

DEPOSITION OF NITROGEN OXIDES TO THE NORTH SEA

Interim report to the Commission of the
European Communities

ITE Project T07057k5
CEC Contract STEP-0003-C(GDF)

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June 1991

SUMMARY

The reaction of nitrogen dioxide with water has been studied using gas-phase measurements of nitrogen dioxide after passing air containing 10-50 ppbV NO₂ through a reaction vessel.

Measurements with distilled or deionised water gave a second-order rate constant of $8.5 \times 10^3 \text{ Ms}^{-1}\text{atm}^{-2}$ at 9.5°C, in good agreement with the temperature-corrected published value of $8.9 \times 10^3 \text{ Ms}^{-1} \text{ atm}^{-2}$.

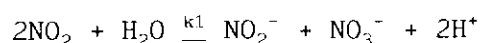
Measurements on sea-water showed an additional first-order reaction, with rate constant $4.4 \times 10^{-4} \text{ Ms}^{-1}\text{atm}^{-1}$ at 9.5°C. Below 15 ppbV NO₂ the reaction of NO₂ by this first-order pathway is more rapid than by the second-order reaction with pure water.

These results imply greater deposition rates for NO₂ to sea-water at low ppbV concentrations than previously estimated from consideration of the second-order reaction alone.

INTRODUCTION

The removal of gases from the atmosphere at the surface of the sea is controlled both by gas phase mass transfer to the sea surface, and by subsequent dissolution of the gases in sea-water. Laboratory kinetic studies of the reactive dissolution of NO_2 in pure water, at concentrations close to those observed in non-urban air (> 10 ppbV), have suggested that dissolution of NO_2 at these concentrations would be slow compared with the rate of gas-phase transfer, and that uptake would be determined by aqueous phase transport and/or reaction, with deposition velocity around 10^{-5} m s^{-1} (Lee & Schwartz, 1981). The rate-determining step is the rate of uptake of NO_2 by sea-water, so it is important to know whether reactions of NO_2 with dissolved materials, or with surface layers, would enhance deposition rates above those calculated for simple dissolution.

The reaction of NO_2 with pure water at concentrations ~ 10 ppbV has been shown to be slow relative to diffusion or convective transport of unreacted NO_2 in solution [designated $\text{NO}_2(\text{aq})$]. In this phase-mixed limit, the forward reaction:



is second-order in $\text{NO}_2(\text{g})$ and $\text{NO}_2(\text{aq})$,

$$\text{i.e.} \quad k_1 = k [\text{NO}_2(\text{aq})]^2 = k^1 [p_{\text{NO}_2}]^2$$

$$\text{where} \quad k^1 = k(H_{\text{NO}_2})^2$$

and H_{NO_2} is the Henry's Law equilibrium constant for NO_2 between air and water, i.e.

$$H_{\text{NO}_2} = \frac{(\text{NO}_2)_{\text{aq}}}{p_{\text{NO}_2}}$$

At concentrations above ~ 100 ppbV NO_2 , this simple relationship breaks down, partly because the dimerisation of NO_2 to N_2O_4 becomes significant, thereby altering aqueous phase diffusion, and because the forward reaction becomes fast relative to convective mixing.

The rate of reaction between NO_2 and water has usually been investigated at much larger gas-phase concentrations than are found in the marine atmosphere. Experiments on the kinetics of this reaction have been reviewed in detail by Schwartz & White (1983). Extrapolation to the concentrations likely to be found over the North Sea (1-10 ppbV) would imply that deposition rates would be entirely controlled by aqueous phase transport of the physically dissolved gas, and that chemical reactions would be unimportant. However, there is the distinct possibility, as noted by Lee & Schwartz (1981) that a "reaction with naturally occurring organic compounds [could be] a major sink process for NO_2 in surface waters". Experimental evidence for first-order reactions of NO_2 with aqueous solutes at low partial pressures of NO_2 has been circumstantial. Several authors have noted a deviation from second-order kinetics at very low partial pressures in their experiments, and attributed the results to reactions with 'impurities'.

Given the potential for such reactions in controlling the uptake of nitrogen oxides by sea-water, an experimental study of the reaction kinetics of NO_2 with water was established, to investigate possible

deviations from second-order kinetics at low potential pressures, and/or enhanced reaction rates in natural waters.

OBJECTIVES

The initial objective was to develop an experimental system for the reaction of NO_2 with water under controlled conditions, and to reproduce published values for the second-order reaction rate of NO_2 with water. Subsequently, a range of waters (including sea-water) were to be examined.

METHODS

Reaction of NO_2 with water was determined by measuring the loss of NO_2 from the gas phase after passing through water, rather than by measuring reaction products. The method of Lee & Schwartz (1981), using conductivity detection, is not applicable to solutions other than pure water. The apparatus is shown schematically in Figure 1. Air from a compressed air gas bottle was passed through a 'Parafil' and activated charcoal filter to remove traces of nitrogen oxides, and passed over a permeation source of nitrogen dioxide to produce a known gas phase concentration. The concentration was calculated from the gravimetric weight loss of the thermostatted permeation tube over time, and air flow measured by an electronic mass flow meter which had been calibrated using a standard volume bubble meter. A part of the flow containing NO_2 was then diverted through a sintered glass frit into a known volume (usually 1 litre) of water. The flow rate into the bubbler vessel was measured by mass flow meter, and kept constant. Gas phase concentrations were varied by changing the gas flow rate over the permeation source, while maintaining constant flow through the reaction vessel. Effluent air was fed to a Scintrex NO_2 analyzer, previously calibrated against the permeation source, and the loss of NO_2 was calculated. The reaction vessel was maintained at c. 10°C in a thermostatted water bath.

RESULTS

1. Reactions with pure water

Preliminary experiments with pure water showed that nitrogen dioxide was removed by reaction in the frit or on the walls of the reaction vessel. The amount removed depended on flow rate through the vessel, but was not dependent on gas concentration. The use of constant aqueous volume and gas flow rate therefore gave a constant offset to the results.

Reaction with pure water (distilled or deionised) over a range of gas-phase concentrations showed the expected second-order kinetics, as shown in Figure 2. The straight line relationship between the loss of NO_2 and the square of the $\text{NO}_2(\text{g})$ concentration is clearly seen, as well as the non-zero intercept attributed to heterogeneous reactions.

The average calculated second-order reaction rate constant, $k^1 (= k \cdot H_{\text{NO}_2}^2)$, is $8.5 (\pm 1.6) \times 10^3 \text{ Ms}^{-1}\text{atm}^{-2}$ at 9.5°C (Table 1), compared with the published value of $4.3 \times 10^3 \text{ Ms}^{-1}\text{atm}^{-2}$ at 25°C (Schwartz & White, 1983). The activation energy for the forward reaction is given by Schwartz & White (1983) as -33kJ mol^{-1} , which would mean a factor of 2.1 difference between 25°C and 9.5°C . The measured mean value for glass-distilled and deionised water (7 experiments) of $8.5 \times 10^3 \text{ Ms}^{-1}\text{atm}^{-2}$ is therefore in very good agreement with the corrected published value of $8.9 \times 10^3 \text{ Ms}^{-1}\text{atm}^{-2}$ at 9.5°C .

The rate constant has been calculated only from data above 20 ppbV NO_2 , as there is evidence of a deviation from linearity at low partial pressures (Figure 2).

2. Reaction with dilute acid.

One experiment was conducted using sulphuric acid at pH2. The resultant second-order rate constant (k^1) was $8.1 \times 10^3 \text{ Ms}^{-1}\text{atm}^{-2}$, not significantly different from the data for pure water.

3. Reactions with precipitation.

The mean rate constant for cloud and snow was $7.0 (\pm 2.0) \times 10^3 \text{ Ms}^{-1}\text{atm}^{-2}$, and not significantly different from the results for pure water (Table 1).

4. Reactions with lake water.

Water sampled from the shore of a fresh-water loch in the Scottish Border Region showed a slightly enhanced rate constant of $1.2 (\pm 0.1) \times 10^4 \text{ Ms}^{-1}\text{atm}^{-2}$ suggesting additional reaction pathways, probably with organic solutes.

Schematic diagram of laboratory experiments to study direct reaction of nitrogen dioxide(NO_2) gas with water.

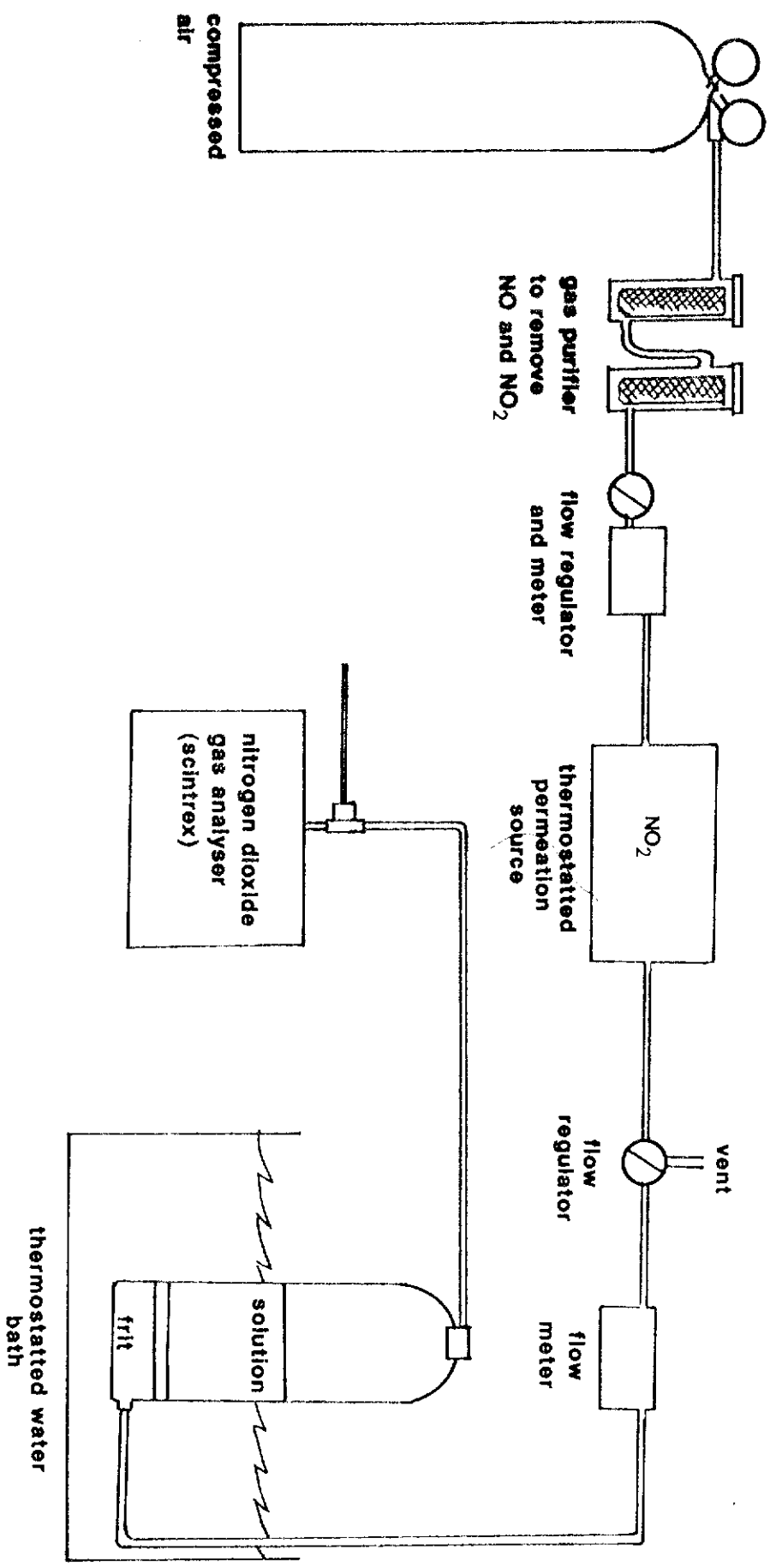
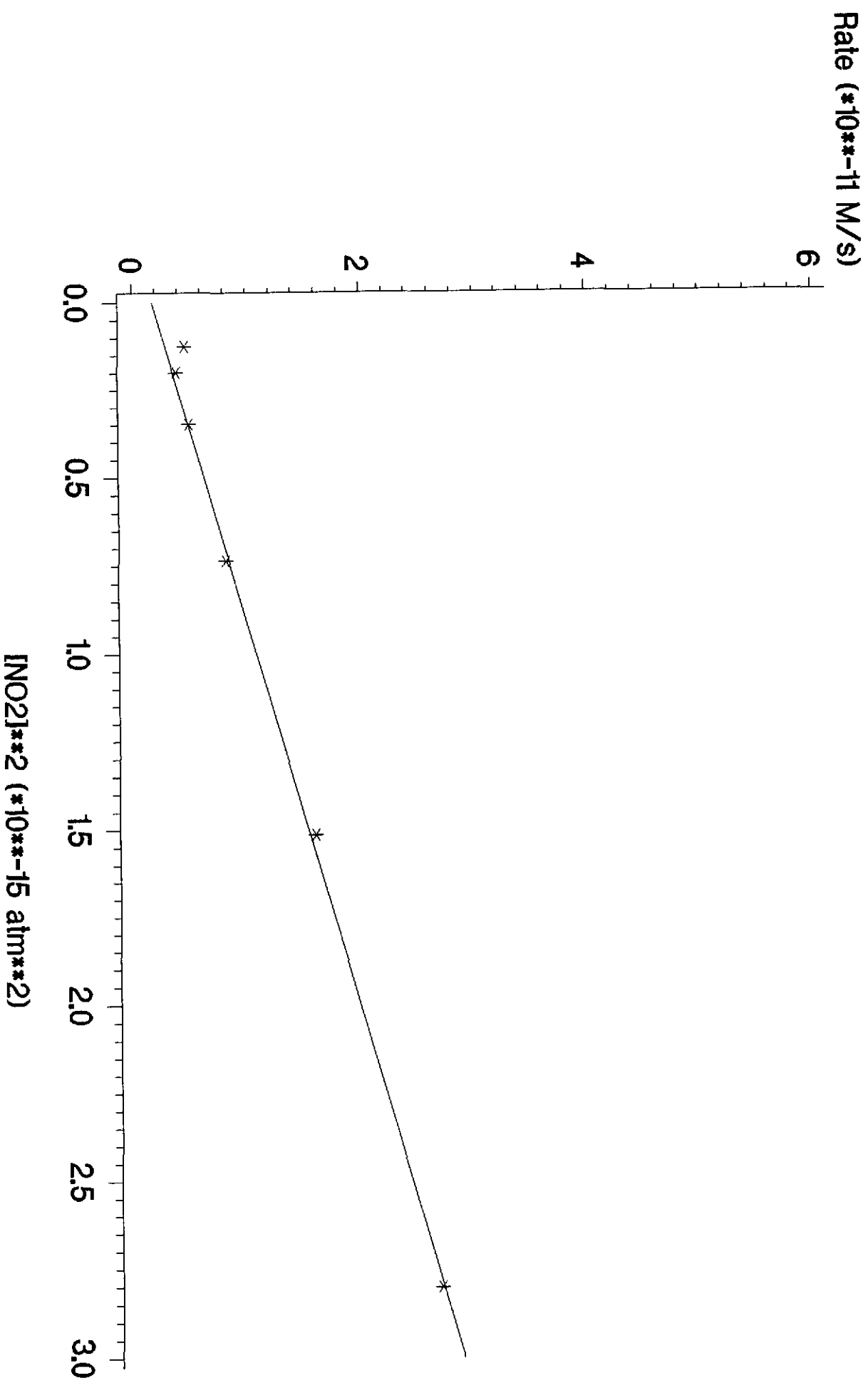


Table 1 - Experimental Results

Exp no.	Solution	Temp °C	Flow rate l/min	$k.H_{NO_2}^2$ $10^{11}M/s/atm^2$	Intercept $10^{-11}M/s$
3	Snow - fresh	10	2.55	0.149	0.661
4	Deionised	10	2.55	0.669	0.490
5	Deionised	10.5	2.55	0.869	0.555
6	Snow - old	10	2.50	0.818	0.994
7	Snow - old	10	2.50	0.578	1.080
9	Glass - distilled	9.5	2.10	0.768	0.217
10	Glass - distilled	9.5	2.25	0.837	-0.063
11	Deionised	9.5	2.05	0.711	0.176
12	Cloud - old	9.5	2.15	0.774	0.141
13	Sulphuric acid, pH2	9.5	2.30	0.806	0.089
14	Seawater	9.5	2.00	0.890	0.824
15	Seawater (vacuum filter)	9.5	2.10	1.054	1.011
16	Lake water	9.5	2.45	1.098	0.737
17	Lake water	9.5	2.45	1.227	0.555
18	Seawater	9.5	2.60	1.452	1.227
19	Deionised	9.5	2.60	1.159	0.192
20	Lake water	9.5	2.60	1.199	0.631
21	Lake water	9.5	2.65	1.337	0.552
22	Cloud - fresh	9.5	2.45	0.929	0.397
23	Glass distilled	9.5	2.50	0.904	0.182

FIGURE 2

Expt 23 - NO2 and glass distilled water



5. Reactions with sea-water.

Sea water was sampled from the south shore of the Forth estuary. An initial experiment (14 in Table 1) used water filtered through Whatman No 1 filter paper under gravity. There were large fluctuations in NO_2 detected, apparently caused by entrainment of small particles which greatly enhanced the NO_2 signal. It is not clear whether this represents adsorption/reaction of NO_2 on particles, or substances which give a positive response in the NO_2 analyser. Subsequent experiments using vacuum filtered sea-water did not show this behaviour, and gave a mean rate constant of $1.3 (\pm 0.3) \times 10^4 \text{ Ms}^{-1}\text{atm}^{-2}$, significantly greater than pure water. The data in Table 1 conceal an additional feature (Figure 3), which is a marked curvature (concave downwards), suggesting a deviation from simple second-order behaviour. This is shown by a much larger value for the intercept $1.1 (\pm 0.2) \times 10^{-11} \text{ Ms}^{-1}$ for sea water, compared with $0.25 (\pm 0.21) \times 10^{-11} \text{ Ms}^{-1}$ for pure water.

Subtraction of the mean second-order reaction rate for pure water gives the result shown in Figure 4 for experiment 18. There is an additional first-order reaction between NO_2 and seawater, with a reaction rate given by:

$$\text{rate} = 4.4 \times 10^{-4} p_{\text{NO}_2} + 5.1 \times 10^{-12} \text{ Ms}^{-1}$$

FIGURE 3

Expt 18 - NO₂ and seawater (vac.filt.)

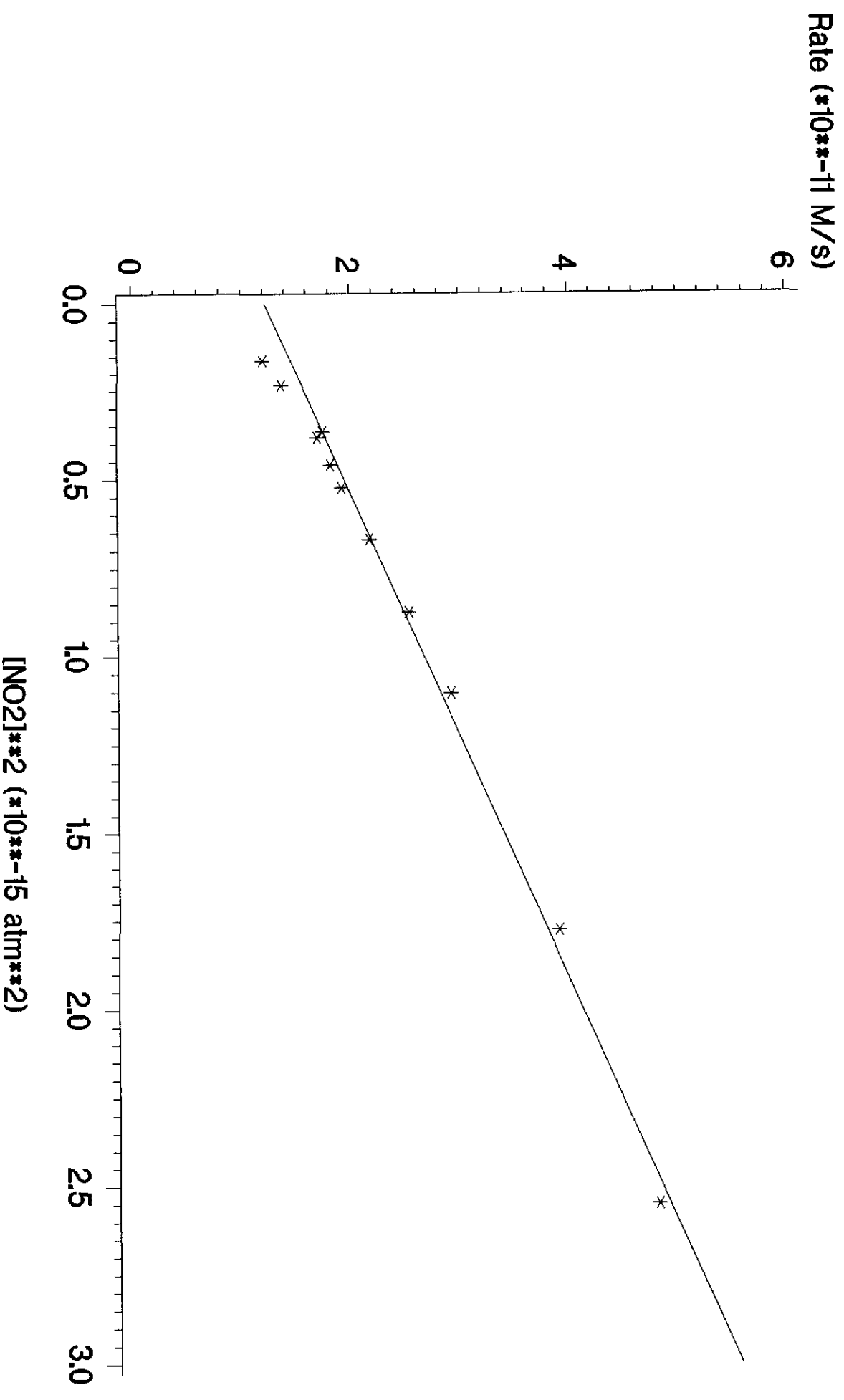
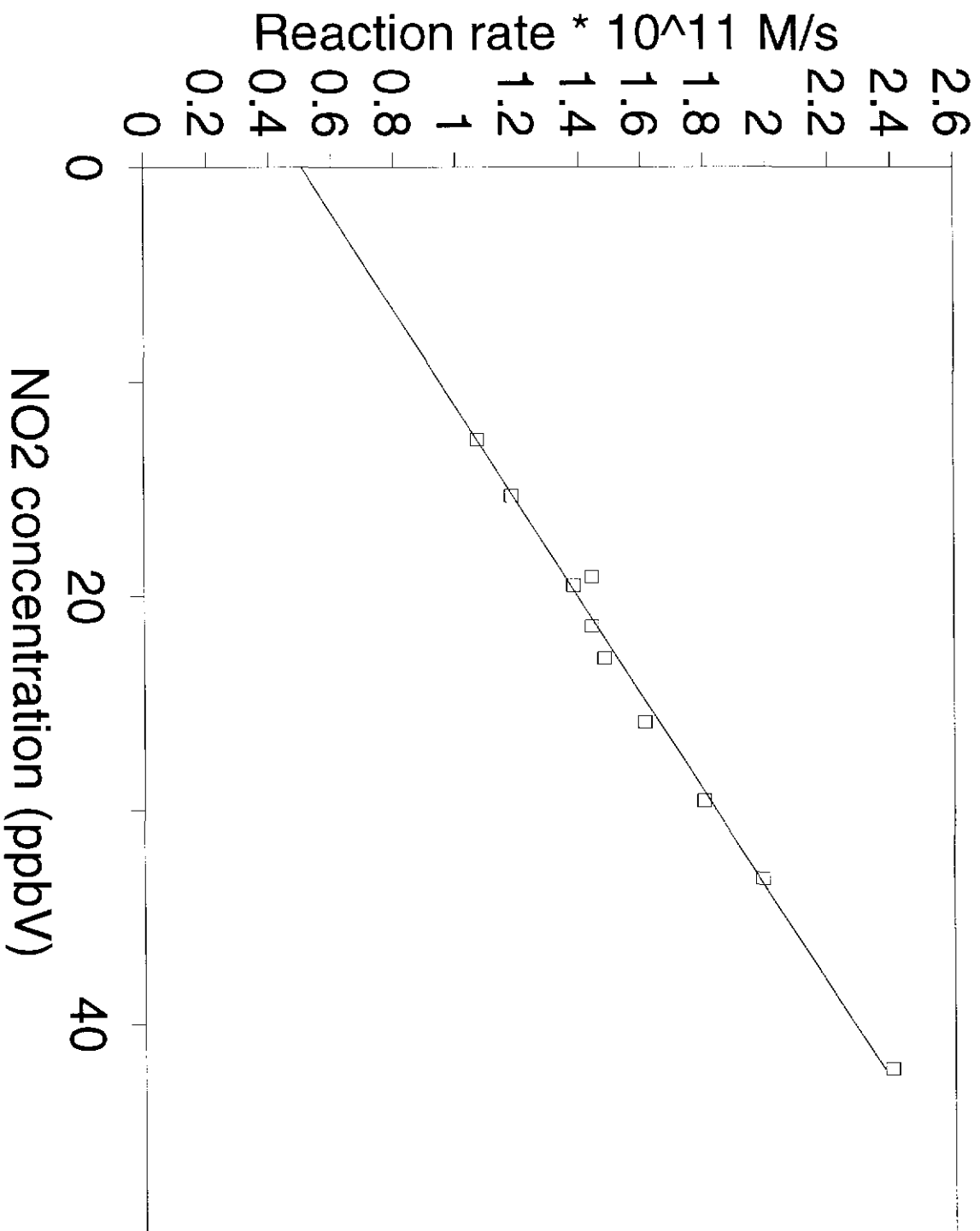


FIGURE 4

Reaction rate (sea water- dist.water)



DISCUSSION

The original objective has been achieved, in that the experimental method has reproduced the recommended literature values for the second-order reaction of NO_2 with water at low partial pressures, using a novel experimental approach.

Direct measurement of the reaction between NO_2 and sea-water has demonstrated additional first-order reaction, which is fast compared with the second-order reaction at low partial pressures. The uptake rate of NO_2 at 10 ppbV by the first-order process at 9.5°C is $4.4 \times 10^{-12} \text{ M s}^{-1}$, compared with $8.5 \times 10^{-13} \text{ M s}^{-1}$ for the second-order process. The importance of the first-order process is relatively much greater below 10 ppbV.

There was a larger apparent reaction rate at zero gas concentration (by extrapolation) with sea-water than with pure water. This results from heterogeneous reactions in the apparatus and is likely to be related to surface-active solutes in sea-water or greater ionic strength. These aspects will be investigated in more detail in future.

REFERENCES

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