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Evaluation of the Rate of Uptake of Nitrogen Dioxide by Atmospheric and Surface Liquid Water

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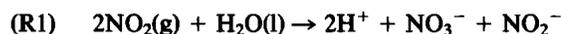
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The rate of uptake of NO₂ by liquid water according to (R1), 2NO₂(g) + H₂O(l) → 2H⁺ + NO₃⁻ + NO₂⁻, is shown to be unaffected by O₂ (0.2 atm). Hence the rate constant and Henry's law solubility constant of NO₂ previously obtained may be employed to evaluate the rates of aqueous phase reactions of NO₂ in the ambient atmosphere. Reactions (R1) and (R2), NO₂(g) + NO(g) + H₂O(l) → 2H⁺ + 2NO₂⁻, are quite slow at representative atmospheric partial pressures and cloud liquid water content; the characteristic times range upward from 10³ - 10⁴ hours at 10⁻⁷ atm, increasing with decreasing partial pressures of the gases. Direct acidification of cloud liquid water by (R1) or (R2) is also unimportant. Catalytic enhancement of (R1) is potentially important for catalyst concentrations of order 10⁻⁷ M, assuming sufficiently fast rate constants (~10⁸ M⁻¹ s⁻¹). Iron-catalyzed reaction in particular, however, is found to be unimportant. Reaction of NO₂ with dissolved S(IV) is potentially important, based upon an assumed upper limit rate constant of 2.5 × 10⁷ M⁻¹ s⁻¹. Deposition of NO₂ to surface (ocean or lake) water is shown to be controlled by aqueous phase mass transport and/or reaction and is much slower than heretofore assumed.

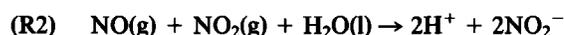
INTRODUCTION

Nitrogen oxides (NO_x = NO + NO₂) are important trace atmospheric constituents because of their catalytic role in the production and destruction of ozone in the troposphere and stratosphere [Crutzen, 1979; Kley *et al.*, 1981a]. These species also serve as precursors to the formation of nitric acid, an important constituent in acid precipitation [Likens *et al.*, 1979]. The removal of NO_x from the atmosphere may take place by two distinct processes: (1) oxidation to gas phase HNO₃ followed by incorporation into cloud or rainwater or dry deposition, and/or (2) incorporation of NO_x into atmospheric or surface liquid water followed by aqueous phase reaction. The first process has been studied extensively, and both the homogeneous gas phase reactions [Crutzen, 1979; Baulch *et al.*, 1980] and the subsequent processes for wet and dry removal of HNO₃ [e.g., Levine and Schwartz, 1981] appear to be well delineated. In contrast, the second process has received considerably less attention. Neither the uptake of NO_x by atmospheric liquid water nor the contribution of this process to acid precipitation has been satisfactorily assessed [National Academy of Sciences, 1977]. Similarly, little quantitative information is available concerning the rate of dry deposition of NO₂ directly to surface water, i.e., lakes and oceans.

The potential importance of aqueous phase reactions of the nitrogen oxides may be appreciated in view of the high concentrations of dissolved nitrogen species that would result if the reactions



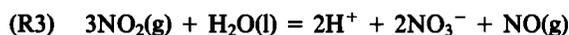
and/or



were to proceed significantly toward equilibrium under ambient conditions [Schwartz and White, 1981a]. For example, (R1) would at equilibrium lead to an aqueous phase

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HNO₃ concentration of 1.3 × 10⁻⁴ M (pH = 3.9) for p_{NO₂} = 10⁻⁹ atm at 25°C. For (R1) and (R2) both at equilibrium, i.e., corresponding to the overall equilibrium



the aqueous phase HNO₃ concentration in equilibrium with partial pressures of NO and NO₂ of 10⁻⁹ atm would be 6.5 × 10⁻³ M (pH 2.2). The high thermodynamic driving force for reaction as well, perhaps, as the rapid reactive dissolution of NO₂ in water at common laboratory pressures [Latimer and Hildebrand, 1940; Pauling, 1956; Cotton and Wilkinson, 1980] have led a number of previous investigators to assume that these reactions are rapid also under ambient conditions, i.e., with cloud water or rainwater [Georgii, 1963; Cooper *et al.*, 1976; Söderlund and Svensson, 1976; Matteson, 1979; Herrmann and Matteson, 1980; Rodhe *et al.*, 1980; Martin *et al.*, 1981], with liquid-water-containing clear air aerosols [Hidy and Burton, 1975; Orel and Seinfeld, 1977; Peterson and Seinfeld, 1979; Middleton and Kiang, 1979; Parungo and Poeschel, 1980], with surface water [Liss, 1976; Hicks and Liss, 1976; Kabel, 1976, 1979; Slinn *et al.*, 1978], or with liquid water contained within vegetation [Hill, 1971; Hill and Chamberlain, 1976]. The acidity resulting from assumption of equilibria (R1) and (R2) has been shown as well to exert a major influence upon aqueous phase concentrations of sulfur IV and resultant sulfate formation rates as a consequence of the highly pH-dependent solubility of sulfur IV [Orel and Seinfeld, 1977; Peterson and Seinfeld, 1979; Beyak and Peterson, 1980; Middleton and Kiang, 1979]. In contrast, other authors have minimized the importance of direct interaction of NO_x with liquid water, citing the 'insolubility' or 'limited solubility' of NO and NO₂ in liquid water [Nash, 1970; Graedel *et al.*, 1975; Barnes, 1979]. Recently, Liljestrand and Morgan [1981] have asserted that (R1) is 'kinetically slow' under conditions pertinent to equilibrium with rainwater but that (R2) is 'kinetically fast' but that and have presented an interpretation of precipitation composition in the context of these equilibria.

Despite the importance of and interest in (R1) and (R2) as

TABLE 1. Comparison of Measured Rates of Reaction (R1) in Nitrogen and Air

Carrier Gas	p_{NO_2} , 10^{-7} atm	
	1.0	0.50
Nitrogen	$3.5 \pm 4\%$	$1.05 \pm 7\%$
Air	$3.4 \pm 5\%$	$1.10 \pm 8\%$

$R_1^{(\text{aq})}$, 10^{-11} M s⁻¹; indicated values represent averages and standard deviations of four determinations. $T = 22^\circ\text{C}$; characteristic time of convective mixing [Lee and Schwartz, 1981] = 2.14 s.

they pertain to the ambient atmosphere, no quantitative evaluation of the rate of these reactions under ambient conditions has previously been given. In this paper we carry out such an evaluation employing recent laboratory data and further measurements reported here. Additionally, we employ available literature data to examine the rates of other potentially important aqueous phase reactions of NO₂ pertinent to in-cloud processes and to uptake by surface water.

Recent work in our laboratory [Lee and Schwartz, 1981] has established that the reactive dissolution of NO₂ in water at low partial pressures (10^{-7} – 10^{-4} atm) proceeds in the absence of other substances according to (R1), i.e., that the reaction proceeds according to second-order aqueous phase kinetics:

$$R_1^{(\text{aq})} = k_1 [\text{NO}_2(\text{aq})]^2 \quad (1)$$

$R_1^{(\text{aq})}$ represents the rate of reaction in the aqueous phase (units M s⁻¹). From the measured dependence of $R_1^{(\text{aq})}$ upon p_{NO_2} and upon the rate of convective mixing applied to the gas-liquid system it was possible to determine both the second-order rate constant, $k_1(1.0 \pm 0.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 22°C), and the Henry's law coefficient of NO₂, $H_{\text{NO}_2}(7.0 \pm 0.5 \times 10^{-3} \text{ M atm}^{-1}$ at 22°C). The latter quantity relates the equilibrium concentration of the physically dissolved gas to its partial pressure above solution:

$$[\text{NO}_2(\text{aq})] = H_{\text{NO}_2} p_{\text{NO}_2} \quad (2)$$

Under phase-mixed conditions, i.e., condition (2) satisfied, it is possible to express $R_1^{(\text{aq})}$ in terms of p_{NO_2} as

$$R_1^{(\text{aq})} = k_1 H_{\text{NO}_2}^2 p_{\text{NO}_2}^2 \quad (3)$$

The value of $k_1 H_{\text{NO}_2}^2$ obtained by Lee and Schwartz [1981] was shown to agree closely with that inferred from studies of the kinetics of nitrous acid decomposition and formation [Abel and Schmid, 1928; Abel et al., 1928; Schmid and Bähr, 1964]. Additionally the aqueous phase rate constant k_1 was found to agree rather closely with that determined by pulse-radiolysis measurements [Grätzel et al., 1969], and the value of H_{NO_2} agreed closely with that which has been inferred on the basis of thermochemical cycles involving NO₂(aq) [Schwartz and White, 1981a]. These results may be applied to the evaluation of the rate of (R1) in the ambient atmosphere. However, first it remains to be established that O₂ has no effect upon the rate or mechanism of NO₂ uptake by liquid water, since the previous studies were carried out with exclusion of O₂.

EXPERIMENTAL RESULTS

The experimental apparatus, procedure, and materials have been described previously [Lee and Schwartz, 1981]. Briefly, NO₂ at low partial pressure in N₂ or air was

contacted with liquid water in the form of finely divided bubbles introduced through a fritted disk that comprised the bottom surface of an all glass cylindrical reactor. The extent of formation of ionic products and, in turn, the rate of (R1) were monitored continuously by measurement of the electrical conductivity of the solution; the stoichiometry of the reaction was determined by analysis of products (NO₂⁻ and NO₃⁻). Air (ultrazero, Matheson) and N₂ (ultra-high purity, Matheson) were used alternately as diluent gas under otherwise identical conditions. Rates of reaction (R1) are shown in Table 1. These measurements have been carried out at low p_{NO_2} to decrease the rate of the second-order reaction (R1) and thereby enhance sensitivity to any influence of O₂. Within the precision of the measurements oxygen was found to have no effect on the rate of reaction for p_{NO_2} as low as 5×10^{-8} atm. These results establish that in the presence of O₂ as well as its absence the reactive dissolution of NO₂ in liquid water proceeds according to (R1). The possibility of an additional, oxygen-mediated pathway for the reactive uptake of NO₂ by water at these low partial pressures is ruled out, and consequently values of H_{NO_2} and k_1 determined by Lee and Schwartz [1981] may be utilized in evaluating the rates of aqueous phase reactions of NO₂ in the ambient atmosphere.

DISCUSSION

The foregoing results permit evaluation of the rate of (R1) in liquid water clouds, liquid-water-containing clear air aerosols, and surface water (lakes and oceans). Additionally, knowledge of H_{NO_2} permits estimation of the rates of other reactions of NO₂ in these media. This discussion addresses the rates and characteristic times of these reactions under conditions representative of the ambient atmosphere.

We first consider (R1). Here it is assumed that the same mechanism for establishing this equilibrium obtains in atmospheric liquid water as in the laboratory, i.e., that there are no catalytic processes occurring in parallel that would more rapidly establish this equilibrium. We return to consideration of possible catalytic pathways subsequently. The several rates and characteristic times of interest are as follows:

$$R_1^{(\text{g})} = -\frac{1}{2} dp_{\text{NO}_2}/dt \quad (\text{atm s}^{-1}) \quad (4)$$

$$R_1^{(\text{aq})} = d[\text{NO}_3^-]/dt \quad (\text{M s}^{-1}) \quad (5)$$

$$\tau_1^{(\text{NO}_2)} = p_{\text{NO}_2}/2R_1^{(\text{g})} \quad (\text{s}) \quad (6)$$

$$\tau_1^{(\text{eq})} = [p_{\text{NO}_2} - p_{\text{NO}_2}^{(\text{eq})}]/2R_1^{(\text{g})} \quad (\text{s}) \quad (7a)$$

$$\tau_1^{(\text{eq})} = [\text{NO}_3^-]_{\text{eq}}/R_1^{(\text{aq})} \quad (7b)$$

Here $R_1^{(\text{g})}$ is the rate of (R1) referred to the partial pressure of NO₂ gas; $\tau_1^{(\text{NO}_2)}$ and $\tau_1^{(\text{eq})}$ are the characteristic times for removal of gas phase NO₂ by (R1) and for establishing equilibrium (R1), respectively. $[\text{NO}_3^-]_{\text{eq}}$ represents the equilibrium concentration of dissolved nitrate product. The factor of 2 in these equations represents the stoichiometric coefficient of NO₂(g) in (R1). The characteristic time of removal of a material from a reservoir by a particular process, e.g., $\tau_1^{(\text{NO}_2)}$ (or its inverse, which has units of a first-order rate constant), is useful in comparing the relative importance of various processes, in constructing material budgets, etc. [Bolin and Rodhe, 1973; Rodhe, 1978; Junge, 1974; Wagner and Zellner, 1979; Schwartz, 1979]. The characteristic time of establishing a particular equilibrium,

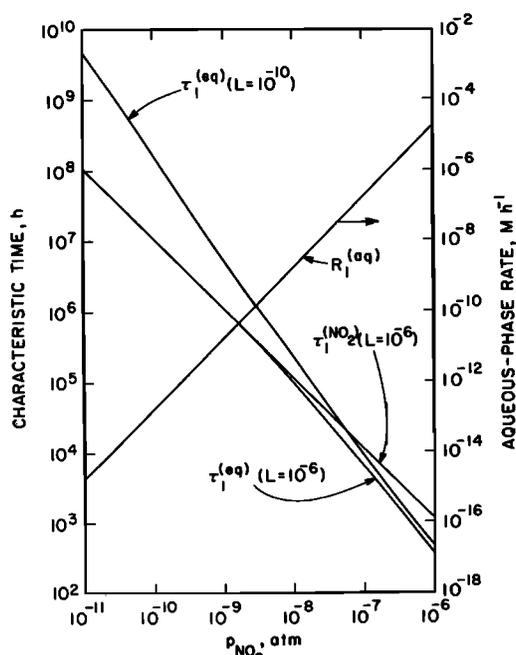


Fig. 1. Rate and characteristic times of reaction (R1), $2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}^+ + \text{NO}_3^- + \text{NO}_2^-$, as function of partial pressure of NO_2 , $T = 25^\circ\text{C}$. $R_1^{(\text{aq})}$ represents reaction rate referred to aqueous phase concentration of products; $\tau_1^{(\text{NO}_2)}$ and $\tau_1^{(\text{aq})}$ represent characteristic times of removal of $\text{NO}_2(\text{g})$ and of establishing equilibrium, respectively. Values of liquid water content L ($\mu\text{g l}^{-1}$) = 10^{-6} and 10^{-10} are representative of liquid water clouds and clear air aerosols, respectively.

e.g., $\tau_1^{(\text{aq})}$, is useful in addressing whether that equilibrium is achieved under conditions of interest, e.g., within a cloud lifetime. This quantity may approximate the characteristic time of removal of a reagent (in situations in which the equilibrium strongly favors product formation) or may be substantially less (in situations in which the equilibrium favors the reagents).

Reaction in Liquid Water Clouds

The rate of aqueous phase reaction $R_1^{(\text{aq})}$ may be evaluated by (3) for known k_1 and H_{NO_2} and specified p_{NO_2} , provided that the aqueous phase is saturated in NO_2 . This assumption is valid for reaction in cloud droplets for which the characteristic time of diffusion is short compared to that of reaction of dissolved NO_2 , as may be readily established by the approach of Schwartz and Freiberg [1981].

Once $R_1^{(\text{aq})}$ has been evaluated, the rate referred to gaseous NO_2 may be evaluated as

$$R_1^{(\text{g})} = LRT R_1^{(\text{aq})} = LRT k_1 H_{\text{NO}_2}^2 p_{\text{NO}_2}^2 \quad (8)$$

Here R is the gas constant, T is the absolute temperature, and L is the liquid water content ($\mu\text{g l}^{-1}$; a liquid water content of 1 g m^{-3} corresponds to $L = 10^{-6}$). It is seen that the rate referred to the gas phase reagent concentration varies linearly with L , whereas the rate referred to the aqueous phase is independent of L .

The characteristic time for removal of gas phase NO_2 by (R1), $\tau_1^{(\text{NO}_2)}$, may be evaluated as

$$\tau_1^{(\text{NO}_2)} = (2LRT k_1 H_{\text{NO}_2} p_{\text{NO}_2})^{-1} \quad (9)$$

Finally, the characteristic time of reaching equilibrium may be evaluated as

$$\tau_1^{(\text{aq})} = \tau_1^{(\text{NO}_2)} (1 - p_{\text{NO}_2}^{(\text{aq})}/p_{\text{NO}_2}) \quad (10)$$

where $p_{\text{NO}_2}^{(\text{aq})}$ must be evaluated for specified p_{NO_2} and L . These several quantities have been calculated as a function of NO_2 partial pressure for $L = 10^{-6}$, corresponding to a moderately dense liquid water cloud [Pruppacher and Klett, 1978] and are shown in Figure 1. The magnitudes of these characteristic times (~ 1 year at $p_{\text{NO}_2} = 10^{-8}$ atm) rule out the possibility that (R1) is a significant sink process for NO_2 in the ambient atmosphere. In particular, $\tau_1^{(\text{NO}_2)}$ may be compared to the characteristic time of removal of NO_2 by gas phase reaction with free radical OH,



which is considered [Crutzen, 1979] to be the principal gas phase sink for NO_2 . This characteristic time, $\tau_4^{(\text{NO}_2)} = (k_4[\text{OH}])^{-1}$ is approximately 1 day, based upon an average OH concentration of 1.2×10^6 molecules cm^{-3} [Sze and Ko, 1980] and $k_4 = 1.0 \times 10^{-11}$ cm^3 molecule $^{-1}$ s $^{-1}$ [Baulch et al., 1980]. The magnitude of $\tau_1^{(\text{aq})}$, similar to that of $\tau_1^{(\text{NO}_2)}$ is also seen to be sufficiently great compared to cloud lifetimes (Pruppacher and Klett [1978] suggest an average value of 7 hours) that this equilibrium cannot be considered to be established under ambient conditions for clouds and a fortiori for rain. Finally, one would note that except for persistent high NO_2 concentrations, (R1) would not contribute significantly to acidification of cloud water or rainwater. Thus, even for $p_{\text{NO}_2} = 1 \times 10^{-7}$ atm in contact with a liquid water cloud for 10 hours, the resultant contribution to cloud acidity would be only 3×10^{-6} M $[\text{H}^+]$ (cf. $[\text{H}^+] = 2.5 \times 10^{-6}$ M for pH 5.6, as dictated by equilibria involving atmospheric CO_2).

The slow rate of (R1) under atmospheric conditions contrasts with the rapid rate of this reaction at higher partial pressures. The principal reason for this is the second-order rate law for this reaction. Additionally, the low value of the Henry's law coefficient serves to inhibit the rate of reaction, despite a high value of k_1 , within a factor of 50 of the diffusion-controlled encounter rate coefficient.

Reaction in Clear Air Aerosols

A treatment similar to that for liquid water clouds may be applied to examination of the rate and characteristic times of (R1) in clear air aerosols. The liquid water content of clear air aerosols is typically 10–100 $\mu\text{g/m}^3$ ($L = 10^{-11}$ – 10^{-10}) [Ho et al., 1980], 4 to 5 orders of magnitude less than used in the calculation for cloud liquid water, and consequently, the rate of reaction referred to NO_2 gas, $R_1^{(\text{g})}$, would be diminished by such a factor. Correspondingly, the residence time for removal of $\text{NO}_2(\text{g})$ by (R1) is increased by the same factor. Thus these processes, which are slow even for liquid water clouds, are seen to contribute inappreciably for clear air aerosols.

Finally, we examine $\tau_1^{(\text{aq})}$ appropriate for aerosols of low liquid water content by evaluating this quantity (equation (7b)), for equilibrium NO_3^- concentration specified by the initial p_{NO_2} , i.e., negligible depletion of $\text{NO}_2(\text{g})$ at equilibrium. This quantity, also shown in Figure 1, is seen to exceed the corresponding quantity for $L = 10^{-6}$ throughout the entire partial pressure range examined, considerably so at low pressures. Characteristic times of such magnitude establish

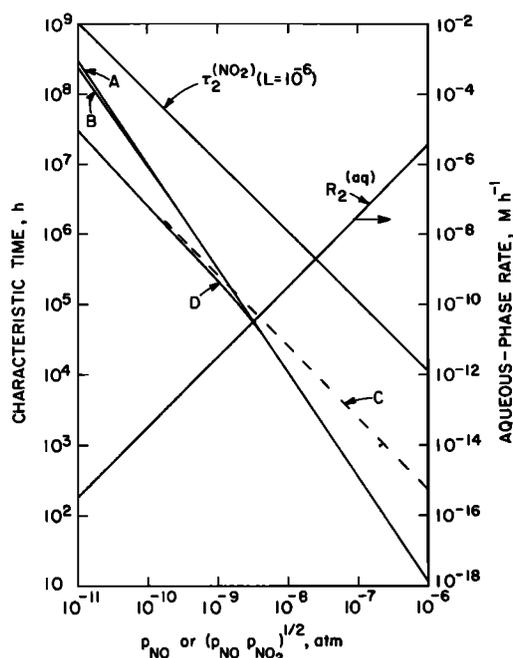


Fig. 2. Estimated rate and characteristic times of reaction (R2), $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}^+ + 2\text{NO}_2^-$; $\tau_2^{(\text{NO}_2)}$ represents characteristic time of removal of $\text{NO}_2(\text{g})$ as function of p_{NO} . Curves A, B, C, and D show characteristic times of achieving equilibrium, $\tau_2^{(\text{eq})}$, as a function of $(p_{\text{NO}} p_{\text{NO}_2})^{1/2}$. Curve A, $L = 10^{-10}$; $[\text{H}^+] = [\text{NO}_2^-]$. Curve B, $L = 10^{-6}$; $[\text{H}^+] = [\text{NO}_2^-]$. Curve C, $L = 10^{-10}$; $[\text{H}^+] = 2.5 \times 10^{-5} \text{ M}$ ($\text{pH} = 5.6$). Curve D, $L = 10^{-10}$; $[\text{H}^+]$ controlled by equilibrium (R2) and CO_2 solubility. $R_2^{(\text{aq})}$ represents reaction rate referred to aqueous phase concentration of products, as function of $(p_{\text{NO}} p_{\text{NO}_2})^{1/2}$.

that contrary to the assumption of previous investigators, equilibrium (1) cannot be assumed to hold for clear air aerosols in the ambient atmosphere, at least in the absence of catalytic pathways.

Rate of Reaction (R2)

The rate and characteristic times associated with (R2) may be treated analogously to (R1). Here the rate expression referred to the gaseous reagents is

$$R_2^{(\text{aq})} = k_2 H_{\text{NO}} H_{\text{NO}_2} p_{\text{NO}} p_{\text{NO}_2} \quad (11)$$

$H_{\text{NO}} = 1.9 \times 10^{-3} \text{ M atm}^{-1}$ at 25°C [Loomis, 1928], and H_{NO_2} has been given above. However, the aqueous phase rate constant k_2 is not well known. A value of $7.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ is obtained from the pulse radiolysis study of Grätzel et al. [1970], whereas the flash photolysis study of Treinin and Hayon [1970] yields the value $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. These values of k_2 yield a range for the overall rate coefficient $k_2 H_{\text{NO}} H_{\text{NO}_2} = (1.0 \text{ to } 13) \times 10^2 \text{ M atm}^{-2} \text{ s}^{-1}$.

An alternative approach to the overall rate constant has been given by Schwartz and White [1981b], who have evaluated this quantity from the kinetics of the reverse reaction, as inferred from the rates of diazotization of amines and of isotope exchange, and the equilibrium constant of (R2). This treatment leads to the value $7 \times 10^2 \text{ M atm}^{-2} \text{ s}^{-1}$, intermediate between the values obtained by direct measurement.

In the calculations that follow we employ the value $k_2 H_{\text{NO}} H_{\text{NO}_2} = 1 \times 10^3 \text{ M atm}^{-2} \text{ s}^{-1}$ toward the high end of the range of values obtained for this quantity. With this value it

is shown, as was the case for (R1), that the reaction is slow under characteristic ambient conditions of reagent partial pressures and liquid water content. Thus, although the values of the several characteristic times and rates obtained will be subject to refinement as the value of the overall rate constant becomes better known, this conclusion will remain unchanged.

The rate and the several characteristic times associated with (R2) are shown in Figure 2. Since this rate is proportional to the product of the partial pressures of the two gases, it is convenient to choose as an abscissa scale the quantity $(p_{\text{NO}} p_{\text{NO}_2})^{1/2}$, i.e., the geometric mean of the two partial pressures. As was found for (R1), the rate of (R2) is seen to contribute negligibly to acidification of liquid water at ambient partial pressures. The characteristic time for removal of gas phase NO_2 by (R2), $\tau_2^{(\text{NO}_2)}$ may be evaluated as

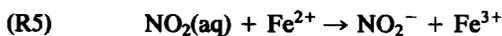
$$\tau_2^{(\text{NO}_2)} = (LRT k_2 H_{\text{NO}} H_{\text{NO}_2} p_{\text{NO}})^{-1} \quad (12)$$

and is seen to vary inversely as p_{NO} . The magnitude of this quantity, which is comparable to that of $\tau_1^{(\text{NO}_2)}$ establishes that (R2) also represents a minor sink path for NO_2 . Finally, we consider the characteristic time of establishing equilibrium (R2). At higher partial pressures this quantity becomes relatively short [~ 10 hours at $(p_{\text{NO}} p_{\text{NO}_2})^{1/2} = 10^{-6} \text{ atm}$], but at more representative partial pressures $(p_{\text{NO}} p_{\text{NO}_2})^{1/2} \leq 10^{-7} \text{ atm}$, $\tau_2^{(\text{eq})}$ is seen to be sufficiently long as to rule out establishment of this equilibrium under ambient conditions. At low partial pressures, the equilibrium concentration of nitrite ion dissolved by (R2) becomes sensitive to other influences on $[\text{H}^+]$; in turn, $\tau_2^{(\text{eq})}$ is affected, as indicated in Figure 2. However, this is significant only at low partial pressures, where $\tau_2^{(\text{eq})}$ is quite large. Thus, as was the case for (R1), it may be concluded that (R2) is so slow under ambient conditions that this equilibrium cannot be assumed to hold. This conclusion applies to reaction in liquid-water-containing aerosols, in liquid water clouds and in rain.

Catalytic Reactions

In this section we consider possible catalytic paths that might occur in parallel with, and much faster than, (R1) as studied here, thereby increasing the importance of this reaction under ambient conditions. In particular, homogeneous transition metal catalysis is considered in view of the capabilities of transition metal ions to undergo the necessary oxidation reduction reactions [Cotton and Wilkinson, 1980] and in view also of the known trace concentrations of transition metal ions in atmospheric liquid water [e.g., Tanaka et al., 1980]. We further specialize to consideration of possible reaction catalyzed by dissolved iron, since the well-studied chemistry of iron and the nitrogen oxides and oxyacids [Abel et al., 1936] both suggests the possibility of iron as a candidate catalyst and provides the information necessary to evaluate the rate of this process.

An example of a potential catalytic mechanism parallel to (R1) consists of the reactions



The free energy change of reaction is -6.21 and $-2.91 \text{ kcal mol}^{-1}$, respectively, evaluated via the standard oxidation potential for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple [Latimer and Hildebrand,

1940] and the standard free energies of formation of the remaining species [Schwartz and White, 1981a]; the standard free energy of formation of NO₂(aq), evaluated using the value $H_{\text{NO}_2} = 7 \times 10^{-3} \text{ M atm}^{-1}$ obtained by Lee and Schwartz [1981] is 15.20 kcal mol⁻¹. The negative free energy of reaction in each case suggests the thermodynamic favorability of the reaction in the direction shown.

To estimate the rate and characteristic times of the catalytic pathway under ambient conditions it is necessary to ascertain the rates of each of the reactions (R5) and (R6). A rough upper limit to the rate constant for reactions such as these can be estimated as $k_c \leq 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; cf. the diffusion-controlled encounter rate constant $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [Benson, 1960]. The characteristic time for reaction of NO₂ referred to the gas phase, by reaction with a catalytic species having concentration [C] is

$$\tau_c^{(\text{NO}_2)} = (\text{LRT } H_{\text{NO}_2} k_c [C])^{-1} \quad (13)$$

For an assumed catalyst concentration [C] = 10⁻⁷ M (cf. dissolved Fe concentrations of this magnitude as reported by Tanaka et al. [1980] in rain samples obtained in Florida) and for $L = 10^{-6}$, $\tau_c^{(\text{NO}_2)} = 16$ hours. Such a value for the characteristic time of NO₂ uptake by in-cloud reaction would be highly significant in the budget of atmospheric NO₂. Similarly, the above conditions would, for $p_{\text{NO}_2} = 10^{-8}$ atm, lead to an acid formation rate of $3 \times 10^{-5} \text{ M h}^{-1}$. Such a high rate indicates a potentially important process for acidification of cloud liquid water for the rate constants of (R5) and (R6) even 1 or 2 orders of magnitude less than the encounter rate coefficient.

As indicated above, information is available that permits k_5 to be evaluated; this is done in Appendix B, leading to the value $7.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. This value is some 5 orders of magnitude less than the encounter rate, and hence (R5) would be significant only at high concentrations of Fe²⁺ and high partial pressures of NO₂; e.g., for $[\text{Fe}^{2+}] = 1 \times 10^{-5} \text{ M}$ and $p_{\text{NO}_2} = 1 \times 10^{-7} \text{ atm}$, $R_5^{(\text{aq})} = 1.8 \times 10^{-6} \text{ M h}^{-1}$. With respect to (R6), necessary to complete the catalytic cycle, available evidence, as noted in Appendix B, suggests that this reaction is even slower than (R5). Hence, the iron-catalyzed mechanism, (R5) and (R6), while possibly occurring at a substantially greater rate than the direct, uncatalyzed reaction, would not appear to enhance the rate of (R1) sufficiently to make this process significant in the budget of ambient NO₂. It should, however, be emphasized that other catalytic mechanisms not examined here should be considered potentially significant, since the rates of electron transfer reactions may greatly exceed that found for (R5) and indeed may approach the diffusion-controlled limit [Cotton and Wilkinson, 1980].

Other Reactions

In addition to catalytic mechanisms one must also consider the possibility of the reaction of NO₂ with other dissolved substances present in cloud water. One such potential reagent that must be considered is sulfur IV, since NO₂ is a fairly strong oxidizing agent, comparable to Br₂ [Cotton and Wilkinson, 1980]. The reaction of NO₂ with S(IV) has been studied by Nash [1970], who compared the reactivity of NO₂ toward various solutes by measuring the efficiency of the several solutes in absorbing NO₂ (3 ppm) bubbled through aqueous solution. In this study, S(IV) was shown to be some 200-fold less reactive to NO₂(aq) than *o*-methoxyphenol, the

most reactive solute found. This finding allows an upper bound to be given for the rate constant for second-order NO₂(aq)-S(IV) reaction. Since the rate constant for reaction of NO₂ with *o*-methoxyphenol cannot exceed the diffusion controlled encounter rate constant ($5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the rate constant for reaction with S(IV), $k_{\text{S(IV)}}$, cannot exceed $2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

To evaluate the aqueous phase reaction rate, an estimate is also needed for S(IV) concentrations. Little information appears to be available concerning S(IV) concentration in cloud liquid water. However, Dana [1980] suggests that dissolved S(IV) in the rain at rural sites in the northeastern United States is in equilibrium with gaseous SO₂ and dissolved, nonvolatile acid. S(IV) concentrations of the order of $3 \times 10^{-6} \text{ M}$ are reported; this concentration corresponds to $p_{\text{SO}_2} = 1.5 \times 10^{-8} \text{ atm}$.

If $[\text{S(IV)}] = 3 \times 10^{-6} \text{ M}$ and the upper limit $k_{\text{S(IV)}} = 2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ are employed to evaluate the characteristic time for removal of NO₂ by reaction in cloud liquid water ($L = 10^{-6}$), the value $\tau_{\text{S(IV)}}^{(\text{NO}_2)} = 20$ hours is obtained, which would be highly significant in the budget of atmospheric NO₂. This process would become even more significant for increased p_{SO_2} or $p\text{H}$, which would lead to still lower values of $\tau_{\text{S(IV)}}^{(\text{NO}_2)}$. In this context, however, it should be noted that for concentrations of S(IV) substantially greater than that employed in the present calculation ($3 \times 10^{-6} \text{ M}$), the rate of reaction of dissolved NO₂ (evaluated for $k_{\text{S(IV)}} = 2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) becomes sufficiently fast compared to the rate of diffusive mass transport within cloud droplets of 10- μm diameter that the aqueous phase can no longer be treated as saturated in NO₂. In this situation the rate of aqueous phase reaction of NO₂ continues to increase with [(S(IV))], although no longer linearly, as would be the case if the aqueous phase remained saturated in NO₂. Criteria for the onset of this effect and expressions for evaluating the rate under these conditions have been given by Schwartz and Freiberg [1981].

In concluding this discussion it should again be emphasized that these calculations are based on an assumed upper limit value for $k_{\text{S(IV)}}$, as evaluated above; the actual value may be substantially less than this assumed value. Also, we would point out that the above discussion pertains only to direct, uncatalyzed reaction of NO₂ with S(IV), whereas the possibility exists as well of catalytic pathways for this reaction, either homogeneous or heterogeneous, e.g., with carbon particles [Cofer et al., 1981]. Finally, it should be noted that while the occurrence of reaction between dissolved NO₂ and S(IV) has been recognized [Nash, 1970, 1979; Takeuchi et al., 1977; Sato et al., 1979], information is lacking regarding the identity of the products, reaction stoichiometry, and kinetics.

Deposition to Surface Water

The rate of deposition of a gas to surface water in the ambient atmosphere is conveniently evaluated [Liss, 1971] as $J_G = K_G[G]$, where J_G represents the deposition flux, $[G]$ represents the concentration of gas phase material, and K_G represents the overall mass transfer coefficient referred to the gas phase. As discussed in Appendix A, the overall mass transfer coefficient may be evaluated as

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{ak_L HRT} \quad (14)$$

where k_G and k_L are the gas and liquid phase mass transfer coefficients and α represents an enhancement coefficient, the magnitude of which depends on the equilibrium reactive solubility of the gas, the kinetics of reaction, and the rates of aqueous phase convective and diffusive mass transport.

By using the criteria developed in Appendix A it is possible to ascertain readily whether the rate of uptake of NO₂ by surface water is so fast that the rate is controlled by gas phase mass transport, as has been assumed by previous investigators [Liss, 1976; Hicks and Liss, 1976; Kabel, 1976, 1979; Slinn *et al.*, 1978]. The situation of gas-phase-controlled mass transport may arise in either of two ways. First, the gas may be sufficiently soluble, by physical (Henry's law) dissolution alone without further reaction, that deposition to the surface is limited by gas phase resistance. As noted in Appendix A (condition (A6)), the criterion for this situation is that the Henry's law coefficient greatly exceed $H^{(phys)} (\equiv k_G/k_L RT)$. To test this condition, we take $k_G = 1 \text{ cm s}^{-1}$, characteristic of the average gas phase mass transfer coefficient appropriate for a low molecular weight gas above surface water [Slinn *et al.*, 1978]; average values of k_L have been suggested to be 10–20 cm h^{-1} for ocean water [Slinn *et al.*, 1978] and 1–5 cm h^{-1} for lakes [Liss, 1976]. The resulting values of $H^{(phys)}$ range from 7–140 $M \text{ atm}^{-1}$, 3 to 4 orders of magnitude greater than H_{NO_2} . Thus the uptake of NO₂ by surface water cannot be gas phase mass transport controlled as a consequence of a high physical solubility of the gas.

The second mechanism for gas-phase-controlled deposition is that of physical dissolution followed by rapid chemical reaction to form a much more soluble product. We have already noted that NO₂ is capable, thermochemically, of undergoing such reactions, i.e., yielding the much more soluble nitrite or nitrate ions. (In the terminology of Appendix A, η , the ratio of the total concentration of dissolved material at equilibrium to the concentration of the physically dissolved gas, greatly exceeds unity.) Thus the question that must be addressed here is whether the reaction of physically dissolved NO₂ is sufficiently fast. As shown in Appendix A, this condition may be tested by comparing the characteristic time for aqueous phase reaction of physically dissolved NO₂,

$$\tau_r^{(\text{NO}_2)} \equiv - \frac{1}{[\text{NO}_2(\text{aq})]} \frac{\partial[\text{NO}_2(\text{aq})]}{\partial t} \quad (15)$$

with the quantity $D_{\text{aq}}(HRT)^2/k_G^2$. Here D_{aq} is the aqueous phase diffusion coefficient of the dissolved gas, which may be taken as $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for NO₂ in water, estimated using the semi-empirical correlation of Wilke and Chang [1955]. For $k_G = 1 \text{ cm s}^{-1}$, the resulting value of $D_{\text{aq}}(HRT)^2/k_G^2$ is $6 \times 10^{-7} \text{ s}$; thus, according to the criterion (All'') developed in Appendix A, in order for the deposition of NO₂ to be controlled predominately (>90%) by gas phase mass transport $\tau_r^{(\text{NO}_2)}$ must be less than $6 \times 10^{-9} \text{ s}$. For $\tau_r^{(\text{NO}_2)}$ greater than this value but less than $6 \times 10^{-5} \text{ s}$ both gas phase mass transport and aqueous phase mass transport and reaction must be considered. Finally, for $\tau_r^{(\text{NO}_2)}$ greater than $6 \times 10^{-5} \text{ s}$ the uptake of NO₂ by surface water will be controlled predominately (>90%) by aqueous phase reaction and/or mass transport.

In order to evaluate $\tau_r^{(\text{NO}_2)}$, assumption must be made regarding the mechanism whereby NO₂ reacts in surface water. As demonstrated by Lee and Schwartz [1981], there is

no evidence for any first-order reaction of NO₂ with liquid water. The present results permit this conclusion to be extended also to reaction in the presence of dissolved O₂. For reaction of NO₂ with a second dissolved NO₂ molecule or with dissolved NO, $\tau_r^{(\text{NO}_2)}$ may be evaluated as $(k_1 H_{\text{NO}_2} p_{\text{NO}_2})^{-1}$ or as $(k_2 H_{\text{NO}} p_{\text{NO}})^{-1}$, respectively; for partial pressures of NO₂ and NO of 10^{-7} atm , the rate and solubility constants given above yield $\tau_r^{(\text{NO}_2)} = 14$ and 70 s, respectively, for the two reactions and correspondingly greater for lower partial pressures. Thus reaction of dissolved NO₂ by (R1) or (R2) is also too slow, by orders of magnitude, for the rate of uptake of NO₂ by surface water to be appreciably influenced by gas phase resistance to mass transport, much less controlled by it. The possibility yet remains that NO₂ may react with other substances present in surface water; this is considered below. Certainly, however, in the absence of such other reactions it is established that the uptake of NO₂ by surface water is controlled by aqueous phase mass transport and/or reaction; i.e., the overall mass transport coefficient is given simply by

$$K_G = \alpha k_L HRT \quad (16)$$

Thus, in order to estimate this rate of uptake it is necessary to evaluate the enhancement coefficient α for representative conditions.

As discussed in Appendix A, α ranges from unity (for slow reactions) upwards. For $\alpha = 1$, i.e., uptake governed solely by aqueous phase convective mass transport of the physically dissolved gas, the rate of uptake of a sparingly soluble gas such as NO₂ is quite low. Thus for $k_L = 10 \text{ cm h}^{-1}$ and $H = 7 \times 10^{-3} M \text{ atm}^{-1}$, $K_G = 5 \times 10^{-4} \text{ cm s}^{-1}$. We note further that the condition that uptake of the gas be aqueous phase controlled places a bound on α , viz. $\alpha \leq 0.1 k_G/k_L HRT$ (equation (A16)). For representative values of k_G (1 cm s^{-1}) and k_L (10 cm h^{-1}) and for $H = 7 \times 10^{-3} M \text{ atm}^{-1}$, the resulting bound on α is 200. At this point it might be noted that for $\alpha \leq 200$, i.e., $K_G \leq 0.1 \text{ cm s}^{-1}$, the partial residence time of NO₂ with respect to dry deposition to surface water becomes quite large. If this residence time is approximated [Slinn *et al.*, 1978] as Z_{mix}/K_G , where Z_{mix} is the mixing height, then for $Z_{\text{mix}} = 1 \text{ km}$, the characteristic time of dry deposition is at least 300 hours, greatly in excess of the characteristic time of removal of NO₂ by gas phase reaction, e.g., with OH radical, as noted above.

We now address values of α necessary to evaluate the flux of NO₂ into surface water. To examine whether aqueous phase reaction of NO₂ is sufficiently fast to cause appreciable enhancement of this flux above that given by convective mixing of the physically dissolved gas it is necessary, as shown in Appendix A, to compare $\tau_r^{(\text{NO}_2)}$ to τ_{cd} , a characteristic time that reflects the competition between convective and diffusive mass transport, evaluated as $\tau_{\text{cd}} = D_{\text{aq}}/k_L^2$. In particular, it is shown (equation (A17')) that for $\tau_{\text{cd}}/\tau_r \leq 0.3$, the reaction is so slow that the rate of uptake becomes controlled predominately by aqueous phase convective mass transport of the physically dissolved gas ($\alpha < 1.1$); i.e., the rate of uptake is independent of the rate of aqueous phase reaction. Values of τ_{cd} corresponding to representative values of k_L are given in Table 2 as are the partial pressures (p^*) of NO₂ and NO that would, by (R1) and (R2), respectively, result in $\tau_r^{(\text{NO}_2)} = \tau_{\text{cd}}/0.3$. For partial pressures of NO₂ and NO lower than p^* the uptake of NO₂ is governed solely

TABLE 2. Partial Pressures of NO₂ and NO for the Onset of Enhancement of Uptake of NO₂ by Surface Water by Reactions (R1) and (R2)

	k_L^a , cm h ⁻¹	τ_{cd}^b , s	$p_{NO_2}^{*c}$, atm	p_{NO}^{*c} , atm
Lake	3	30	7×10^{-9}	7×10^{-8}
Ocean	20	0.6	2×10^{-7}	2×10^{-6}

^a Representative values of k_L are from *Liss* [1976] and *Slinn et al.* [1978] for lake and ocean surfaces, respectively.

^b Evaluated as $\tau_{cd} = D_{aq}/k_L^2$.

^c For enhancement coefficient $\alpha = 1.1$.

by aqueous phase mass transport, whereas for partial pressures greater than p^* there is significant enhancement of the rate of uptake as a consequence of aqueous phase reaction (R1) or (R2), respectively.

Examination of the values of p^* given in Table 2 shows that the partial pressures at which α departs significantly from unity are within the range commonly found in regions affected by pollutant nitrogen oxides, especially for low values of k_L . For values of p_{NO_2} or p_{NO} within an order of magnitude of the respective value of p^* , α can be evaluated conveniently as

$$\alpha = 1 + \tau_{cd}/3 \tau_r \quad \tau_{cd}/\tau_r \leq 3 \quad (17)$$

For still higher partial pressures the approximation

$$\alpha k_L = (D_{aq}/\tau_r)^{1/2} \quad \tau_{cd}/\tau_r \geq 2.3 \quad (18)$$

is suitable.

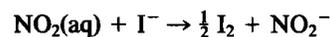
To conclude this discussion, it remains necessary to consider other potential aqueous phase reactions of NO₂ that may affect the deposition of this gas to surface water. Before considering specific reactions it is instructive to draw some general conclusions. We have noted above that for aqueous phase reaction of NO₂ to be sufficiently fast that the uptake is controlled by gas phase mass transport, $\tau_r^{(NO_2)}$ must be less than 6×10^{-9} s. In general, for a second-order reaction of NO₂ with a dissolved reagent R, $\tau_r^{(NO_2)}$ may be evaluated as $(k_R[R])^{-1}$ where [R] is the reagent concentration and k_R is the rate constant. Since k_R cannot exceed the diffusion-controlled encounter rate constant $5 \times 10^9 M^{-1} s^{-1}$, the reagent concentration required for the uptake of NO₂ to be controlled by gas phase mass transport must exceed $3 \times 10^{-2} M$. Concentrations of this magnitude are found in sea water only for Cl⁻, Na⁺, Mg²⁺, and SO₄²⁻, with which NO₂ does not appear to exhibit any interaction at all (much less diffusion-controlled reaction) [*Hofsteyer and Kwanten*, 1972]. Thus in contradiction to the assumption of the several authors noted above that because of the high reactivity of NO₂ its uptake to surface water would be controlled by gas phase mass transport, it may be concluded that the reaction of NO₂ in surface water cannot be sufficiently fast as to lead to gas phase mass transport controlled uptake.

A similar consideration may be given as to whether there is any aqueous phase reagent present in sufficient concentration in natural waters that reaction with dissolved NO₂ can be fast enough (still with assumed upper limit k_R) that the uptake of NO₂ is even significantly affected by gas phase resistance to mass transport. Again for $k_R = 5 \times 10^9 M^{-1} s^{-1}$, the minimum reagent concentration in order that the uptake of NO₂ not be controlled entirely by aqueous phase mass transport and/or reaction is $3 \times 10^{-6} M$. Examination

of inorganic species present in seawater in this concentration range [*Holland*, 1978] also suggests no substance that is likely to react with NO₂ by oxidation or reduction reaction. Hence it would appear that the uptake of NO₂ in seawater and fresh water is controlled entirely by aqueous phase mass transport and/or reaction.

Last, we consider the range of reagent concentrations that might give rise to values of α significantly greater than unity, still assuming upper limit values for k_R . For $k_L = 20$ and 3 cm h⁻¹ for oceans and lakes, respectively, the condition $\tau_{cd} \leq 0.3 \tau_r$ necessary for α to fall within 10% of unity allows bounds to be placed on [R] of $1 \times 10^{-10} M$ and $2 \times 10^{-12} M$, respectively. Reagent concentrations in excess of these values may potentially give rise to values of α significantly greater than unity, depending on the value of k_R .

Little information is available that permits exhaustive examination of substances in this concentration range that may react with NO₂. However, one such species for which considerable information is available is iodide ion. Reaction with I⁻ has recently been suggested [*Garland et al.*, 1980] to contribute significantly to the uptake by seawater of ozone, which has a solubility in water very similar to that of NO₂ ($H_{O_3} = 1.1 \times 10^{-2} M \text{ atm}^{-1}$ at 25°C). The oxidation of I⁻ by NO₂,



has long been recognized [*Raschig and Prahl*, 1929; *Szabó et al.*, 1956], although the rate constant for this reaction, k_{I^-} , has not been measured. An upper limit value to this rate constant may be derived from the measurements of *Nash* [1970], again by assuming that the rate of reaction of NO₂ with *o*-methoxyphenol is diffusion controlled. The resulting upper limit value for k_{I^-} is $2.8 \times 10^6 M^{-1} s^{-1}$. This value indicates that for $k_L = 20$ cm h⁻¹, [I⁻] must exceed $1.8 \times 10^{-7} M$ in order that α depart significantly from unity. *Wong* [1976] reports surface concentrations of I⁻ in ocean water ranging from $(0.4 \text{ to } 1) \times 10^{-7} M$. Hence there is only a slight enhancement of the rate of uptake of NO₂ to ocean water resulting from reaction with I⁻.

In addition to inorganic species with which NO₂ may react, the possibility exists as well of rapid aqueous phase reaction of NO₂ with dissolved organic species present in surface water that might give rise to values of α appreciably greater than unity. Such reactions have also been proposed recently as a sink for O₃ [*Garland et al.*, 1980]. Little is known concerning the reactivity of NO₂ to naturally occurring dissolved organic materials. However, it seems quite reasonable to suppose that NO₂ reacts rapidly with substances such as humic acids (which consist of polymeric substituted phenols [*Stevenson and Butler*, 1969]) in analogy to the high reactivity of NO₂ toward *o*-methoxyphenol [*Nash*, 1970]; *Stevenson and Swaby* [1964] report nitrosation of humic acid by nitrous acid under conditions in which dissolved NO₂ would be present [*Abel and Schmid*, 1928]. Marine humic acid concentrations of 100–400 µg/l have been reported [*Stuermer and Harvey*, 1977], and a molecular weight of ca. 500 is given. [*Stuermer and Harvey*, 1974]. suggesting concentrations of the order of $5 \times 10^{-7} M$. For a rate constant taken as $1 \times 10^9 M^{-1} s^{-1}$, one obtains $\tau_r^{(NO_2)} = 2 \times 10^{-3}$ s, well less than estimated values of τ_{cd} , 0.6–3.0 s (Table 2). The resulting values of the enhancement coefficient α , evaluated as $(\tau_{cd}/\tau_r)^{1/2}$, range from 20 to 120; i.e., a

considerable enhancement of the rate of uptake over that given by convective mixing of the physically dissolved material. It should be stressed that the above values must be considered only a first estimate in view of the assumptions made. Nevertheless, this estimate would strongly implicate reaction with naturally occurring dissolved organic compounds as a major sink process for NO₂ in surface waters. We would note also that the value of the humic acid concentration employed in the present calculation (250 μg/l) represents only a fraction of dissolved organic carbon present in ocean water, typically 1 mg/l or more [Wangersky, 1972] and that reaction of NO₂ with other dissolved organic substances might also be expected. Also, we would note that because of their surface active properties, many organic substances tend to concentrate at or near the air-sea interface [Garrett, 1970; Williams, 1967], leading to a possible enhancement of the rate of reaction of NO₂ with these materials above that estimated here.

To conclude the discussion of NO₂ reaction with natural organic materials, a final observation appears pertinent. Hill and Chamberlain [1976] report that the rate of uptake of NO₂ (at 1–2.5 × 10⁻⁷ atm) by a vegetation canopy is comparable to that of SO₂ and O₃ (K_G ~ 1.7–2.8 cm s⁻¹). Although it might be argued that the rate of uptake of SO₂ is due to its high solubility (as HSO₃⁻) in water contained in plant tissue, this cannot be the mechanism for the rapid uptake of NO₂ or O₃. Rather, it seems necessary to invoke a rapid sink for both these gases by reaction with plant materials. In the case of NO₂ this requires direct reaction with organic material present in plant tissues rather than reactive dissolution by (R1) followed by subsequent reaction, as has been previously supposed [Hill, 1971].

CONCLUSIONS

By comparison of the rate of (R1), 2NO₂(g) + H₂O(l) → 2H⁺ + NO₂⁻ + NO₃⁻, in N₂ and air it is established that this reaction is insensitive to the presence of O₂. This result permits the Henry's law coefficient for NO₂ and rate constant for (R1) obtained by Lee and Schwartz [1981] to be employed in evaluating the rates of aqueous phase reactions of NO₂ under ambient conditions. It is found that the rates of (R1) as well as (R2), NO(g) + NO₂(g) + H₂O(l) → 2H⁺ + 2NO₂⁻ are quite slow at ambient partial pressures of these gases—too slow to allow these reactions to reach equilibrium either in cloud liquid water (~1 g/m³) or in liquid-water-containing clear air aerosols and too slow as well to represent a significant sink process for ambient NO₂. Catalytic pathways for these reactions are potentially important. A catalytic mechanism for (R1) involving Fe, however, is too slow to contribute appreciably to the rate of uptake of NO₂ by cloud liquid water for representative Fe concentration. Based on an upper limit estimate of the rate constant of reaction of NO₂ with dissolved sulfur IV, 2.5 × 10⁷ M⁻¹ s⁻¹, it appears that NO₂ may react at an appreciable rate with S(IV) dissolved in cloud liquid water.

The rate of NO₂ deposition to surface water was examined. The uptake is slow, being controlled by aqueous phase mass transport and/or reaction and not by gas phase mass transport, as has been previously assumed. Reactions (R1) or (R2) enhance the rate of uptake over that given by the physical solubility of NO₂ and the convective mixing rate of the surface water only at high NO₂ or NO pressure. Reaction

of NO₂ with trace inorganic and organic species present in natural waters was also considered. It would appear that reaction with materials such as humic acids may enhance the rate of NO₂ uptake appreciably above that governed solely by convective mixing of the physically dissolved material. Nevertheless the rate of NO₂ removal from the atmosphere by this process remains very slow compared to gas phase reactions, e.g., oxidation to HNO₃ by reaction with OH radical.

APPENDIX A: FACTORS GOVERNING RATE OF UPTAKE OF A REACTIVE GAS TO SURFACE WATER

The rate of uptake of a reactive gas to surface waters depends in general on the rate of mass transfer in the gas and aqueous phases and on the rate of aqueous phase reaction of the dissolved gas. Frequently, however, only one of these processes will be controlling, depending on the relative magnitude of these rates and on the physical and reactive solubility of the gas. Here we adduce criteria that must be satisfied in order that the rate of uptake be controlled by one or another of these mechanisms and present expressions for the rate of uptake as controlled by these mechanisms.

The rate of uptake of a reactive gas may be expressed [Slinn *et al.*, 1978] in terms of the gas phase mass transfer coefficient as

$$J_G = K_G[G] \quad (A1)$$

where

$$\begin{aligned} J_G & \text{ material flux, mol cm}^{-2} \text{ s}^{-1}; \\ [G] & \text{ is the bulk concentration of the gas, mol cm}^{-3}; \\ K_G & \text{ is the overall mass transfer coefficient referred to the} \\ & \text{ gas phase, cm s}^{-1}. \end{aligned}$$

The overall gas phase mass transfer coefficient combines the effects of both gas and aqueous phase mass transfer and aqueous phase reactive uptake [Liss, 1971]:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{\alpha k_L HRT} \quad (A2)$$

Here k_G and k_L are the mass transfer coefficients characterizing the gas and liquid phases, respectively, and α is an enhancement coefficient reflecting the increased rate of uptake of a gas that undergoes subsequent reaction in the aqueous phase. The enhancement coefficient describing the rate of uptake of a gas undergoing reversible first-order aqueous phase reaction is given by [Hoover and Berkshire, 1969; Danckwerts, 1970; Liss, 1971]

$$\alpha = \frac{\eta}{1 + (\eta - 1) \tanh \kappa^{1/2}/\kappa^{1/2}} \quad (A3)$$

where η is the ratio, at equilibrium, of the total concentration of the dissolved material to that of the physically dissolved gas and κ is a dimensionless reaction rate constant,

$$\kappa \equiv \frac{\tau_{cd}}{\tau_r} \frac{\eta}{\eta - 1}$$

Here τ_{cd} is a characteristic time describing the competition between convective and diffusive mass transport,

$$\tau_{cd} \equiv D_{aq}/k_L^2$$

and τ_r is the characteristic time of reaction,

$$\tau_r = k_r^{-1}$$

Here D_{aq} is the aqueous phase diffusion coefficient of the dissolved reagent gas and k_r is the first-order rate coefficient. For a reaction other than first-order, (A3) approximates α provided that we identify

$$\tau_r = -[\text{reag}]/(\partial[\text{reag}]/\partial t)$$

where $-\partial[\text{reag}]/\partial t$ represents the rate of decrease of the aqueous phase reagent concentration by reaction.

Gas-Phase-Controlled Uptake

From (A2) we may set the criterion for gas-phase-controlled mass transport as

$$k_G \leq 0.1 \alpha k_L HRT \quad (\text{A4})$$

which, when combined with (A3) yields

$$\frac{\eta - 1}{\eta} \frac{\tanh \kappa^{1/2}}{\kappa^{1/2}} + \frac{1}{\eta} \leq 0.1 \frac{k_L HRT}{k_G} \quad (\text{A5})$$

Condition (A5) may be satisfied in a number of ways. First, we note that the function $F(x) = \tanh x/x \leq 1$ for all values of the argument x , and hence satisfaction of the condition

$$0.1 k_L HRT \geq k_G \quad (\text{A6})$$

is sufficient to assure satisfaction of (A5) and hence of (A4) irrespective of the values of η and κ ; i.e., the gas is sufficiently soluble by physical (Henry's law) dissolution alone that the rate of uptake is controlled entirely by gas phase mass transfer. Equation (A6) may be used to estimate the value of the Henry's law coefficient of a gas (in water) $H^{(\text{phys})}$ such that for $H \geq 10 H^{(\text{phys})}$, the rate of uptake of the gas by surface water is controlled by gas phase mass transport irrespective of the kinetics of subsequent aqueous phase reaction:

$$H^{(\text{phys})} \equiv k_G/k_L RT \quad (\text{A7})$$

In order to obtain an estimate of $H^{(\text{phys})}$ we evaluate this quantity for representative values of k_G and k_L . For $k_G = 1 \text{ cm s}^{-1}$ and $k_L = 10 \text{ cm h}^{-1}$, characteristic of the mixed layer of the atmosphere and of the surface layer of ocean water, respectively [Slinn *et al.*, 1978], $H^{(\text{phys})} \approx 10 \text{ M atm}^{-1}$. Henry's law coefficients substantially greater than 10 M atm^{-1} are characteristic only of highly soluble gases, e.g., CH_3OH (200 M atm^{-1}), H_2O_2 ($1 \times 10^5 \text{ M atm}^{-1}$) (as evaluated from data tabulated by Wagman *et al.* [1968]) or HNO_3 ($2 \times 10^5 \text{ M atm}^{-1}$) [Schwartz and White, 1981a].

We now address the more interesting situation in which the rate of uptake of the reactive gas is sufficiently fast to be controlled by gas phase mass transport (condition (A5) satisfied) as a consequence of chemical reaction in the aqueous phase and not simply because of a high physical solubility of the gas. In this case, condition (A6) is not satisfied. We set

$$\lambda \equiv k_L HRT/k_G < 10$$

With this definition, condition (A5) now becomes

$$\tanh \kappa^{1/2}/\kappa^{1/2} \leq \mu \quad (\text{A8})$$

where $\mu \equiv 0.1\lambda - (1 - 0.1\lambda)/(\eta - 1)$.

We note that the function $y = F(x) = \tanh x/x$ is a monotonically decreasing function of x . Hence the condition (A8), $F(\kappa^{1/2}) \leq \mu$, is equivalent to

$$\kappa^{1/2} \geq F^{-1}(\mu) \quad (\text{A9})$$

and in turn

$$\kappa \geq [F^{-1}(\mu)]^2 \quad (\text{A10})$$

where $F^{-1}(y)$, the inverse of $F(x)$, is a monotonically decreasing function of x . For values of the argument $y < 0.5$, $F^{-1}(y)$ is closely approximated as y^{-1} . Hence for values of $\mu < 0.5$, condition (A10) becomes

$$\kappa \geq \mu^{-2} \quad \mu \leq 0.5 \quad (\text{A10}')$$

or, by substitution,

$$\tau_r \leq \left(\frac{\eta}{\eta - 1} \right) \tau_{cd} \mu^2 \quad \mu \leq 0.5 \quad (\text{A11})$$

Condition (A11) is both necessary and sufficient for the aqueous phase reaction of the gas to be so fast that the uptake by surface water is controlled by gas phase mass transport. It may be seen that a less stringent condition, which is therefore necessary but not sufficient, is

$$\tau_r \leq 0.01 \left(\frac{\eta}{\eta - 1} \right) \tau_{cd} \lambda^2 \quad \lambda < 5 \quad (\text{A11}')$$

Condition (A11') may be readily tested to address whether further examination, by condition (A11), is required. Additionally, we note that for the situation of particular interest in which the reactive solubility of the material is much greater than the physical solubility, i.e., $\eta \gg 1$, condition (A11') becomes

$$\tau_r \leq 0.01 \tau_{cd} \lambda^2 \quad \lambda < 5 \quad \eta \gg 1 \quad (\text{A11}'')$$

Finally, we observe that $\tau_{cd} \lambda^2 = D_{aq}(HRT)^2/k_G^2$, and hence condition (A11') is equivalent to

$$\tau_r \leq 0.01 D_{aq}(HRT)^2/k_G^2 \quad \lambda < 5 \quad \eta \gg 1 \quad (\text{A11}''')$$

This condition serves as a criterion for demonstrating that the aqueous phase reaction is potentially fast enough that the uptake of the gas to surface water is controlled by gas phase mass transport. If, however, this condition is not satisfied, then it is established that the reaction is not sufficiently fast for uptake to be controlled by gas phase mass transport, i.e., that aqueous phase mass transport and/or reaction must be considered.

Aqueous-Phase-Controlled Uptake

By analogy to (A4), (A5), and (A8), the condition that must be satisfied in order that the uptake of a reactive gas be controlled entirely by aqueous phase mass transport or reaction is

$$\tanh \kappa^{1/2}/\kappa^{1/2} \geq \nu \quad (\text{A12})$$

where $\nu \equiv 10\lambda - (1 - 10\lambda)/(\eta - 1)$. As before, condition (A12) is equivalent to a bound on κ ,

$$\kappa \leq [F^{-1}(\nu)]^2 \quad (\text{A13})$$

For values of $\nu \leq 0.5$, condition (A13) is equivalent to

$$\kappa \geq \nu^{-2} \quad \nu \leq 0.5 \quad (\text{A13}')$$

or, by substitution,

$$\tau_r \geq \left(\frac{\eta}{\eta - 1} \right) \tau_{cd} \nu^2 \quad \nu \leq 0.5 \quad (\text{A14})$$

Condition (A14) is both necessary and sufficient for the aqueous phase reaction to be so slow that the uptake to surface water is controlled by aqueous phase reaction and/or mass transport. It may be seen that a more stringent condition, which is therefore sufficient but not necessary, is

$$\tau_r \geq 100 \left(\frac{\eta}{\eta - 1} \right) \tau_{cd} \lambda^2 \quad \lambda \leq 0.05 \quad (\text{A14}')$$

Finally, we again specialize to cases of high reactive solubility, i.e., $\eta \gg 1$, for which condition (A14') becomes

$$\tau_r \geq 100 \tau_{cd} \lambda^2 \quad \lambda \leq 0.05 \quad \eta \gg 1 \quad (\text{A14}'')$$

or, equivalently,

$$\tau_r \geq 100 D_{aq} (HRT)^2 / k_G^2 \quad \lambda \leq 0.05 \quad \eta \gg 1 \quad (\text{A14}''')$$

If condition (A14''') is satisfied, then it is established that aqueous phase reaction is sufficiently slow that the uptake of the gas is controlled entirely by aqueous phase mass transport and/or reaction and that gas phase mass transport is sufficiently fast that it presents no ($\leq 10\%$) resistance to uptake of the material. The criteria (A11''') and (A14''') permit the controlling phase for uptake of reactive gases by surface waters to be readily identified. In particular, if it is established that the uptake is controlled by aqueous phase mass transport and/or reaction, then the overall mass transport coefficient referred to the gas phase material is simply

$$K_G = \alpha k_L HRT \quad (\text{A15})$$

The condition that gas phase resistance to mass transport be small relative to aqueous phase, expressed in terms of α , is

$$\alpha \leq 0.1 k_G / k_L HRT \quad (\text{A16})$$

It is instructive to examine expression (A3) for α in somewhat more detail, since frequently, depending on the magnitudes of η and κ , this expression may be considerably simplified, resulting in ease of estimating this quantity as well as enhanced physical insight.

Low κ . For low values of the dimensionless rate coefficient κ the tanh function in (A3) may be expanded in a power series, yielding, to first order,

$$\alpha \approx 1 + \tau_{cd} / 3\tau_r \quad \tau_{cd} / \tau_r \leq 3 \quad \eta \geq 100 \quad (\text{A17})$$

where the indicated bound for the applicability of the approximation represents a 10% error in α . The approximation (A17), except for the factor of 3, has been given previously in this context [Slinn *et al.*, 1978] on the basis of qualitative arguments. For still lower values of τ_{cd} / τ_r , α is seen to approach unity,

$$\alpha \approx 1 \quad \tau_{cd} / \tau_r \leq 0.3 \quad (\text{A17}')$$

where, again, the indicated bound represents a 10% error in α . In this limit the reaction of the gas is so slow that the rate of uptake is controlled entirely by convective mixing of the physically dissolved material.

Intermediate and high κ . For values of $\kappa^{1/2} \geq 1.5$ the tanh function is equal to unity within 10%, and hence

$$\alpha \approx \frac{\eta \kappa^{1/2}}{\kappa^{1/2} + \eta - 1} \quad \kappa \geq 2.3 \quad (\text{A18})$$

This expression may be simplified further depending on the relative values of $\kappa^{1/2}$ and η . For intermediate values of κ such that $\kappa^{1/2} \ll \eta - 1$,

$$\alpha \approx \left(\frac{\eta}{\eta - 1} \right) \kappa^{1/2} = \frac{1}{k_L} \left(\frac{\eta}{\eta - 1} \right)^{3/2} \left(\frac{D_{aq}}{\tau_r} \right)^{1/2} \quad (\text{A19})$$

$$2.3 \leq \kappa \ll (\eta - 1)^2$$

In particular, for $\eta \gg 1$, and for a reaction m th order in the reagent gas ($\tau_r^{-1} = H^{m-1} p^{m-1} k_m$)

$$\alpha k_L = (D_{aq} H^{m-1} p^{m-1} k_m)^{1/2} \quad \eta \gg 1 \quad (\text{A20})$$

This expression for the rate of uptake corresponds to the familiar result for the uptake of a reactive gas for a diffusion-controlled reagent concentration profile [Danckwerts, 1970]. For these intermediate values of κ , it is thus seen that reaction is sufficiently fast for the diffusion-controlled concentration profile to be established on a time scale rapid compared to that of convective mixing.

Finally, we consider extremely high values of κ , $\kappa^{1/2} \gg \eta - 1$, for which (A18) becomes

$$\alpha = \eta \quad \kappa \gg (\eta - 1)^2 \quad (\text{A21})$$

In this limit the reaction is sufficiently fast that equilibrium is established on a time scale short relative to that of convection. The uptake then proceeds under convective control but with the equilibrium mixture of reactant and product being the transported substance.

In summary, the several expressions developed here, which are summarized in Table A1, may be applied, for known or assumed values of k_G , k_L , D_{aq} , κ , and τ_r to evaluate the rate of uptake of a reactive gas by surface water and to interpret this process as occurring under control of gas phase mass transport, aqueous phase mass transport or aqueous phase chemical reaction.

TABLE A1. Criteria Delimiting Mass Transport Regimes for Uptake of Reactive Gases by Surface Waters

Limit	Criterion	Constraint
$K_G \approx k_G$	$\lambda > 10$ or $\tau_r \leq 0.01 \tau_{cd} \lambda^2 \eta / (\eta - 1)^a$	$\lambda < 5$
$K_G \approx \alpha k_L HRT$	$\tau_r \geq 100 \tau_{cd} \lambda^2 \eta / (\eta - 1)^b$	$\lambda < 0.05$
$\alpha = \eta$	$\kappa \gg (\eta - 1)^2$	
$\alpha = \kappa^{1/2} \eta / (\eta - 1)$	$2.3 \leq \kappa \ll (\eta - 1)^2$	
$\alpha = 1 + \tau_{cd} / 3\tau_r$	$\tau_{cd} \leq 3 \tau_r$	$\eta \geq 100$
$\alpha = 1$	$\kappa \leq 0.3$	

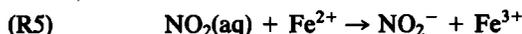
Symbols employed are defined as follows: $\lambda \equiv k_L HRT / k_G$; $\tau_{cd} \equiv D_{aq} / k_L^2$; $\kappa \equiv (\tau_{cd} / \tau_r) (\eta / (\eta - 1))$; $\tau_r \equiv -[\text{reag}] / (\partial[\text{reag}] / \partial t)$.

^a Necessary condition.

^b Sufficient condition.

APPENDIX B: RATE OF FE-CATALYZED REACTIONS (R1)

As noted in the text, the sequence of reactions



represents a potential catalytic path for (R1). Here we evaluate the rate constant k_5 . In a study of the oxidation of Fe^{2+} by nitrous acid,



the observed rate law [Abel *et al.*, 1936] was

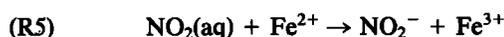
$$\frac{d[\text{Fe}^{3+}]}{dt} = k_{\text{obs}}[\text{Fe}^{2+}][\text{HNO}_2]^2/p_{\text{NO}} \quad (\text{B1})$$

This rate law has been interpreted according to the following mechanism, which is similar to that inferred for nitrous acid decomposition [Abel and Schmid, 1928]:

Rapid equilibrium



Slow, rate determining



Rapid equilibrium



Rapid equilibrium



Equilibria (R8) and (R10) maintain an aqueous phase NO_2 concentration

$$[\text{NO}_2(\text{aq})] = \frac{K_8}{H_{\text{NO}}} \frac{[\text{HNO}_2]^2}{p_{\text{NO}}} \quad (\text{B2})$$

Hence

$$R_7^{(\text{aq})} = \frac{d[\text{Fe}^{3+}]}{dt} = k_5[\text{Fe}^{2+}][\text{NO}_2(\text{aq})] \\ = k_5 \frac{K_8}{H_{\text{NO}}} [\text{Fe}^{2+}][\text{HNO}_2]^2/p_{\text{NO}} \quad (\text{B3})$$

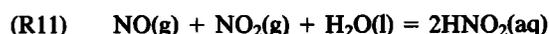
Comparison of (B3) with (B1) gives

$$k_5 = k_{\text{obs}}H_{\text{NO}}/K_8 \quad (\text{B4})$$

In order to evaluate $R_5^{(\text{aq})}$, e.g., in cloud droplets, we require the product $H_{\text{NO}_2}k_5$, which may be evaluated as

$$H_{\text{NO}_2}k_5 = k_{\text{obs}}(H_{\text{NO}}H_{\text{NO}_2}/K_8) \\ = k_{\text{obs}}K_{11} \quad (\text{B5})$$

where K_{11} is the equilibrium constant of the reaction



and has the value $126 \text{ M}^2 \text{ atm}^{-2}$ at 25°C [Schwartz and White, 1981a]. From the value $k_{\text{obs}} = 4.0 \text{ M}^{-2} \text{ atm s}^{-1}$ obtained by Abel *et al.* [1936], $H_{\text{NO}_2}k_5 = 5.0 \times 10^2 \text{ atm}^{-1} \text{ s}^{-1}$. Employing $H_{\text{NO}_2} = 7 \times 10^{-3} \text{ M atm}^{-1}$ [Lee and Schwartz, 1981], we obtain $k_5 = 7.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

The study of Abel *et al.* [1936] also provides qualitative information concerning the rate of (R6). When Fe^{3+} was added to the reaction mixture in 7-fold excess over Fe^{2+} , no noticeable decrease was observed in the net rate of Fe^{3+} formation. Assuming an experimental precision of, say, 10%, then k_6 must be at least a factor of 70 less than k_5 .

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