. The initial rate of the new reaction was measured and found to be 4.7 mm. Hg min.$^{-1}$. This was repeated, the extra gases being added after 15 minutes (when the rate of the original pressure change was 0.05 mm. Hg min.$^{-1}$) and the initial rate of the new

Table 6

(a) Variation of the initial rate of reaction in the presence of high concentrations of nitric oxide with the pressure of added nitrogen, water vapour and carbon dioxide.

$SO_2 = O_2 = 200$ mm. Hg (3.3×10^{-3} mole l^{-1})

$NO = 30$ mm. Hg (4.3×10^{-4} mole l^{-1})

Temperature = 700°C

Pressure N_2 (mm. Hg)	Pressure H_2O (mm. Hg)	Pressure CO_2 (mm. Hg)	Rate (moles SO_3 formed $l^{-1}min^{-1}$)
-	-	-	2.2×10^{-4}
100	-	-	2.3×10^{-4}
200	-	-	2.3×10^{-4}
350	-	-	2.2×10^{-4}
-	10	-	2.3×10^{-4}
-	-	200	2.2×10^{-4}
after extra drying of the sulphur dioxide*			2.2×10^{-4}

(b) Variation of the initial rate of reaction in the presence of low concentrations of nitric oxide with the pressure of added nitrogen, water vapour and carbon dioxide.

$SO_2 = O_2 = 240$ mm. Hg (3.3×10^{-3} mole l^{-1})

$NO = 2.4$ mm. Hg (3.3×10^{-5} mole l^{-1})

Temperature = 900°C

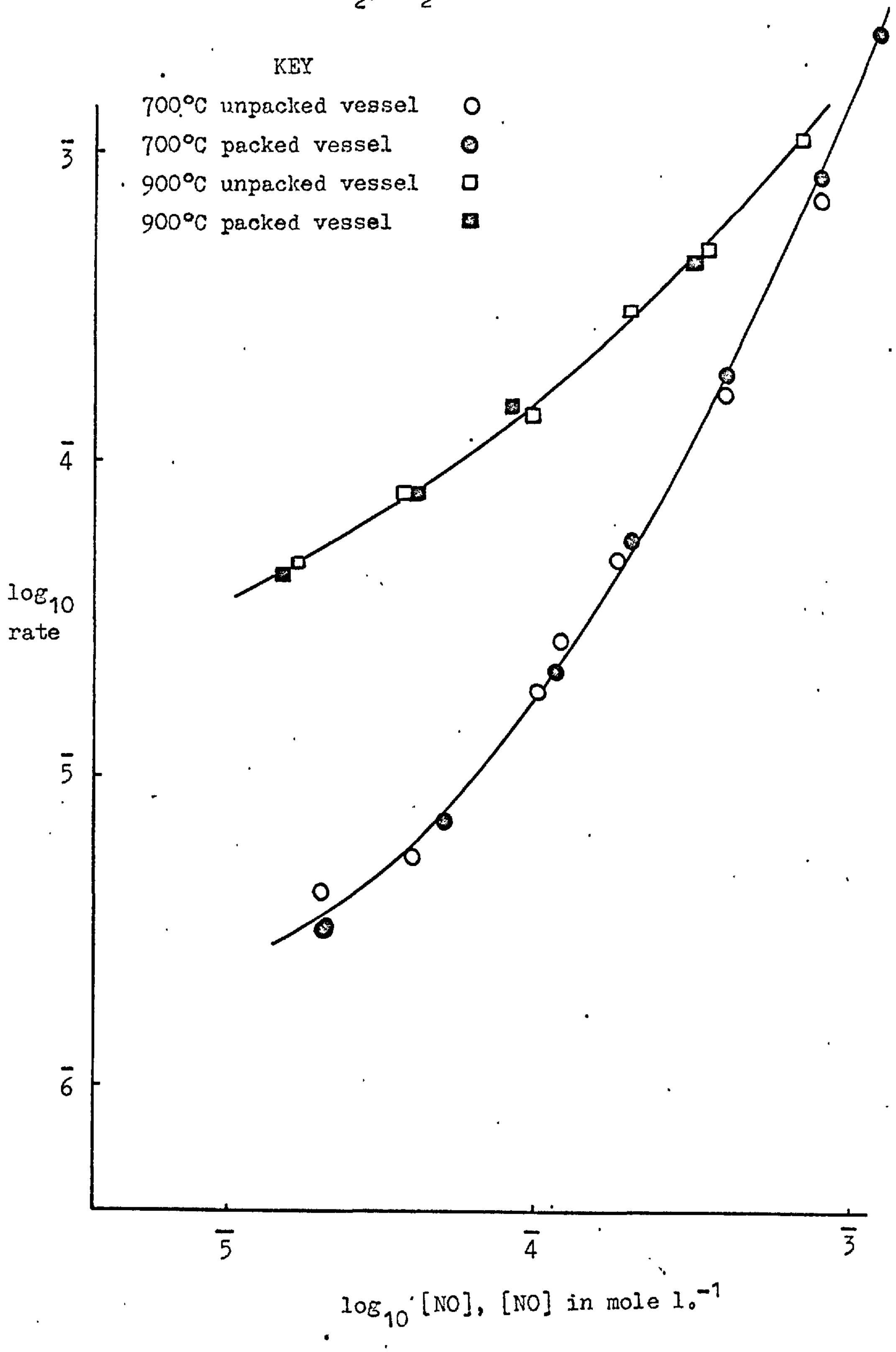
Pressure N_2 (mm. Hg)	Pressure H_2O (mm. Hg)	Pressure CO_2 (mm. Hg)	Rate (moles SO_3 formed $l^{-1}min^{-1}$)
-	-	-	8.5×10^{-5}
110	-	-	8.5×10^{-5}
-	10	-	8.6×10^{-5}
-	-	150	8.4×10^{-5}
after extra drying of the sulphur dioxide*			8.5×10^{-5}

*The sulphur dioxide was dried by distillation from metallic sodium.

Figure 23

Plot of $\log_{10}$ initial rate of reaction versus $\log_{10}$ nitric oxide concentration showing the effect of using a packed vessel.

($[SO_2]=[O_2]= 3.3 \times 10^{-5}$ mole l.$^{-1}$)



reaction was found to be 5.2 mm. Hg min.$^{-1}$. Finally the initial rate of pressure change for a mixture containing 25 mm. Hg nitric oxide, 180 mm. Hg oxygen and 160 mm. Hg sulphur dioxide was found to be 5.7 mm. Hg min.$^{-1}$.

7. Comparison of rate measurements obtained by pressure change measurements and by chemical analysis

The rate of reaction of a typical gas mixture (NO = 12.7 mm. Hg; $SO_2 = O_2 = 200$ mm. Hg) at 700°C was determined by the usual pressure change measurements and the rate of reaction as measured by the loss of sulphur dioxide was then determined for similar mixtures by pumping the contents of the reaction vessel into a cold trap after given intervals of time and analysing the gases for sulphur dioxide as described earlier. The results are compared in Figure 24.

D The reaction between sulphur dioxide and oxygen in the presence of decomposing hydrogen peroxide

Sulphur dioxide and oxygen were mixed with hydrogen peroxide vapour at 50°C. It was observed that, if the gases were kept under these conditions, a slow pressure decrease occurred which corresponded to the loss of sulphur dioxide as measured analytically. If however, the gases were admitted, immediately after mixing, to the reaction vessel at 450°C, no loss of sulphur dioxide could be detected (Table 7).

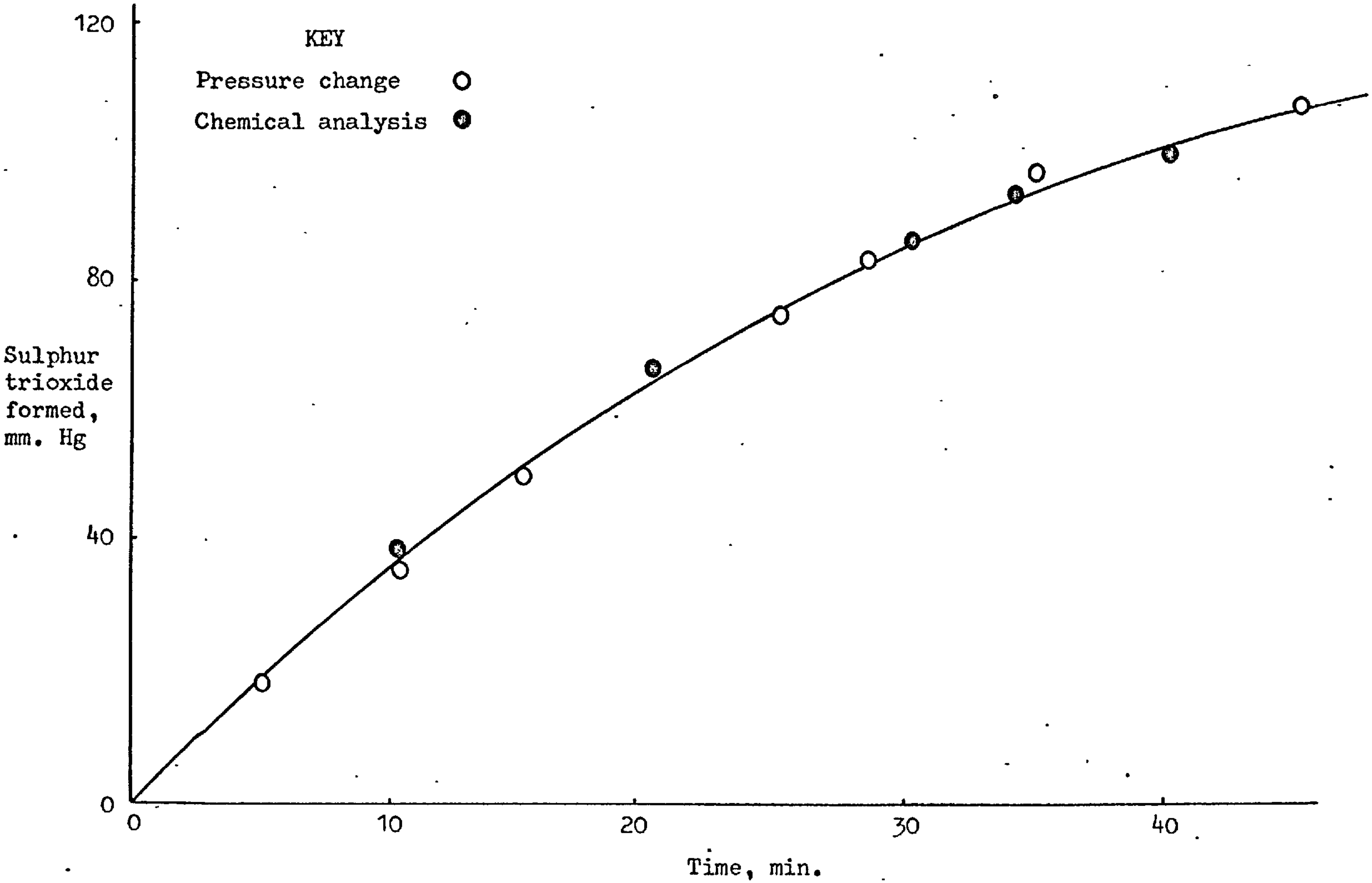


Figure 24

Comparison of pressure change and chemical analysis as criteria of the progress of reaction at 700°C.

($[SO_2]=[O_2]=$ 200 mm. Hg; $[NO]=$ 12.7 mm. Hg)

Table 7

The reaction between sulphur dioxide and oxygen in the presence of decomposing hydrogen peroxide.

Temp. °C	Pressure SO_2 (mm. Hg)	Pressure O_2 (mm. Hg)	Pressure H_2O_2 (mm. Hg)	Duration of reaction (min.)	SO_2 analysis (optical density)	SO_2 lost %
50	25	-	-	-	0.6(3)	-
50	50	-	-	-	1.2(3)	-
50	25	-	10	1	0.6(0)	5
50	25	-	10	10	0.4(3)	32
50	25	25	10	10	0.4(5)	29
450	20	-	-	-	0.5(0)	-
450	40	-	-	-	0.9(7)	-
450	20	-	8	1	0.4(8)	4
450	20	-	8	5	0.5(1)	0
450	20	-	8	10	0.5(0)	0
450	20	20	8	5	0.5(1)	0

E The oxidation of sulphur dioxide in the presence of oxidising fuels

In order to determine the ability to oxidise sulphur dioxide of the species taking part during the oxidation of fuels under oxygen-rich conditions, sulphur dioxide was added to various fuel + oxygen mixtures. A study was made of the consumption of sulphur dioxide and of the effect of this gas on the critical fuel : oxygen ratio required for ignition.

1. Consumption of sulphur dioxide during the oxidation of fuels

(a) Carbon monoxide

Carbon monoxide (100 mm. Hg) was oxidised in the presence of sulphur dioxide (10-20 mm. Hg) and excess oxygen (100 mm. Hg) at 700 and 900°C. No ignition was observed and no loss of sulphur dioxide could be detected in either case (Table 8).

(b) Ethanol

Ethanol (20 mm. Hg) was oxidised at 500°C in the presence of sulphur dioxide (40 mm. Hg) and excess oxygen (200 mm. Hg). Oxidation occurred explosively but no sulphur dioxide was consumed. The addition of ethanol to a sulphur dioxide + oxygen + nitric oxide mixture caused no measureable change in the rate of oxidation of the sulphur dioxide as observed in the absence of ethanol (Table 9).

Table 8

The oxidation of sulphur dioxide in the presence of carbon monoxide.

Temp. (°C)	Pressure SO_2 (mm.Hg)	Pressure O_2 (mm.Hg)	Pressure CO (mm.Hg)	Duration of reaction (min.)	SO_2 analysis (optical density)	% SO_2 lost	CO_2:CO in products
700	10	100	-	-	0.9(2)	-	-
700	10	100	100	2	0.9(0)	0	CO_2 only
700	10	100	100	10	0.9(3)	0	CO_2 only
700	20	100	100	10	1.8(5)	0	CO_2 only
900	10	100	-	-	0.7(5)	0	-
900	20	100	-	-	1.5(2)	0	-
900	20	100	100	2	1.5(6)	0	CO_2 only
900	20	100	100	10	1.4(7)	0	CO_2 only
900	10	100	100	10	0.7(7)	0	CO_2 only

Table 9

The oxidation of sulphur dioxide at 500°C in the presence of ethanol.

Pressure SO_2 (mm. Hg)	Pressure O_2 (mm. Hg)	Pressure NO (mm. Hg)	Pressure ethanol (mm. Hg)	Duration of reaction (min.)	SO_2 analysis (optical density)	% SO_2 lost
40	200	-	-	2	0.9(7)	-
40	200	-	-	90	0.9(9)	0
40	200	-	20	2	0.9(9)	0
40	200	-	20	90	0.9(8)	0
20	200	-	20	90	0.4(5)	0
40	200	10	0	2	0.9(0)	7
40	200	10	20	2	0.9(2)	5
40	200	10	0	90	0.0(2)	100
40	200	10	20	90	0.0(0)	100

No explosion was observed in the presence of nitric oxide.

(c) Benzene

Benzene (30 mm. Hg) was oxidised at 500°C in the presence of sulphur dioxide and excess oxygen without ignition. No loss of sulphur dioxide could be detected. The temperature was increased to 700°C under which conditions the oxidation of benzene occurred rapidly, in some cases being accompanied by ignition; at this temperature some sulphur dioxide was oxidised (Table 10).

(d) Ethane and ethylene

Experiments with both these fuels were performed at 700°C and sulphur dioxide was again found to be consumed when the oxidation of the fuel took place either slowly or explosively (Table 11).

2. The effect of sulphur dioxide and nitrogen on the oxygen-rich ignition limit for various fuels

In the experiments involving the oxidation of benzene at 700°C, it was observed that, when sulphur dioxide was present, the fuel : oxygen ratio had to be increased if ignition was to occur.

Quantitative measurements of this increase were made at 700°C for acetone, acetylene, benzene, ethane, ethylene, n-hexane and cyclohexane in the presence of a constant pressure of oxygen (200 mm. Hg). All the ignitions observed were accompanied by an

Table 10

The oxidation of sulphur dioxide in the presence of benzene.

Temp. (°C)	Pressure SO_2 (mm. Hg)	Pressure O_2 (mm. Hg)	Pressure benzene (mm. Hg)	Duration of reaction (min.)	SO_2 analysis (optical density)	% SO_2 lost
500	30	300	-	2	0.6(6)	-
500	30	300	30	2	0.6(8)	0
500	30	300	30	150*	0.6(5)	0
700	10	200	-	2	0.9(2)	-
700	40	200	-	2	3.6(4)	-
700	10	200	10	2	0.7(4)	20
700	10	200	10	30	0.6(4)	30
700	10	200	15	2	0.6(6)	30
700	40	200	10	2	0.8(3)	10

* Analysis of the products by gas chromatography showed that 90% of the benzene had been oxidised to carbon dioxide.

Table 11

The oxidation of sulphur dioxide at 700°C in the presence of ethane and ethylene.

Pressure SO_2 (mm. Hg)	Pressure O_2 (mm. Hg)	Pressure ethane (mm. Hg)	Pressure ethylene (mm. Hg)	Duration of reaction (min.)	SO_2 analysis (optical density**)	% SO_2 lost
5	400	-	-	2	0.1(1)	-
10	200	-	-	2	0.2(2)	-
50	200	-	-	2	0.5(8)	-
5	200	25	-	2*	0.07(7)	25
5	400	25	-	2	0.09(5)	15
10	200	25	-	2*	0.1(8)	20
50	200	25	-	2*	0.5(0)	15
5	200	-	25	2*	0.06(6)	40
10	200	-	25	2*	0.1(5)	30
40	200	-	25	2*	0.3(8)	15

* indicates that the oxidation occurred explosively

** values for the optical density are all adjusted to the same dilution audible "click" and a "flash-back" to the pre-mix vessel. The results are shown in Table 12 and in Figures 25-27.

Table 12

The minimum values for the fuel:oxygen (200 mm. Hg) ratio at which ignitions were observed when the temperature of the reaction vessel was 700°C.

Fuel	Fuel:oxygen
Acetone	40 : 200
Acetylene	15 : 200
Benzene	8 : 200
Ethane	21 : 200
Ethylene	21 : 200
n-Hexane	10 : 200
Cyclohexane	14 : 200

Figure 25

Graph of oxygen-rich ignition limit showing the % increase in the fuel required for various amounts of additive at 700°C.

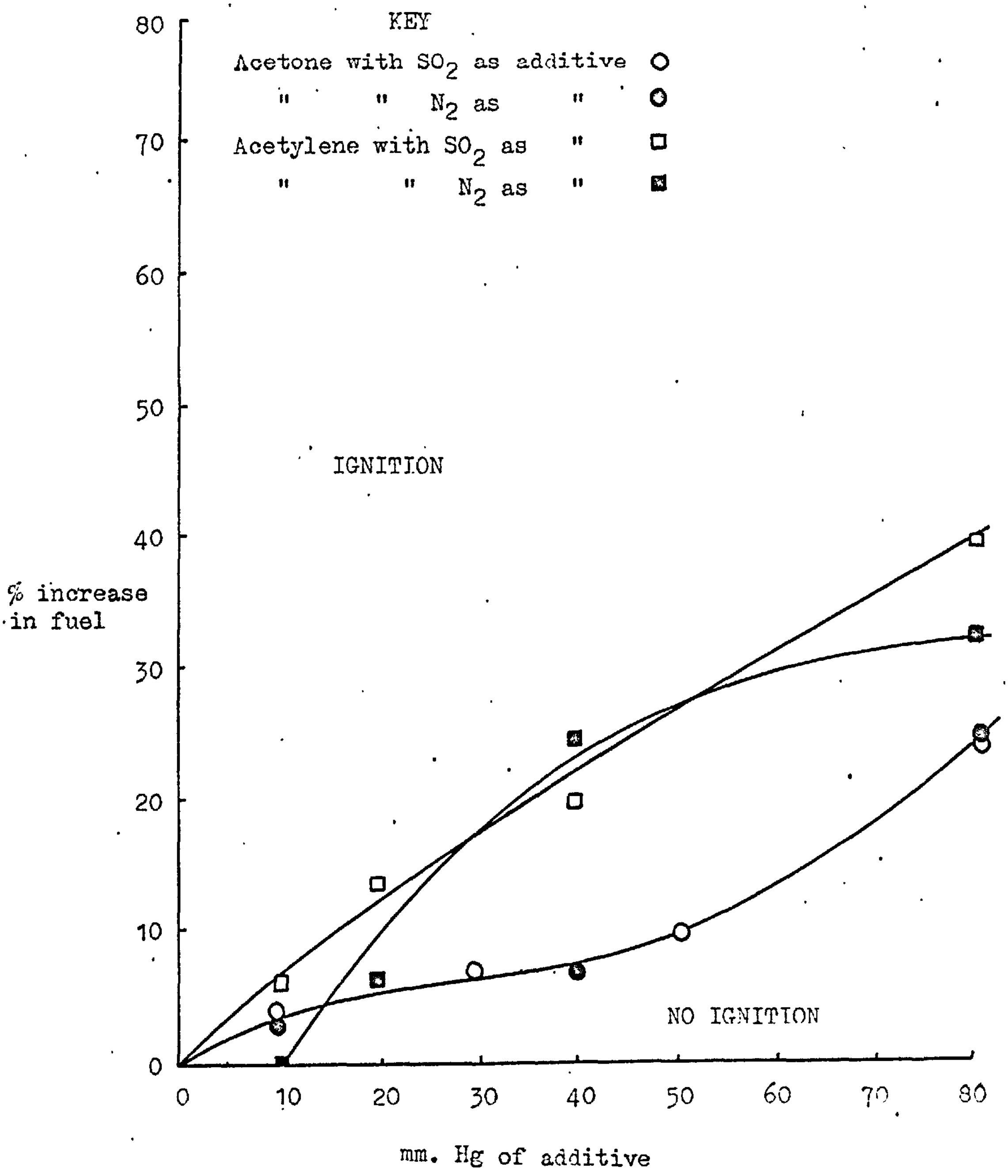


Figure 26

Graph of oxygen-rich ignition limit showing the % increase in the fuel required for various amounts of additive at 700°C.

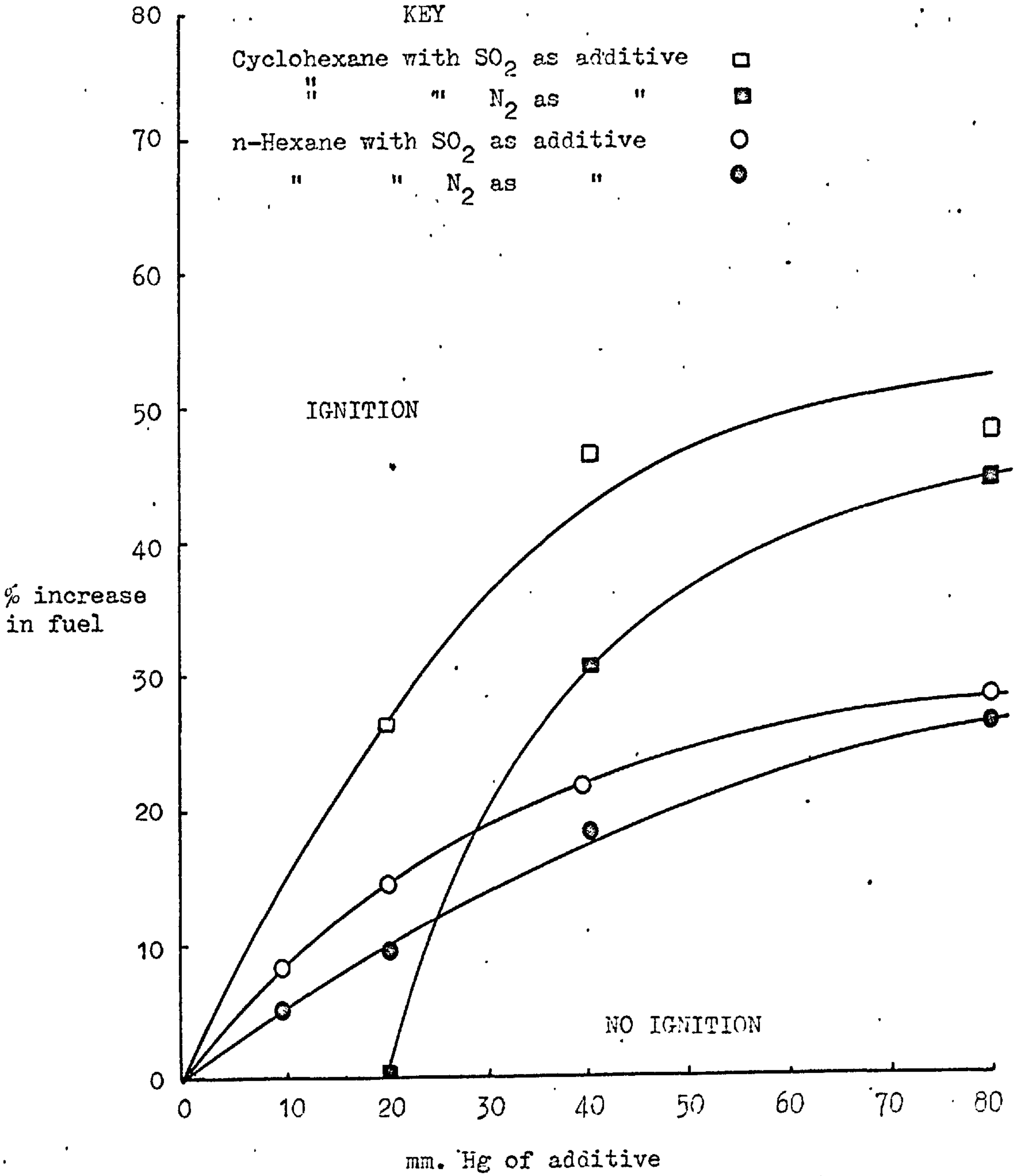
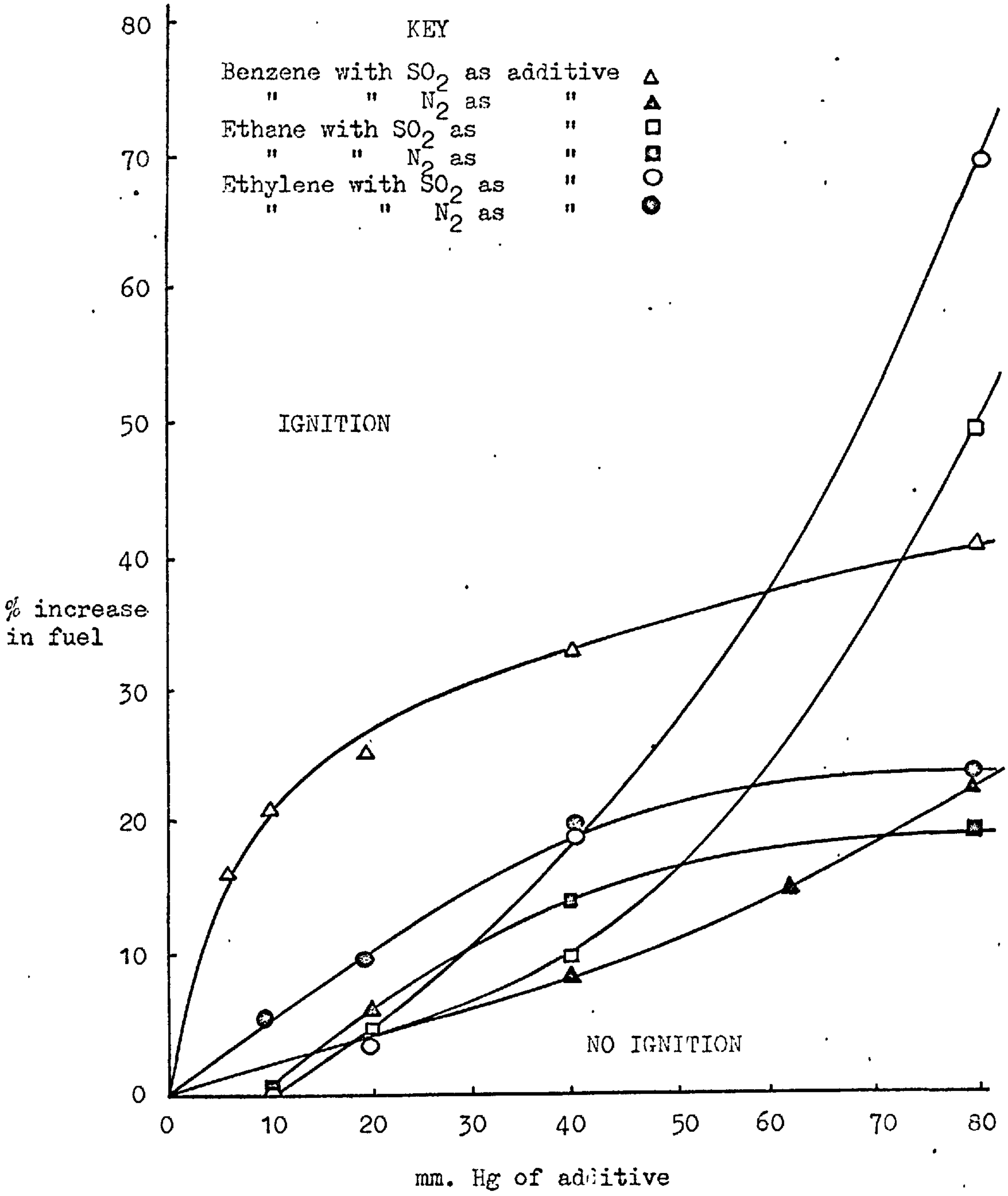


Figure 27

Graph of oxygen-rich ignition limit showing the % increase in the fuel required for various amounts of additive at 700°C.



DISCUSSION

DISCUSSION

CONTENTS

DISCUSSION

A Introduction

The initial experiments showed, as had been expected, that condensation of sulphur trioxide had to be prevented before the overall pressure change could be related directly to the extent of the reaction:

$$SO_2(\text{gas}) + \tfrac{1}{2}O_2(\text{gas}) \longrightarrow SO_3(\text{gas})$$

The reaction in the absence of added catalysts lent itself to study by means of pressure change measurements only over a narrow range of conditions. At low temperatures, the rate of reaction was undetectably low and at high temperatures, where the rate was measurable the equilibrium between sulphur dioxide and sulphur trioxide lay almost completely over on the side of the sulphur dioxide and so the total pressure change became very small. However it is the intermediate region where the reaction is moderately rapid, and there is a detectable quantity of sulphur trioxide produced, that is of particular interest in the study of sulphur trioxide formation in flue gases.

The study of the effect of oxidising species found in flue gases on the oxidation of sulphur dioxide was started with nitric oxide as this was known to have some catalytic effect on the reaction at lower temperatures. The addition of nitric oxide was indeed found to have a powerful catalytic influence, but the magnitude of its effect depended on the concentration of nitric oxide present. The other species studied were hydroxyl radicals from decomposing hydrogen peroxide and the species produced during the oxidation of carbon monoxide. Finally investigations were made of the effect of adding sulphur dioxide to oxidising organic fuels; oxygen-rich conditions were chosen for these experiments as these were thought to be most favourable for the oxidation of added sulphur dioxide, it being known[7] that no sulphur trioxide is produced in fuel-rich flames.

B Adsorption of sulphur trioxide

When a catalyst of vanadium pentoxide on pumice was used at 700°C, the accompanying pressure decrease corresponded to a much greater loss of sulphur dioxide than the predicted equilibrium value. On substitution of a platinum wire catalyst, however, the initial pressure drop corresponded to the predicted equilibrium value but a slow continuing pressure decrease was also observed. These results suggest that reaction products are being adsorbed slowly on to the walls of the apparatus, and in the case of the vanadium pentoxide catalyst, rapidly absorbed into the pores of the pumice. In agreement with this, any "extra" pressure decrease in the case of the platinum catalyst was found to disappear, when the vacuum line in contact with the reacting gases was heated to ca. 200°C. However, when it is considered that the vapour pressure of α- SO_3 (the least volatile form) is 73 mm. Hg at 25°C and 630 mm. Hg at 50°C, it would appear that the above observations can be explained by the presence of several mm. Hg pressure of water vapour leading to the condensation of sulphuric acid, the vapour pressure of which is ca. 2 mm. Hg at 100°C. This seems unlikely, however, as neither careful drying of the gases nor the deliberate addition of 2-3 mm. Hg water vapour had any large effect on this extra pressure decrease. This loss of sulphur dioxide occurred with both greased and greaseless taps at room temperature and was eliminated only by heating the line, inferring that the sulphur trioxide was being adsorbed onto the cool glass surfaces of the vacuum line. Similar losses of sulphur trioxide in contact with clean glass surfaces have been observed by other workers[31].

The loss of activity of platinum wire catalysts observed when ordinary silicone-greased taps were used in the heated section of the line did not recur when greaseless taps were used. No attempt was made to determine whether the poisoning of the platinum took place when the silicone grease was heated alone or only when it was heated in the presence of reaction products.

To overcome these condensation effects, all further experiments were carried out with the vacuum line in the region of the reaction vessel heated to 180°C and sealed with greaseless taps as illustrated in Figure 5. The rate of pressure loss due to condensation of sulphur trioxide under these conditions was ca. 0.005 mm. Hg/min. when several cm. Hg of sulphur trioxide were present and is likely to be even less at the start of a reaction when very little sulphur trioxide has been formed. All kinetic measurements were of initial reaction rates corresponding to pressure changes greater than 0.1 mm. Hg/min., so that the effect of condensation could be ignored.

C The reaction in the absence of added catalysts

The study of this reaction was limited to the temperature range 900-1035°C. Below 900°C the rate of reaction was too low for convenient measurement; calculation on the basis of the observed activation energy shows that in fact the rate of reaction for 200 mm. Hg sulphur dioxide and 200 mm. Hg oxygen would be less than 1 mm. Hg per day at 750°C. Above 1035°C the total pressure change became very small (ca. 12 mm. Hg) although the rate was quite large (ca. 3 mm. Hg min.$^{-1}$). Even within this range reliable rate measurements were difficult to make, and the results were not readily reproducible. Although it has been previously reported[30] that the oxidation of sulphur dioxide may be catalysed by silica, a four-fold increase in the surface to volume ratio did not have a significant effect on the rate of reaction. This result appears to show that the reaction observed is essentially homogeneous.

The rate of this reaction was not appreciably affected by the addition of inert gases so that the effects of changes in the sulphur dioxide and oxygen pressures can be directly attributed to changes in reactant concentrations. It can be seen from Figures 14 and 15 that the rate of the uncatalysed reaction is almost independent of the oxygen pressures and is approximately first order with respect to sulphur dioxide. The considerable scatter in the experimental results makes it difficult to draw more precise conclusions. However, the Arrhenius plot for an equimolar mixture of sulphur dioxide and oxygen (Figure 13) gives a straight line indicating that the activation energy, and hence presumably the rate-controlling step, does not change over the temperature range studied. The activation energy calculated from this slope is 80 kcal. mole^{-1}. The fact that the rate is considerably more dependent on the concentration of sulphur dioxide than on that of any other species present suggests that the rate-controlling step may well be, as at much higher temperatures, collisional activation of the sulphur dioxide molecule:

$$SO_2 + M \longrightarrow SO_2^* + M \, .$$

According to Gaydon[2] the theoretical activation energy of this process is 73.6 kcal. mole^{-1}. The experimental measurements give a value of 56 kcal. mole^{-1}, but this is attributed to lowering of the activation energy by contributions from the vibrational energy of the sulphur dioxide molecule. More recently, however, Levitt[59] has obtained an experimental value of 73.2 kcal. mole^{-1} for this activation energy when using a shock-heated mixture of sulphur dioxide and argon. Levitt[59] considers that the quenching step is probably

$$SO_2^* + M \longrightarrow SO_2 + M$$

which requires no activation energy, while Gaydon[2] considers the reaction

$$SO_2^* + SO_2 = SO + SO_3 + 25.6 \text{ kcal} \qquad \text{(A)}$$

to take place to an appreciable extent.

In the present system ($SO_2 = O_2 = 200$ mm. Hg at ca. 1200°K), where only sulphur dioxide and oxygen are present, the occurrence of reaction (A) seems probable as the only molecules available for deactivating the SO_2^* are sulphur dioxide and oxygen. This would lead to the reaction sequence:

$$\begin{array}{lcl} M + SO_2 & \longrightarrow & M + SO_2^* \\ SO_2 + SO_2^* & \longrightarrow & SO + SO_3 \\ SO + O_2 & \longrightarrow & SO_3 + 95 \text{ kcal}^{65}. \end{array}$$

Alternatively, if oxygen was the deactivating species, the following reactions could occur:

$$\begin{array}{lcl} M + SO_2 & \longrightarrow & M + SO_2^* \\ SO_2^* + O_2 & \longrightarrow & SO_3 + O \\ SO_2 + O & \longrightarrow & SO_3. \end{array}$$

Both these schemes would lead to the same overall reactions:

$$SO_2 + M \longrightarrow SO_2^* + M$$
$$SO_2^* + O_2 + SO_2 \longrightarrow 2SO_3$$

if the first step was rate-controlling. However, considering the observed irreproducibility, which is due largely to the small overall pressure change occurring, it is probably not justifiable to propose a more detailed reaction mechanism and an alternative experimental approach must be considered if this reaction is to be studied more fully.

D The reaction berween sulphur dioxide and oxygen in the presence of nitric oxide

1. Different regions

The experimental results show that the reaction in the presence of nitric oxide can be divided into two distinct regions with different kinetic characteristics: viz. the reaction at high nitric oxide concentrations where the rate of formation of sulphur trioxide is proportional to the second power of the nitric oxide concentration and to the first power of the oxygen concentration and the reaction at low concentrations of nitric oxide which is more complex and where the order with respect to nitric oxide is lower and variable, that with respect to oxygen is one and that with respect to sulphur dioxide is somewhat less than one.

In both regions it was observed that the addition of inert gases (Table 6) and a four-fold increase in surface:volume ratio had little influence on the rate of formation of sulphur dioxide indicating that the reactions concerned were truly homogeneous processes. This is in agreement with recent work by Shaw[53] who used a flow system for studying the reaction with low concentrations of sulphur dioxide and nitric oxide. He observed some catalysis by silica but found that this became insignificant when the concentration of nitric oxide was greater than 10^{-5} mole l^{-1}; this concentration was always exceeded in the present work, since it was not possible to obtain accurate rate measurements at lower concentrations of nitric oxide.

In order to confirm that nitric oxide was acting as a true catalyst and was not being extensively removed from the system, a sulphur dioxide + oxygen + nitric oxide mixture was allowed to equilibrate at 700°C for 1 hour and a further quantity of an equimolar mixture of sulphur dioxide and oxygen was then added. If allowance is made for the first-order dependence of the reaction rate on the oxygen concentration (Figure 21), the observed rate of reaction between the newly added gases is in good agreement with the predicted rate showing that at the most only 10% of the nitric oxide is removed from the system during the initial reaction period.

2. The reaction in the presence of high concentrations of nitric oxide

The kinetics of the reaction at high nitric oxide concentrations were strikingly similar to those for the oxidation of nitric oxide to nitrogen dioxide. The rate of formation of sulphur trioxide was independent of the sulphur dioxide concentration and was proportional to the first power of the oxygen concentration and to the second power of the nitric oxide concentration (Figure 17). The apparent activation energy was zero (Figure 28).

The probability that the reaction

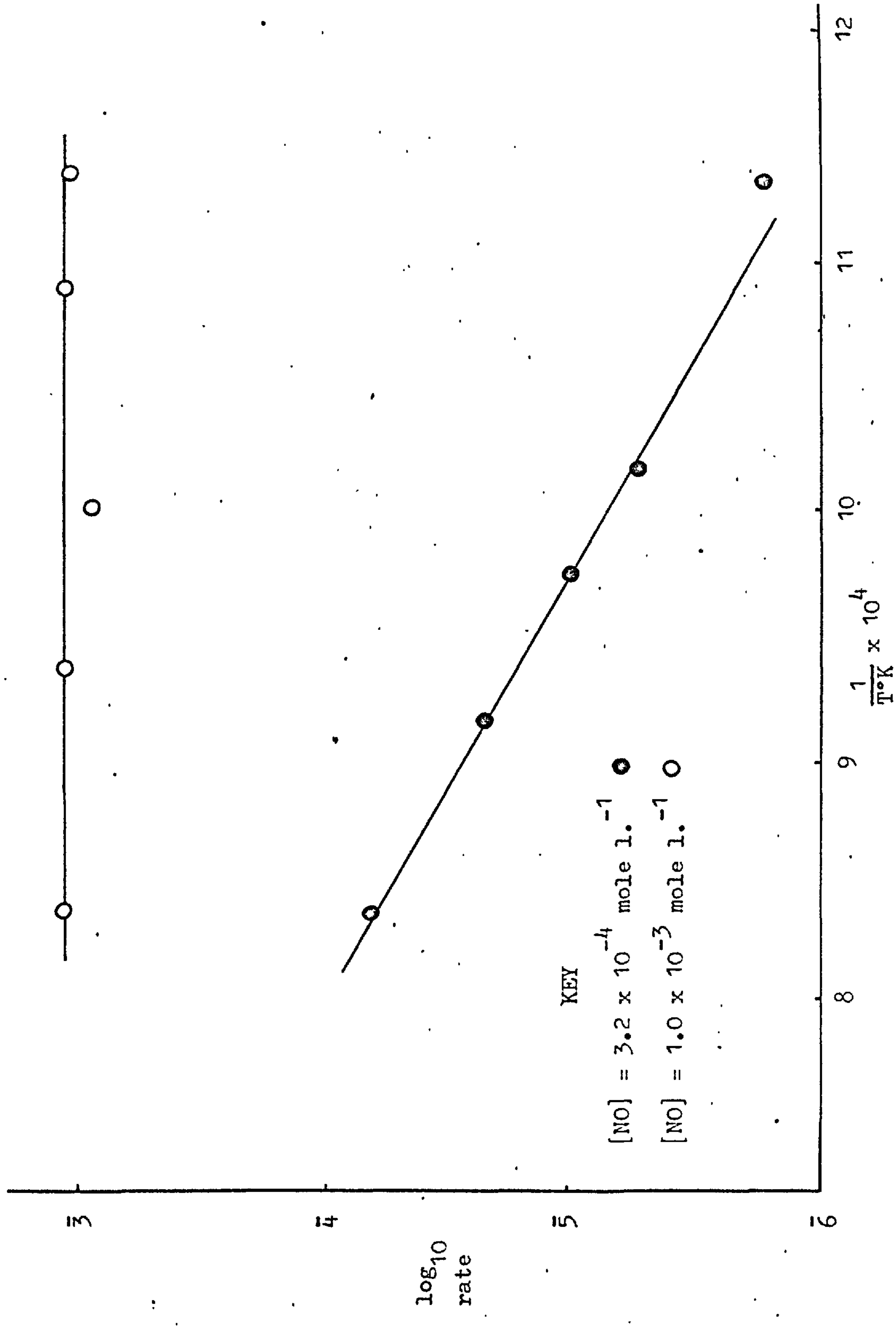
$$2NO + O_2 \longrightarrow 2NO_2$$

is the rate-controlling step is borne out by the agreement between the experimental values for the rate of formation of sulphur trioxide and the predicted values of the rate of formation of nitrogen dioxide. The value of the latter in a system containing for example 50 mm. Hg nitric oxide, 200 mm. Hg oxygen and 200 mm. Hg sulphur dioxide at 800°C can be calculated to be 1.32×10^{-8} mole l^{-1} sec $^{-1}$ from the rate constant $k_{2NO + O_2} = 8 \times 10^{9}$ cc.^{2} mole^{-2} sec.$^{-1}$ [35], this value being independent of temperature. The observed rate of formation of sulphur trioxide under these conditions was found to be 1.23×10^{-8} mole l^{-1} sec.$^{-1}$. The very good agreement between these two values shows that the formation of nitrogen dioxide must be the rate-controlling step in an overall

Figure 28

An Arrhenius plot for the reactions between sulphur dioxide and oxygen in the presence of nitric oxide.

($[SO_2]=[O_2]= 3.3 \times 10^{-3}$ mole $1.^{-1}$)



reaction sequence of the type:

$$2NO + O_2 \longrightarrow 2NO_2 \qquad (1)$$

$$NO_2 + SO_2 \rightleftharpoons SO_3 + NO . \qquad (2)$$

The possible intermediate equilibrium

$$NO + O_2 \rightleftharpoons NO_3$$

$$NO_3 + NO \longrightarrow 2NO_2$$

in the nitric oxide/nitrogen dioxide system will, under normal conditions, have no effect on the reaction as the second-stage is considered to be very fast.

Since experimental measurements have been made at the start of reactions where the concentrations of sulphur trioxide are low, it is possible to ignore any effect of the not inappreciable reverse reaction between nitrogen dioxide and sulphur trioxide reported by Reuben et al.[38].

Using the present apparatus it was found to be impossible to assess the importance of individual reaction steps. Thus it was not possible to determine whether the sulphur dioxide was oxidised directly by the nitrogen dioxide or if an intermediate decomposition of the nitrogen dioxide was involved e.g.

$$M + NO_2 \longrightarrow M + NO + O \qquad (3)$$

$$O + SO_2 \longrightarrow SO_3 . \qquad (4)$$

This course is, however, unlikely as it has been shown earlier that the rate of oxidation of sulphur dioxide was exactly the same as the rate of formation of nitrogen dioxide. It has been shown[41] that the reaction:

$$O + NO_2 \longrightarrow NO + O_2$$

is fast and hence would compete with reaction (4) causing a discrepancy between the rates of formation of nitrogen dioxide and sulphur trioxide.

3. The reaction in the presence of low concentrations of nitric oxide

When the concentration of nitric oxide is reduced to low values, the rate of reaction is no longer proportional to the square of the nitric oxide concentration. A comparison of reaction rates (Figure 29) does show, however, that the uncatalysed reaction makes no appreciable contribution to the rate of the reaction in the presence of nitric oxide.

Recent studies of the oxidation of nitric oxide[34,35,48] have shown that nitrogen trioxide can exist as an intermediate in the reaction i.e.

$$NO + O_2 \rightleftharpoons NO_3 \qquad (5)$$

$$NO + NO \longrightarrow 2NO_2 \qquad (6)$$

Under normal conditions, nitrogen trioxide should play no further part in the overall reaction, but when the concentration of nitric

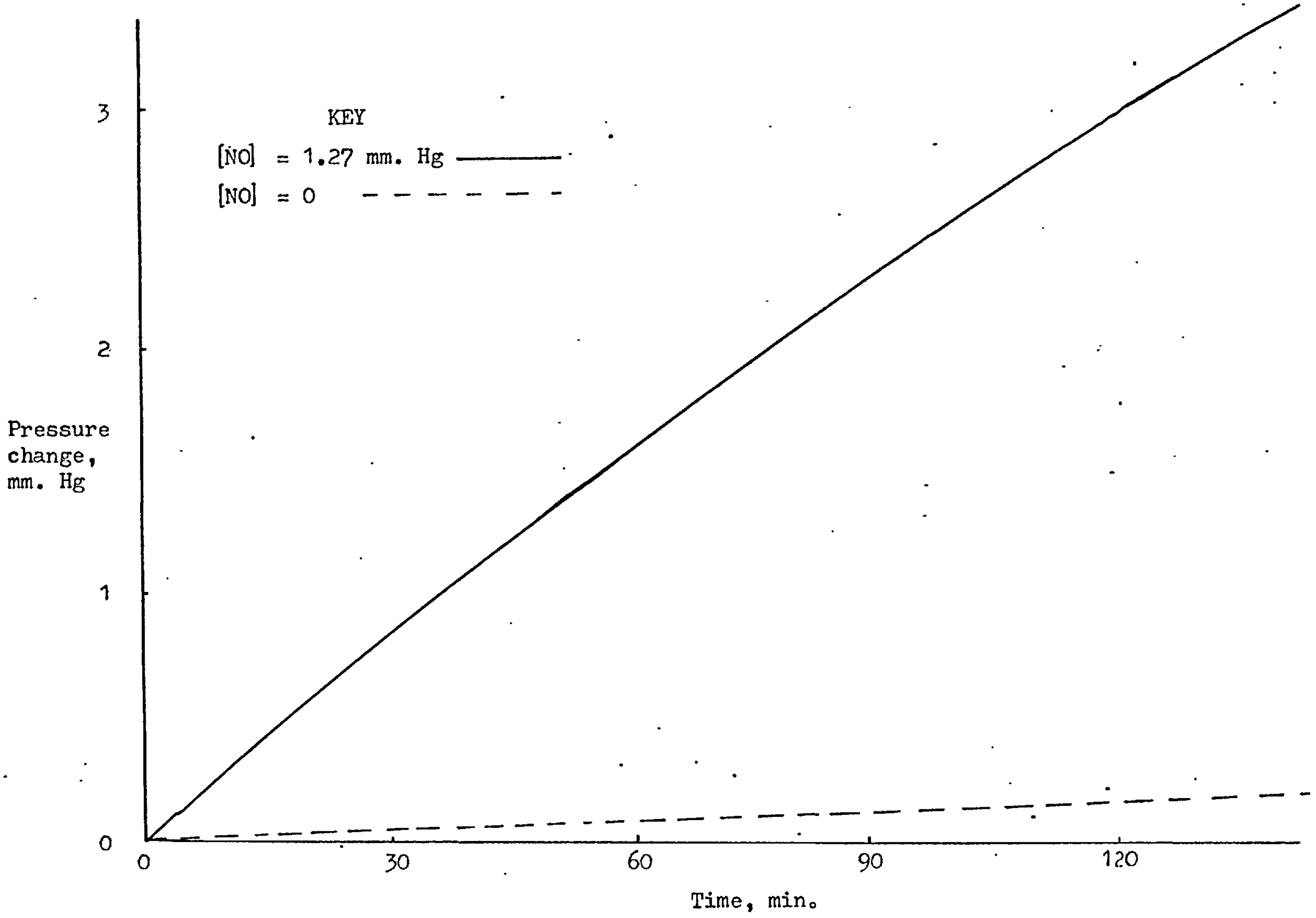


Figure 29

Comparison of the rates of reaction in the presence and absence of nitric oxide at 900°C. ($[SO_2]=[O_2]=$ 240 mm. Hg) oxide becomes low in comparison with that of other oxidisable species in the system (e.g. sulphur dioxide) competition for the nitrogen trioxide e.g.

$$NO_3 + SO_2 \longrightarrow NO_2 + SO_3 \qquad (7)$$

may become important.

Since the activation energies of reactions (5) and (6) are very low, reaction (7) will be expected to become important only at high temperatures and low nitric oxide concentrations, the very conditions under which the reaction deviates from the relatively simple kinetics found at high concentrations of nitric oxide. In this region the rate of reaction increases slightly with the sulphur dioxide concentration (Figure 22) and is proportional to the first power of the oxygen concentration. The order of the reaction with respect to nitric oxide decreases with decreasing nitric oxide concentration and with increasing temperature. A dependence of rate on the first power of the nitric oxide concentration can be identified under some conditions, although the order apparently drops to a variable and fractional value at very low concentrations of nitric oxide (Figure 17).

On the basis of the arguments above the following reaction scheme may be proposed:

$$NO + O_2 \rightleftharpoons NO_3 \qquad (5)$$

$$NO_3 + NO \longrightarrow 2NO_2 \qquad (6)$$

$$NO_2 + SO_2 \longrightarrow SO_3 + NO \qquad (2)$$

$$NO_3 + SO_2 \rightleftharpoons SO_3 + NO_2 \qquad (7)$$

the reaction between nitrogen dioxide and sulphur trioxide (-7) being ignored as all rate measurements were made at the beginning of the reaction when the concentration of sulphur trioxide is low.

Applying stationary state analysis, it is possible to write:

$$[NO_3] = \frac{k_{+5}\,[NO][O_2]}{k_{-5} + k_6\,[NO] + k_7\,[SO_2]}$$

$$[NO_2] = \frac{2k_6\,[NO_3][NO] + k_7\,[NO_3][SO_2]}{k_2\,[SO_2]}$$

and $-\dfrac{d[SO_2]}{dt}\left(\text{i.e. } \dfrac{d[SO_3]}{dt}\right) = k_2\,[NO_2][SO_2] + k_7\,[NO_3][SO_2]$.

On substitution of the above values for $[NO_3]$ and $[NO_2]$ into the equation for the rate of loss of sulphur dioxide $\left(-\dfrac{d[SO_2]}{dt}\right)$ we obtain:

$$-\frac{d[SO_2]}{dt} = \frac{k_{+5}\,[NO][O_2]}{k_{-5} + k_6\,[NO] + k_7\,[SO_2]}\,(2k_6\,[NO] + 2k_7\,[SO_2])$$

which on rearrangement gives:

$$-\frac{d[SO_2]}{dt} = 2k_{+5}\,[NO][O_2]\left(1 - \frac{k_{-5}}{k_{-5} + k_6\,[NO] + k_7\,[SO_2]}\right).$$

This equation gives an interpretation of the observed kinetic relationships that is in good agreement with the experimental results in the region where a first-order dependence of rate on nitric oxide concentration is found. Thus the experimental observation that the reaction rate increases slightly with sulphur dioxide concentration can be correlated with this equation, where, as $[SO_2]$ increases, the term

$$\frac{k_{-5}}{k_{-5} + k_6 [NO] + k_7 [SO_2]}$$

becomes smaller and the overall rate should tend towards the value

$$2k_{+5} [NO][O_2].$$

On the other hand the first order dependence of the rate on the concentrations of nitric oxide and oxygen is consistent with the fairly small influence of the term above at reasonably high $[SO_2]:[NO]$ ratios (i.e. $k_7 [SO_2]$is constant and much greater than $[NO]$). Similarly the fact that the transition from second order kinetics in nitric oxide to those of lower order takes place at increasingly high concentrations of nitric oxide as the temperature is raised is consistent with reaction (7) possessing an appreciably higher activation energy than reaction (6).

This may be contrasted with the observed second-order dependence of the rate on the concentration of nitric oxide that was found in the high nitric oxide concentration studies. In that region the pre-equilibrium

$$NO + O_2 \rightleftharpoons NO_3$$

was ignored as the ensuing reaction

$$NO_3 + NO \longrightarrow 2NO_2$$

is fast and has a low activation energy. However, when the nitric oxide concentation is very low, the competition for the nitrogen trioxide must be considered.

If the above mechanism correctly represents the course of the NO-catalysed oxidation of sulphur dioxide, then for a concentration of sulphur dioxide which is constant and large compared with that of nitric oxide, the equation reduces to

$$-\frac{d[SO_2]}{dt} = 2k_{+5}\,[NO][O_2].$$

It is then possible to calculate, for the region where this equation holds, an activation energy for the reaction:

$$NO + O_2 \rightleftharpoons NO_3 \, . \qquad (5)$$

Using the rate measurements shown in Figure 18, concentrations of nitric oxide, sulphur dioxide and oxygen of 3.2×10^{-4} mole l^{-1}, 3.3×10^{-3} mole l^{-1} and 3.3×10^{-3} mole l^{-1} respectively and temperatures from 800 to 900°C a value of E_{+5} may be obtained ($E_{+5} = 27.8$ kcal.mole^{-1}). The Arrhenius plot is shown in Figure 28, and it is interesting to note the deviation from a straight line at low temperatures, where the rate of reaction (6) is of about the same magnitude as that of reaction (5).

E The oxidation of sulphur dioxide in the presence of other oxidising species

1. Introduction

The NO-catalysed oxidation of sulphur dioxide has been shown to involve a redox cycle of the type

$$2NO + O_2 \longrightarrow 2NO_2$$
$$NO_2 + SO_2 \longrightarrow SO_3 + NO \ .$$

It is possible of course that such oxidation may be brought about by oxygen atoms produced by the action of nitric oxide on molecular oxygen

$$NO + O_2 \longrightarrow NO_2 + O$$
$$NO_2 \longrightarrow NO + O \ .$$

The oxidation of carbon monoxide also probably involves oxygen atoms and it was therefore thought of interest to study the oxidation of sulphur dioxide in the presence of oxidising carbon monoxide

$$2CO + O_2 \longrightarrow 2CO_2$$
$$CO_2 + SO_2 \longrightarrow CO + SO_3 \ .$$

In addition, other oxygen-containing species may be able to oxidise sulphur dioxide. Obvious examples include free radicals of the type

O_nH_m and also, in view of the fact that sulphur dioxide undergoes appreciable oxidation in the presence of flue gases, oxygenated free radicals produced by the combustion of organic fuels.

Several series of experiments have been carried out, therefore, on the fate of sulphur dioxide in systems involving such species. Attention has been focussed on some comparative kinetic parameters (e.g. explosion limits of organic fuels in the presence and absence of sulphur dioxide) and on the extent of conversion of sulphur dioxide to trioxide in such systems.

2. The oxidation of sulphur dioxide in the presence of decomposing hydrogen peroxide

As mentioned earlier the silica reaction vessel was pre-washed with 40% hydrofluoric acid since it has been shown[53] that an acidic vitreous surface has the least catalytic effect on the heterogeneous decomposition of hydrogen peroxide vapour. Under the conditions used, therefore, the breakdown of hydrogen peroxide should take place almost entirely homogeneously to give hydroxyl radicals[53]. According to Hoare et al.[53], the half life of hydrogen peroxide at the temperature of the reaction vessel (450°C) is ca. 3 sec..

It was observed that, if the reaction mixture of hydrogen peroxide vapour and sulphur dioxide, with or without oxygen, was allowed to stand in the pre-mix vessel at 50°C, a loss of sulphur dioxide occurred.

This effect was detected by a fall in pressure and was confirmed by chemical analysis (Table 7). This has been attributed to the reaction

$$H_2O_2 + SO_2 \longrightarrow H_2SO_4$$

which may initially occur on the walls of the pre-mix vessel, but which will take place also in the condensed phase as soon as sufficient sulphuric acid is present.

However, only a small fraction ($\sim$5%) of the sulphur dioxide was lost during the first minute in the pre-mix vessel (Table 7), and any error due to this cause was minimised by transferring the gases to the reaction vessel within this period of time.

No loss of sulphur dioxide occurred when the gases were admitted to the hot reaction vessel at 450°C; this suggests that hydroxyl radicals undergo no appreciable reaction with sulphur dioxide at this temperature.

3. The oxidation of sulphur dioxide in the presence of oxidising carbon monoxide.

Carbon monoxide was oxidised with excess oxygen at 700°C and at 900°C in the presence of small quantities of sulphur dioxide. No loss of sulphur dioxide was detected. The carbon dioxide:carbon monoxide ratio was checked by gas-chromatogrphy when oxidation was sensibly complete. These observations are in agreement with those of Tipper and Williams[25], who observed that sulphur dioxide inhibited the explosive oxidation of carbon monoxide although no consumption of sulphur dioxide could be detected. Sulphur dioxide apparently acts as an efficient "energy sink" for some species in the oxidation chain, probably carbon dioxide[60]. The transfer of energy is not sufficient, however, to lead to a reaction sequence of the type:

$$CO_2^* + SO_2 \longrightarrow CO_2 + SO_2^*$$
$$SO_2^* + O_2 \longrightarrow SO_3 + O$$

even though these reactions have been postulated as the main route for the oxidation of sulphur dioxide in flue gases[60].

4. The oxidation of sulphur dioxide in the presence of oxidising organic compounds

The effect of sulphur dioxide on the oxidation of organic compounds has been studied both by comparison of the conversions of sulphur dioxide to trioxide in individual systems and by observation of the effect of sulphur dioxide on the explosion limits of fuel-oxygen systems. In the first case, although some oxidation of sulphur dioxide was observed, no direct correlation was found between the amount of fuel oxidised and the conversion of sulphur dioxide. Individual measurements are reported in Tables 8,9,10 and 11. In the case of ethanol, nitric oxide was also added, but in this case the oxidation of sulphur dioxide was adequately described by the kinetic parameters discussed in section D2 and no additional effect was observed due to the presence of ethanol.

On the other hand, the presence of sulphur dioxide appeared to have a very real effect on explosion limits. Thus, for an ignition to occur in an oxygen-rich system (i.e. a system containing the minimum quantity of fuel for an ignition), it was found that more fuel had to be added to a given quantity of oxygen when sulphur dioxide (or nitrogen) was present. When acetone, acetylene, n-hexane or cyclohexane was the fuel, the effect of a given pressure of sulphur dioxide was slightly greater than that of an equal pressure of nitrogen, but when benzene was the fuel the effect of the sulphur dioxide was much greater. However, for ethane and ethylene small pressures of sulphur dioxide had slightly less effect than equal pressures of nitrogen, while large pressures of sulphur dioxide had a much larger inhibiting effect than the same pressures of nitrogen. (Table 12 and Figures 25-27).

It is to be expected that sulphur dioxide would be a more efficient explosion inhibitor than nitrogen as it is a larger molecule with more ability to absorb energy and hence deactivate chain-carriers. There is also the possibility of a rapid reaction between sulphur dioxide and oxygen atoms acting as a chain terminating step, although measurements of sulphur trioxide concentrations indicate, as expected, that such reactions are not important.

However it was also observed that the inhibiting power of a small quantity of sulphur dioxide depended on the nature of the fuel.

Thus, if the effect of sulphur dioxide on the explosion limit is expressed in terms of the increase in fuel concentration needed to re-establish explosive conditions, then a plot of this percentage increase against the number of carbon-carbon bonds in the molecule of the organic fuel, presents an almost straight line (Figure 30) On the other hand, no correlation could be observed with such factors as percentage unsaturation in the fuel molecule.

The inhibiting effect of nitrogen and sulphur dioxide is contrary to observations in fuel-rich systems[61] where Burgoyne has found that the addition of nitrogen lowers the ignition pressure for fuel-rich mixtures of benzene and oxygen.

Studies of the mechanism of oxidation of organic gases have usually been carried out under stochiometric or fuel-rich conditions to enable partially oxidised intermediates to be isolated[62,63]. In such cases the initial attack usually consists in the removal of a hydrogen atom to give an organic radical[62,63]

$$RH + X \longrightarrow R + XH \qquad \text{(where X is oxygen or an oxygenated radical)}$$

$$R + O_2 \longrightarrow RO_2$$

$$RO_2 \longrightarrow CO \text{ and other products.}$$

On the other hand in the case of benzene it has been suggested that hydroxylation occurs since phenolic intermediates can be detected[64].

However before rapid degradative oxidation can occur, fission of

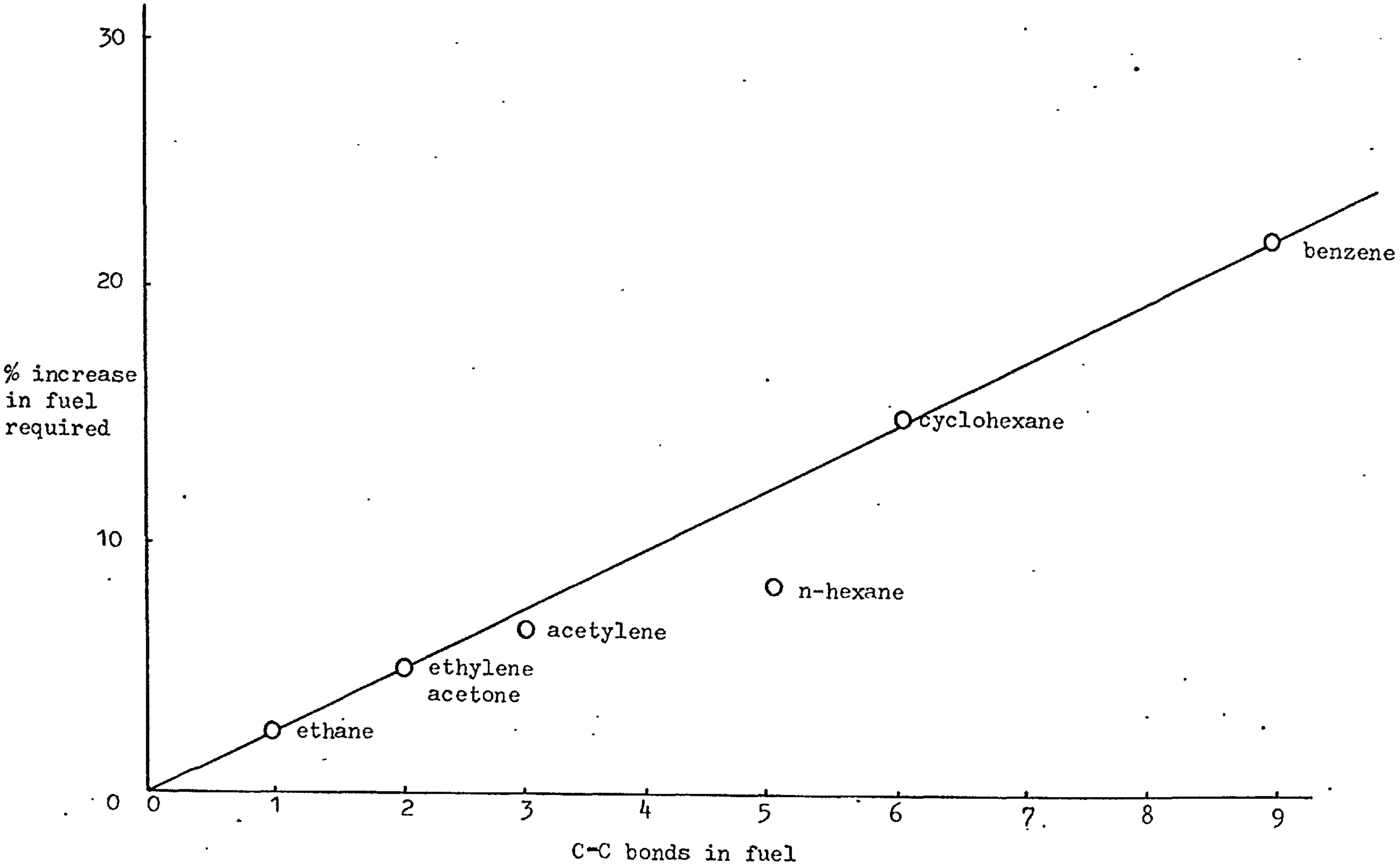


Figure 30

A plot of the initial slopes from figures 25, 26 and 27 versus the number of carbon-carbon bonds in the fuel.

the carbon-carbon bonds is essential and it would appear that sulphur dioxide is, in some way, capable of protecting these bonds.

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