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NO_x ABSORPTION RATE STUDIES IN SODIUM HYDROXIDE SOLUTION

K. Ofose-Asiedu, U.S.T. Kumase, Ghana and
S.H. Wu, Sino-Arab Chemical Fertilizer Co. Ltd, China

ABSTRACT

The kinetics of absorption of NO₂/N₂O₄ and of NO/NO₂/N₂O₃ from nitrogen diluent gas into 0.5 and 1.0 sodium hydroxide solutions at 25°C have been studied experimentally.

In those trials with NO₂ concentrations greater than 2×10^{-7} gmol/cm³ (4500 p.p.m), nitric oxide was observed to appear in the exit gas stream which suggests there may be an acidic layer present at the liquid surface.

The absorption rate of NO₂ at these concentrations is proportional to the square of the NO₂ gas concentration confirming that N₂O₄ is the main dissolving and reacting species.

A linear plot of $3 \times \text{NO}$ formed against NO₂ absorbed indicates that virtually all the nitrous acid HNO₂ by N₂O₄ hydrolysis decomposes to nitric oxide and nitric acid which is strong evidence for the presence of an acidic liquid surface layer in the absorber.

The absorption rate constant $H\sqrt{KD}$ for first order irreversible hydrolysis of N₂O₄ was found to be 0.136 m/s at 25°C which is significantly larger than values observed by previous researchers.

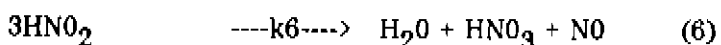
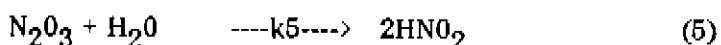
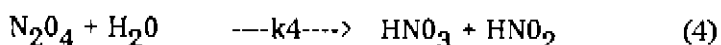
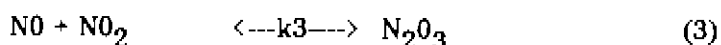
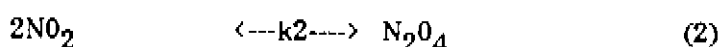
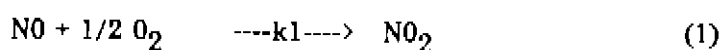
The absorption rate constant assuming first order irreversible dissolution and hydrolysis of N₂O₃ at 25°C was found to be 2.71 m/s for $(H\sqrt{KD})$ N₂O₃. Komiyama (1982) reported a value of 2.35 m/s at 15°C.

INTRODUCTION

In the absorption of gaseous nitrogen oxides by sodium hydroxide solution, three process mechanisms are believed to be involved :

- a) Gas-phase equilibrium reactions;
- b) NO_x absorption mechanism; and
- c) Utilization of the hydroxyl ions.

The gas-phase equilibrium reactions of interest when oxides of nitrogen are mixed in the presence of water vapour and oxygen are :



Reaction 1 has been extensively studied, (Bodenstein, 1918), and the rate constant is given by :

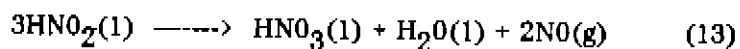
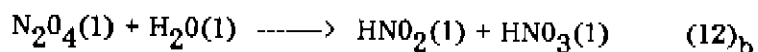
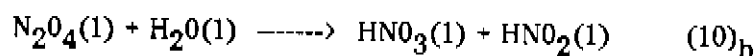
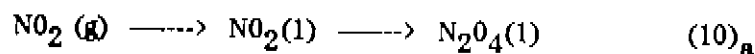
$$k_1 = 2.17 \times 10^{-11} \exp \left(\frac{1399}{T} \right) \text{ m}^4 \text{ N}^{-2} \text{ s}^{-1}$$

Equilibrium constants for reactions 2 and 3 are taken from the literature, (Verhoek & Daniels, 1931; Beattie & Bell, 1947; Horftlizer & Kwanten, 1964), and their respective values are given as follows :

$$k_2 = 6.98 \times 10^{-15} \exp \left(\frac{6866}{T} \right) \text{ m}^2 \text{ N}^{-1}$$

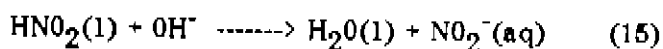
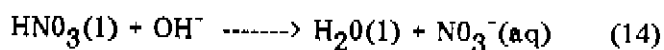
$$k_3 = 6.53 \times 10^{-13} \exp \left(\frac{4740}{T} \right) \text{ m}^2 \text{ N}^{-1}$$

Since nitric oxide is almost insoluble in water, only three absorption reactions involving three major species: NO_2 , N_2O_3 and N_2O_4 , occur simultaneously in the liquid film. These absorption reactions are represented as follows :



Reactions 11 and 12 are believed to be very fast while reaction 10 is considered to be a relatively slow reaction (Andrew & Hanson, 1961; Chambers & Sherwood, 1937; Dekker et al, 1959; Komiyama & Inoue, 1978; Wendel & Pigford, 1958).

The nitric and the nitrous acids produced in reactions 10 to 12 react with the hydroxyl ions in the bulk liquid phase to form nitrate and nitrite ions :



In addition, there is a possibility that the nitrous acid produced decomposes to give nitric oxide viz reaction 13 (Andrew & Hanson, 1961; Chambers & Sherwood, 1937; Komiyama & Inoue, 1978).

The purpose of this study is to evaluate the mechanism of the absorption process and evaluate the NOx absorption rate parameters which will allow more representation model equations to describe the complete NOx absorption process.

EXPERIMENTAL PROGRAM AND RESULTS

The absorption rate measurements were made using a planar disc surface diffusion cell under the conditions specified below, and the equipment used for the absorption study is shown in Figure 1.

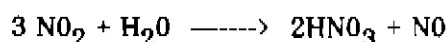
Cell diameter	10.5 cm
Liquid surface area	86.6 cm ²
Liquid temperature	25°C
Feed gas flow rate	1000 ccs/min
Liquid film coefficient	3.9 x 10 ⁻³ cm/s
Gas agitator speed	375 r.p.m
Gas film coefficient	6.5 x 10 ⁻⁶ gmol/(cm ² atmos s)

Initially 20 trials were carried out using nitrogen oxide gas straight from the NO₂ supply bottle diluted with nitrogen.

It was not immediately appreciated that NO was appearing during the absorption runs and only the total nitrogen oxides NOx absorption rate was being measured. This gave a curved data plot in Figure 2. It was later realised that it is necessary to monitor separately the concentrations of NO₂ and NO species as the gas flows through the cell.

A further 16 trials were carried out observing both NO₂ and NO concentrations entering and leaving the absorber. The observed absorption rate of NO₂ species is plotted against the exit NO₂ gas concentration in Figure 3. Some difficulty was experienced in getting steady reproducible concentrations at the bottom of the range <250 ppm and gas analysis by mass spectrometry will be required for accurate investigation at lower concentrations.

Figure 4 shows a plot of NO₂ absorbed against three times the observed formation of NO which appears to confirm the following equation.



Finally a set of 18 trials was carried out with various mixtures of NO and NO₂ in nitrogen most of the NO to NO₂ ratios being less than one.

A plot of the rate of NO₂ absorption against the product of the outlet NO and NO₂ concentrations is shown in Figure 5. All the points fall on or above a straight line having a slope of unity which appears to confirm that the main absorbing species is N₂O₃ for points on or near the line. Points falling above the line are thought to have a substantial contribution due to N₂O₄ absorption.

DISCUSSION

Komiyama (1980) published a mathematical model and solution predicting the rate of absorption of NO₂/N₂O₄ into alkaline solutions based on the steady state film theory for absorption with chemical reaction.

At high concentrations of NO₂ (>10⁻⁸ gmole/cm³, 224 ppm) the main species dissolving and reacting is assumed to be N₂O₄. The rate of absorption with rapid first order irreversible reaction is predicted by the expression.

$$R_{N_2O_4} = H\sqrt{KD}(N_2O_4)_g$$

In this concentration range there is also likely to be significant gas film resistance so that $(N_2O_4)_g$ should be changed to the gas concentration at the liquid surface.

At NO_2 concentrations less than 10^{-8} gmole/cc and with relatively low liquid film mass transfer coefficients the primary dissolving species is assumed to be NO_2 which dissolves, diffuses and dimerizes to N_2O_4 which then hydrolyses within the liquid film.

The absorption rate is given by the expression,

$$R_{NO_2} = 2\sqrt{\frac{k}{3} H_{N_2O_4} K_c D_{NO_2}} H_{NO_2}^{0.5} (NO_2)_g^{1.5}$$

Where K_c is the gas phase equilibrium constant

$$K_c = \frac{(N_2O_4)_g}{(NO_2)_g} \text{ (m}^3/\text{gmol)}$$

K is the first order hydrolysis rate constant for N_2O_4 (sec^{-1})

At low concentrations of NO_2 ($<10^{-9}$ gmol/cm³, 22ppm) or with high liquid film coefficients the main dissolving species is NO_2 which physically diffuses into the bulk of the liquid phase where it is assumed to dimerize and undergo hydrolysis,

$$R_{NO_2} = H_{NO_2} K_L (NO_2)_g$$

Physical mass transfer by molecular diffusion is controlling. Log plots of rate against concentration for each of the three mechanisms will show straight lines having increasing slopes at increasing concentrations of $(NO_2)_g$.

Komiyama's rate data covers the complete range of absorption mechanisms down to 2×10^{-10} gmol/cm³ (5 ppm) and appears to enable good estimates of the model parameters to be made.

Using appropriate data points taken from Komiyama's absorption rate measurements with the correct value of K_c at 15°C reported by Verhoek and Daniels ($0.406 \text{ m}^3/\text{gmol}$) the following parameter values have been estimated :

$$\begin{aligned} H_{NO_2} &= 0.556 \\ D_{N_2O_4} &= 0.9 \times 10^{-9} \text{ m}^2/\text{s} \\ H_{N_2O_4} &= 50.7 \\ D_{NO_2} &= 1.0 \times 10^{-9} \text{ m}^2/\text{s} \\ K_{N_2O_4} &= 1640 \text{ s}^{-1} \\ H\sqrt{KD} &= 0.062 \text{ m/s} \end{aligned}$$

Komiyama used $K_c = 0.486 \text{ m}^3/\text{gmol}$ and obtained the following parameter values at 15°C :

$$\begin{aligned} H_{NO} &= 0.556 \\ D_{N_2O_4} &= 0.9 \times 10^{-9} \text{ m}^2/\text{s} \\ H_{N_2O_4} &= 48.2 \end{aligned}$$

$$D_{\text{NO}_2} = 1.0 \times 10^{-9} \text{ m}^2/\text{s}$$

$$K_{\text{N}_2\text{O}_4} = 554 \text{ s}^{-1}$$

$$H/\sqrt{KD} = 0.034 \text{ m/s}$$

The difference between the two sets of values is not entirely explained by the differing values of K_c employed and it would appear that there is some other explanation. The Komiyama parameters reported above will predict conservatively low rates of absorption.

Komiyama has not reported absorption rate data for NO/NO_2 mixtures in nitrogen at low concentrations $<10^{-7} \text{ gmole/cm}^3 \text{ NO}_x$ (2000 ppm) and with various liquid film mass transfer coefficients. This data is relevant to predicting the back end performance of alkali absorption towers where the NO to NO_2 ratio could be greater than unity.

In the present study, the absorption rate constant for NO/NO_2 mixtures at 25°C (i.e. H/\sqrt{KD} for N_2O_3 dissolving and hydrolysing) is 2.71 m/s which is slightly greater than Komiyama's reported value of 2.55 m/s at 15°C . This suggests that the hydrolysis rate constant k may be substantially increased by the 10 degree temperature rise.

CONCLUSIONS AND RECOMMENDATIONS

1. The absorption of pure NO_2 from nitrogen into 0.5M alkaline solutions has been studied and the absorption rate constant at 25°C has been measured (0.136 m/s). This is significantly higher than the rate constants observed for absorption into water and acid solutions reported by previous workers.
2. At the higher concentration range ($> 4500 \text{ ppm}$) the absorption of $\text{NO}_2/\text{N}_2\text{O}_4$ appears to be accompanied by evolution of NO which reduced the overall rate of absorption of nitrogen oxides as compared with absorption in the absence of NO evolution.
3. The observed rates of $\text{NO}_2/\text{N}_2\text{O}_4$ absorption at 25°C are in close agreement with those observed by Komiyama at 15°C .
4. Absorption of various ratios and concentrations of NO/NO_2 mixtures resulted in absorption of both species taking place but with NO_2 absorption being much greater than NO absorption suggesting that N_2O_3 absorption is being suppressed. Under none of the conditions was the N_2O_4 absorption mechanism suppressed by the N_2O_3 mechanism. In general the rate of absorption of NO_2 was increased by the presence of NO however the highest rates of NO_x absorption were obtained with low ratios of NO to NO_2 . Study of the detailed results for NO/NO_2 mixture absorption suggests the absorption of N_2O_4 is not suppressed by the presence of NO since equimolar absorption rates of NO and NO_2 were not observed.

At low ratios of NO to NO_2 (<0.5) the N_2O_3 absorption mechanism did not appear to operate as evidence by the NO_2 absorption rates falling on the absorption rate curve established for $\text{NO}_2/\text{N}_2\text{O}_4$ see Figure 6. In addition the NO concentration was observed to be either unchanged or increased in passing through the absorption cell.

The existence of an acidic layer at the liquid surface could lead to reduced efficiency of CO_2 co-absorption. However the presence of such a layer seems less probable in the presence of low concentration nitrogen oxides present near the back end of an absorption system.

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NOMENCLATURE

- D_i Liquid phase diffusivity of species i , m/s
 H_i Henry's law constant of species i dimensionless
 (equal to $\frac{\text{liquid phase concentration}}{\text{gas phase concentration}}$ at equilibrium
 K_j First order hydrolysis reaction rate constant, 1/s
 K_L Liquid film mass transfer coefficient, m/s
 K_j Gas phase equilibrium constant, m²/gmol
 R Rate of absorption per unit interfacial area, gmol/m³s
 $(NO_x)_g$ Gas phase concentration of NO_x species, gmol/m³

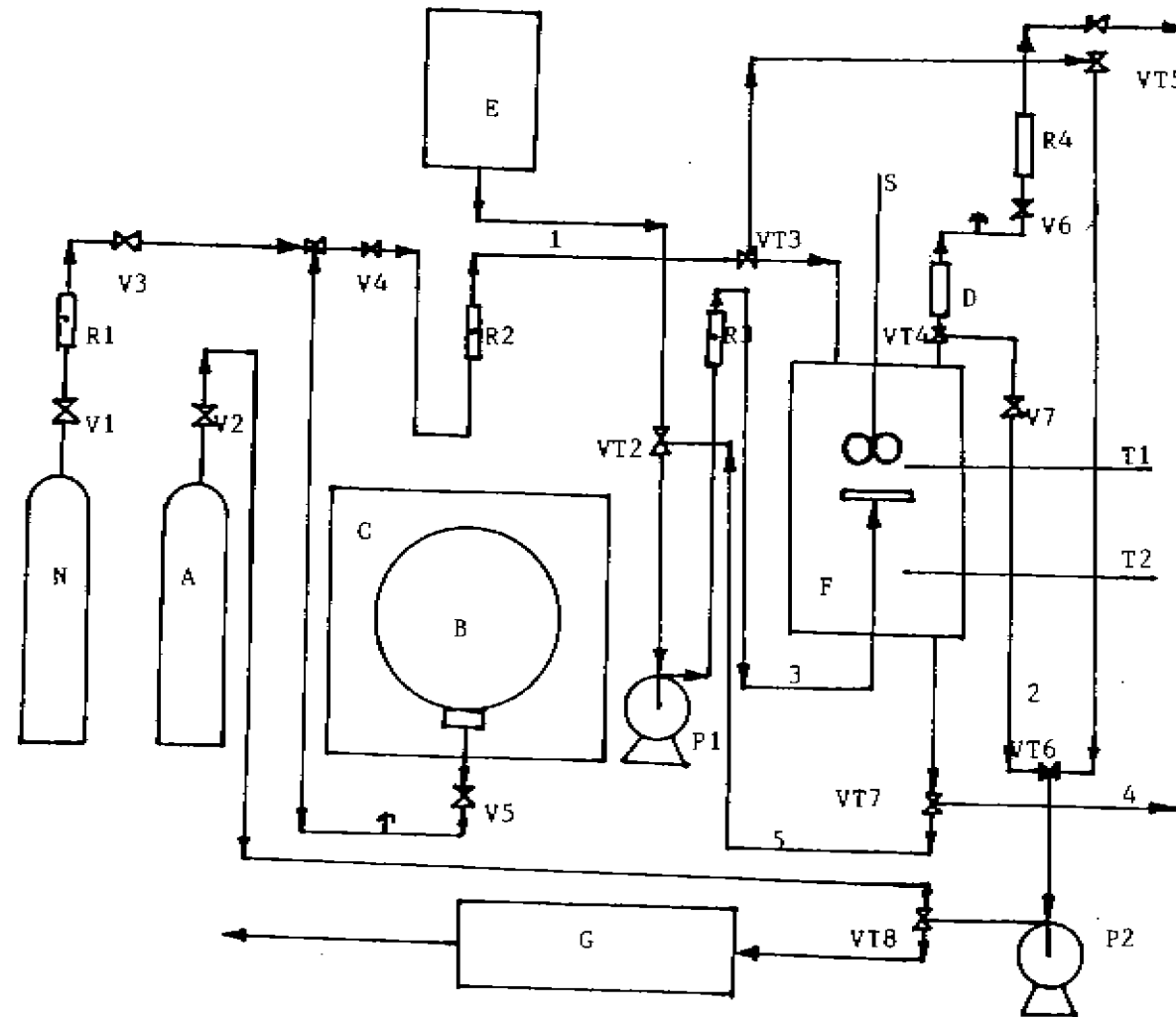


FIG.1 . Schematic diagram of the experimental apparatus.

N : Nitrogen cylinder, A : NO cylinder, B : Black PVC mixing bag, C: Encloser barrel

D : Dryer, E: NaOH storage tank, F: Absorber, G : KNOX analyser, S: stirrer, R : Rotameter,
V : valve, VT: 3-way valve, P: pump and T : thermocouple.

I : inlet gas stream, 2: outlet gas stream, 3: liquid inlet stream, 4: liquid outlet
stream, 5 : liquid recirculate stream

Fig 2 Preliminary experimental runs with unknown mixtures of NO₂ and NO (NO_x) absorbing in 0.5M NaOH solution at 298°K

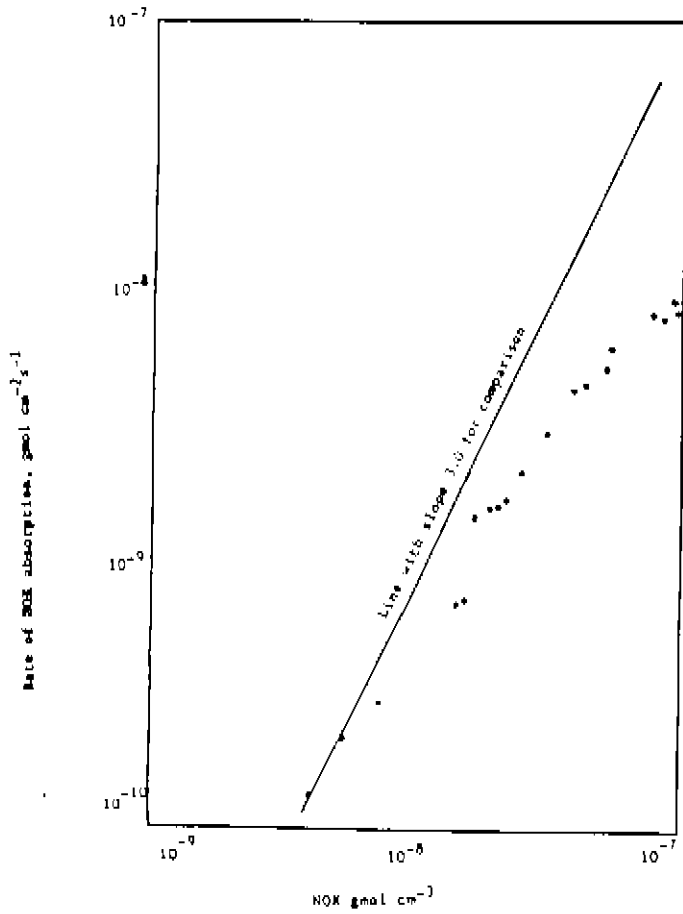


Fig 3 Graph of the rate of absorption of NO₂ - N₂ mixture by 0.5M NaOH solution at 298°K

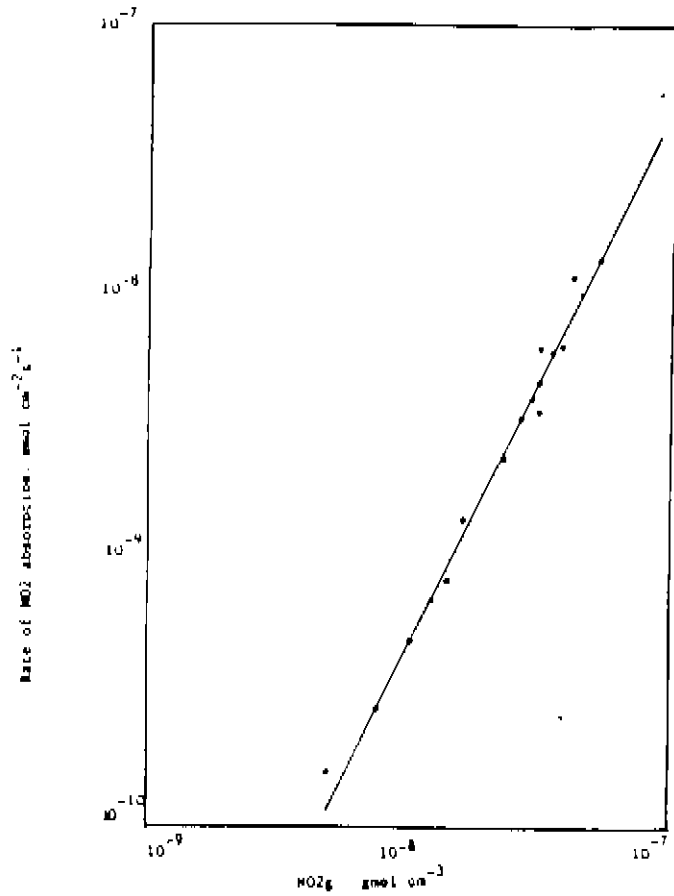


Fig 4 Graph of concentration change of NO₂ by absorption against required change in NO₂ concentration to form NO as observed from trials on NO₂ - N₂ absorption into 0.5 NaOH solution at 298°K () trial numbers shown against each data point.

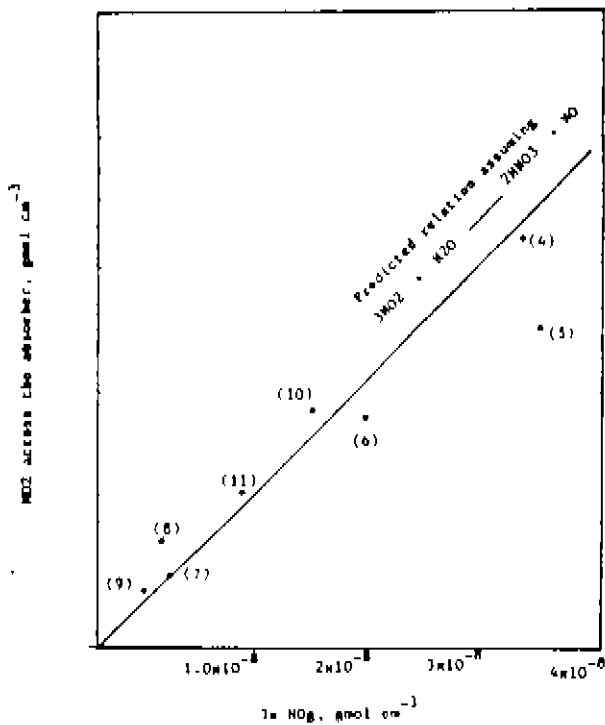


Fig 5 Graph of Rate of absorption of NO₂ from various mixtures of NO₂ and NO in nitrogen into 0.5M NaOH solution at 298°K.

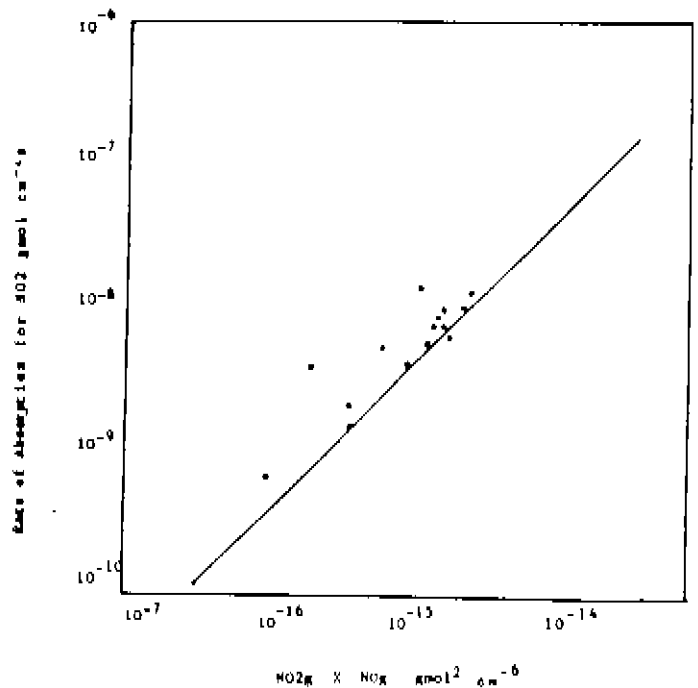


Fig . 6 Rate of absorption of NO₂ against NO₂g for
absorption from NO₂ and NO into 0.5M NaOH solution at 298°K

