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KINETICS OF REACTIVE DISSOLUTION OF NITROGEN OXIDES INTO AQUEOUS SOLUTION

Stephen E. Schwartz

Environmental Chemistry Division
Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

Warren H. White

Center for Air Pollution Impact and Trend Analysis
Washington University
St. Louis, Missouri 63130

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1. INTRODUCTION

It would be difficult to cite a process so common to the industrial chemical scene and yet posing so severe a challenge to our comprehension of its fundamental mechanisms as that of the absorption of nigrogen oxides in water to produce nitric acid.

Carberry (1959)

The reactive dissolution of nitrogen oxides into aqueous solution, i.e., physical dissolution of NO_2 and/or NO followed by aqueous-phase reaction to form nitrous and/or nitric acids, has been postulated to be potentially important as a mechanism of removal of these oxides from the atmosphere, as a means of acidification of precipitation, and as an influence on the composition of atmospheric aerosols (Durham et al., 1981; Lee and Schwartz, 1981a; Liljestrand and Morgan, 1981; Liss, 1976; Orel and Seinfeld, 1977; Söderlund and Svennson, 1976) (see also Chapter 9 in this volume by Anderson and Chapter 10 by Stedman and Shetter). Aqueous-phase reactions of nitrogen oxides are also of interest in environmental science in connection with the mechanism of toxicity of these gases to animals (Goldstein et al., 1977; Mustafa et al., 1979; Pryor and Lightsey, 1981) and to vegetation (Hill, 1971; National Research Council, 1977). These reactions are of interest as well in the search for possible water-based scrubbers for removal of nitrogen oxides from flue gases (Counce, 1980; Faucett et al., 1978) and in development and interpretation of wet analytical methods for analyses of these gases in flue gases (Driscoll, 1974) or ambient air (National Research Council, 1977).

To quantitatively describe aqueous-phase reactions of the nitrogen oxides, it is necessary to develop an understanding of the fundamental equilibrium and kinetic properties of this system. In a previous article (Schwartz and White, 1981) we reviewed the chemical equilibria in this system and presented a fairly consistent picture of these equilibria, including the Henry's law (solubility) equilibria of the reactive oxides NO_2, N_2O_3, and N_2O_4. (The Henry's law constant of NO, which is reversibly and nonreactively soluble in aqueous solution in the absence of other reactive substances, is well established.) It was shown that the nitrogen oxides exhibit only limited solubility according to Henry's law but substantially greater reactive solubility, i.e., by undergoing oxidation or reduction to the much more soluble nitrite or nitrate anions. At low partial pressures of these gases, characteristic of atmospheric conditions, such reactive dissolution will be controlled largely if not entirely by the chemical kinetic rate. Here we examine the kinetics of these reactions.

A parallel route for incorporation of the nitrogen oxides into aqueous solution is gas-phase reaction to form the oxyacid (nitrous or nitric acid) followed by uptake of the gaseous acid by liquid water. Gas-phase formation of HNO_2 and HNO_3 takes place in the atmosphere largely by free-radical reactions the kinetics of which are reasonably well described (Baulch et al., 1980; Crutzen, 1979); direct formation of HNO_2 or HNO_3 by gas-phase molecular reaction, if it occurs at all, is quite slow (Carberry, 1959; England and Corcoran, 1974; Kaiser and Wu, 1977a,b). Aqueous-phase reactions of HNO_2 and HNO_3 (i.e., establishing the respective ionization equilibria) would be expected to be quite fast (Eigen et al., 1964), and consequently the rate of dissolution of gaseous HNO_2 and HNO_3 will be limited entirely by mass transport. Such mass-transport rates are rather well described theoretically for conditions pertinent to either cloud droplets (Freiberg and Schwartz, 1981) or falling raindrops (Hales, 1972), and the rates of in-cloud and below-cloud scavenging of nitric acid vapor have recently been evaluated on this basis (Levine and Schwartz, 1982). Consequently, we do not address these processes further here.

To facilitate the discussion of studies of the aqueous-solution kinetics of the nitrogen oxides, we first present a brief, general review in Section 2 of the kinetics of gas–liquid reactions. In general, the reactive dissolution of a gas into a liquid is a complex process that involves mass transport in both phases and solution-phase reaction of the dissolved gas and whose rate is governed by the combined rates of these several processes. Consequently, to present an interpretation of various laboratory studies, it is necessary to consider these mass-transport processes in some detail. In Section 3 we introduce a nomenclature that facilitates the discussion of the nitrogen oxide reactions in particular by taking into account the rapid equilibria between the so-called simple oxides (NO_2 and NO) and the compound oxides (N_2O_4 and N_2O_3).

The review of the kinetic studies is organized about techniques that have been employed in these studies. These are as follows:

Section 4. Indirect inference from kinetic studies of the decomposition of nitrous acid, kinetics of isotope exchange, diazotization reaction, and so on.

Section 5. Direct measurement of aqueous-phase kinetics.

Section 6. Direct measurement of the rate of uptake of nitrogen oxides by liquid water.

The results of these experiments are expressed as products of various powers of the Henry's law coefficients and kinetic rate constants as appropriate to the various types of experiment. In Section 7 these results are examined in relation to each other to obtain recommended values for the elementary thermochemical and kinetic constants that describe these reactions. Finally, studies of the interaction of nitrogen oxides with dissolved materials are reviewed in Section 8.

As becomes evident below, there is a large body of work pertinent to the reactive dissolution of the nitrogen oxides into aqueous solution. The great majority of this work has been motivated by the role of these reactions in the industrially important manufacture of nitric acid; for a historical account of this technology, the interested reader is referred to the monograph by Chilton (1968). The present chapter relies heavily on this literature. The question thus naturally arises as to whether studies conducted under conditions widely differing from those of the intended application (specifically, partial pressures of the nitrogen oxides orders of magnitude greater than those characterizing the ambient atmosphere) are of utility in the present review. In reply, we would assert that, provided the elementary reactions that comprise the mechanisms are correctly elucidated, the rates inferred from these mechanisms would be applicable under any conditions of interest, specifically including atmospheric conditions of low partial pressures. Nevertheless, we must remember that under laboratory conditions of high partial pressures of the nitrogen oxides, second- and higher-order reactions

Table 1. Reactions of Nitrogen Oxides and Oxyacids[a]

[1] $2NO_2 \overset{w}{=} 2H^+ + NO_2^- + NO_3^-$

[2] $NO + NO_2 \overset{w}{=} 2H^+ \ 2NO_2^-$

[3] $3NO_2 \overset{w}{=} 2H^+ + 2NO_3^- + NO$

[4] $N_2O_4 \overset{w}{=} 2H^+ + NO_2^- + NO_3^-$

[5] $N_2O_3 \overset{w}{=} 2H^+ + 2NO_2^-$

[6] $N_2O_5 \overset{w}{=} 2H^+ + 2NO_3^-$

[7] $2NO_2 = N_2O_4$

[8] $NO + NO_2 = N_2O_3$

[9] $3NO_2 = N_2O_5 + NO$

[10] $3H^+ + 3NO_2^- \overset{w}{=} H^+ + NO_3^- + 2NO$

[11] $NO_2 + NO_2^- = NO_3^- + NO$

[I1] $HNO_3(aq) = H^+ + NO_3^-$

[I2] $HNO_2(aq) = H^+ + NO_2^-$

[a] Reaction numbers correspond to those introduced by Schwartz and White (1981). The prefix G, A, or M to the reaction number is used to denote a gas-, aqueous-, or mixed- (gaseous oxide, aqueous acid) phase reaction. Aqueous acids are expressed as ionized (dissociated) forms. The addition of a prime to a reaction number, e.g., [A11′], denotes nitrous acid expressed as the undissociated form. Equilibria [I1] and [I2] represent the acid dissociation equilibria for nitric and nitrous acid. The symbols $\overset{w}{=}$ and $\overset{w}{\rightarrow}$ refer to equilibria or reactions involving water as a reagent in which H_2O is not explicitly denoted as a reagent. Water activity is taken as unity unless otherwise specified.

Table 2. Equilibria Involving Gaseous and Aqueous Nitrogen Oxides and Oxyacids[a]

Equilibrium Number	Equilibrium	Equilibrium Constant	Value	Units	ΔH° (kcal mol^{-1})
[G7]	$2NO_2(g) = N_2O_4(g)$	$p_{N_2O_4}/p^2_{NO_2}$	6.86	atm^{-1}	−13.7
[G8]	$NO(g) + NO_2(g) = N_2O_3(g)$	$p_{N_2O_3}/p_{NO}p_{NO_2}$	0.535	atm^{-1}	−9.5
[H_{NO}]	$NO(g) = NO(aq)$	$[NO(aq)]/p_{NO}$	1.93(−3)[b]	M atm^{-1}	−2.94
[I2]	$HNO_2(aq) = H^+ + NO_2^-$	$[H^+][NO_2^-]/[HNO_2]$	5.1 (−4)	M	2.5[c]
[M1′]	$2NO_2(g) \overset{w}{=} HNO_2(aq) + H^+ + NO_3^-$	$[HNO_2][H^+][NO_3^-]/p^2_{NO_2}$	4.78(5)	M^3 atm^{-2}	−25.6
[M2′]	$NO(g) + NO_2(g) \overset{w}{=} 2HNO_2(aq)$	$[HNO_2]^2/p_{NO}p_{NO_2}$	1.26(2)	M^2 atm^{-2}	−18.2
[M11′]	$NO_2(g) + HNO_2(aq) = H^+ + NO_3^- + NO(g)$	$[H^+][NO_3^-]p_{NO}/[HNO_2]p_{NO_2}$	3.79(3)	M	−7.4

[a] From Schwartz and White (1981). Equilibrium constants and reaction enthalpies are given for $T = 25°C = 298$ K; equilibrium constants for other temperatures may be evaluated by means of ΔH°.

[b] The notation 1.93(−3) represents 1.93×10^{-3}.

[c] The values for ΔH° [I2] and ΔH° [V2] given by Schwartz and White (1981, Table VII) should be corrected to read 2.5 and −7.0 kcal mol^{-1}, respectively.

will be favored and might mask any first-order reaction that was occurring in parallel, whereas under atmospheric conditions such a first-order mechanism might be dominant. Consequently, we must keep open the possibility of such first-order mechanisms, either with water itself or with other dissolved materials. This possibility can be addressed only by direct experimentation at low partial pressures. As is noted in Section 8, there exist numerous qualitative indications of the existence of such additional pathways for the reactive dissolution of the nitrogen oxides. In this context the present review will serve as well as a guide to the formulation of laboratory experiments to elucidate these pathways.

As noted above, this chapter represents an extension of, and relies heavily on, the authors' previous review (Schwartz and White, 1981) of the chemical and phase (Henry's law) equilibria in this system. In particular, we retain the system of labeling of chemical reactions adopted there; this nomenclature is summarized in Table 1. For convenience, in Table 2 we also present a summary of pertinent equilibrium constant expressions and numerical values for equilibrium constants and for reaction enthalpies. It should be pointed out that we employ as standard states 1 atm (for gases) and 1 M (for solutes); for convenience, units are retained with numerical values of the equilibrium constants (Daniels and Alberty, 1975). The Henry's law equilibrium between a gaseous substance X(g) and the dissolved substance X(aq),

$$\mathrm{X(g)} = \mathrm{X(aq)} \qquad [\mathrm{H_X}]$$

represents a special case of the standard state convention adopted. The equilibrium constant expression for this reaction is

$$H_\mathrm{X} = \frac{[\mathrm{X(aq)}]}{p_\mathrm{X}}, \qquad (1)$$

and it is seen that the Henry's law coefficient (H_X) has units M atm^{-1}

2. KINETICS OF GAS–LIQUID REACTIONS

In this section the formalism used to describe the rates of gas–liquid reactions is briefly outlined. Some of this discussion is merely definitional, i.e., expressing the rates and reagent concentrations in terms of gas- or aqueous-phase species, and the interconversion between the corresponding expressions. However, much of the discussion addresses the relationships between reaction rates and rate constants as a function of the degree of mixing maintained between the reagent concentrations in the two phases. This discussion outlines criteria for ascertaining the mixing condition that describes a given experimental situation and presents expressions for evaluating rates of reactive uptake of gases for these various situations. These expressions are utilized in the analysis presented in the subsequent sections.

2.1. Aqueous-Phase Kinetics

We first consider a general aqueous-phase reaction of stoichiometry

$$m_1\mathrm{X}_1(\mathrm{aq}) + m_2\mathrm{X}_2(\mathrm{aq}) + \cdots \rightarrow n_1\mathrm{Y}_1(\mathrm{aq}) + n_2\mathrm{Y}_2(\mathrm{aq}) + \cdots . \qquad [\mathrm{A12}]$$

The rate of this reaction is defined conventionally and unambiguously (e.g., Johnston, 1966) as

$$\begin{aligned} R_{\mathrm{A12}} &= -\frac{1}{m_1}\frac{d_{12}[\mathrm{X}_1(\mathrm{aq})]}{dt} = -\frac{1}{m_2}\frac{d_{12}[\mathrm{X}_2(\mathrm{aq})]}{dt} = \cdots \\ &= \frac{1}{n_1}\frac{d_{12}[\mathrm{Y}_1(\mathrm{aq})]}{dt} = \frac{1}{n_2}\frac{d_{12}[\mathrm{Y}_2(\mathrm{aq})]}{dt} = \cdots \end{aligned} \qquad (2)$$

Here the subscripted differential is employed to specify the rate of the indicated process, which need not (as in the case of consecutive or parallel reactions) be equal to the net rate of change in the concentration of the indicated species. The rate of aqueous-phase reaction is conventionally expressed in units moles (of reaction, as written) liter^{-1} s^{-1}, i.e., M s^{-1}. Frequently, and in the case of elementary reactions necessarily (Johnston, 1966), the reaction rate expression is given by the molecularity of the reaction, i.e.,

$$R_{\mathrm{A12}} = k_{\mathrm{A12}}[\mathrm{X}_1]^{m_1}[\mathrm{X}_2]^{m_2}, \qquad (3)$$

where the subscript A to the rate constant k denotes that this rate expression refers to the aqueous-phase reaction [A12]. Specializing to a reaction involving a single reagent,

$$m\mathrm{X}(\mathrm{aq}) \rightarrow \text{products}, \qquad [\mathrm{A13}]$$

the rate expression is

$$R_{\mathrm{A13}} = -\frac{1}{m}\frac{d_{13}[\mathrm{X}]}{dt} = k_{\mathrm{A13}}[\mathrm{X}]^m. \qquad (4)$$

An important relationship that, when applicable, relates the forward and reverse rate constants of a reaction may be developed as follows. Provided the forward rate of reaction may be expressed as a product of species concentrations (the exponents need not necessarily be equal to the respective stoichiometric coefficients)

$$R_f = k_f[\mathrm{X}_1]^{p_1}[\mathrm{X}_2]^{p_2}\cdots$$

applicable over the entire extent of reaction, and similarly for the reverse reaction

$$R_r = k_r[\mathrm{Y}_1]^{q_1}[\mathrm{Y}_2]^{q_2}\cdots ,$$

then at equilibrium (where the net rate of reaction is zero) $R_f - R_r = 0$ and hence the ratio of the products of species concentrations is equal to the ratio of rate constants, itself a constant:

$$\frac{[\mathrm{Y}_1]^{q_1}[\mathrm{Y}_2]^{q_2}\cdots}{[\mathrm{X}_1]^{p_1}[\mathrm{X}_2]^{p_2}\cdots} = \frac{k_f}{k_r} = K. \tag{5}$$

The constant K is equal to the equilibrium constant of the reaction (or to some power of the equilibrium constant). Relationship (5) necessarily holds for elementary reactions but is of much greater generality, holding, for example, in the cases of pre- or postequilibria and/or steady-state intermediates. In fact, Eq. (5) may obtain even in cases in which the rate law does not coincide with the molecularity of the reaction. Equation (5) permits evaluation of the reverse-rate constant from a known forward-rate constant and serves as an important check on the validity of an assumed mechanism and/or on the accuracy of measured rate constants.

2.2. Mixed-Phase Kinetics

We now consider a mixed-phase reaction, in which a gaseous reagent X(g) dissolves in water and reacts by aqueous-phase reaction, as described by the mechanism

$$\mathrm{X(g)} \rightleftharpoons \mathrm{X(aq)}$$

$$m\mathrm{X(aq)} \rightarrow \text{products.} \qquad [\mathrm{A13}]$$

Such a situation necessarily involves competition between the rate of reaction of the physically dissolved gas and the replenishment of the concentration of the dissolved gas by mass transport in each of the two phases and dissolution of the reagent gas at the interface. It is beyond the scope of the present review to survey this literature; an excellent treatment is given by Danckwerts (1970). We restrict the present discussion to a brief outline of situations pertinent to studies that are examined in this review. In this outline it is useful to consider the characteristic rate of aqueous-phase reaction as an "independent variable" that may be compared to the rate of aqueous-phase mixing as governed by convection and/or diffusion. At one extreme, that denoted by Danckwerts as the case of a "very slow reaction," we have a situation in which the rate of reaction is sufficiently slow, compared to the rate at which the phase equilibrium is restored, that the concentration of the aqueous-phase reagent is uniform throughout the aqueous phase and equal to the value given by Henry's law evaluated with respect to the bulk gas-phase concentration. (Here and in the discussion that follows we consider gas-phase mass transport to be sufficiently rapid that the gas-phase profile of the reagent concentration is essentially uniform; if this is not the case, the rate of gas-phase mass transport must be ascertained and appropriate corrections applied.)

A second limiting situation of interest is that of convective-controlled uptake. In this situation reaction is sufficiently slow to allow saturation of a region of the liquid near the surface on a time scale that is rapid compared to that of convective mixing. This saturated volume is then convected into the bulk, where reaction proceeds rapidly compared to the time scale of return of this parcel of material to the surface. In this limiting situation the rate of uptake is controlled entirely by the physical (Henry's law) solubility of the gas and the rate of convective mixing. Finally, we consider the extreme of a reaction sufficiently fast that the uptake occurs entirely within a thin film near the interface in which there is a steep concentration gradient of the reagent governed by the competition between reaction and diffusion of the material from the interface; this concentration profile is established rapidly in comparison to the rate of convective mixing.

As may be anticipated, the above situations are idealizations. However, these idealizations may often be closely approached in laboratory studies, permitting interpretation of measured rates of uptake in terms of the fundamental quantities (Henry's law coefficients and kinetic rate constants) of interest. We should note also that studies may be profitably conducted as well under phase-mixing conditions intermediate to these idealized situations, for which semiempirical models are employed to describe the mass transport and kinetics. We proceed now to outline the several mass-transport situations and to develop expressions relating the rate of uptake as measured in laboratory studies to the fundamental quantities of interest.

2.3. Phase-Mixed Limit (Very Slow Reaction)

We first consider reactions in the phase-mixed limit. For Henry's law satisfied, i.e.,

$$[\mathrm{X(aq)}] = \mathrm{H_X} p_{\mathrm{X}}, \tag{6}$$

it is seen that the rate of aqueous-phase reaction of a single reagent X reacting according to [A13] may be expressed in terms of the gas-phase partial pressure p_{X} as

$$R_{\mathrm{A13}} = \mathrm{H_X^{\mathit{m}}} k_{\mathrm{A13}} p_{\mathrm{X}}^{m}. \tag{7}$$

Consequently, it is convenient to define a rate constant k_{M13} for the mixed-phase reaction

$$m\mathrm{X(g)} \rightarrow \text{products} \tag{M13}$$

such that the rate is expressed as

$$R_{\mathrm{A13}} = k_{\mathrm{M13}} p_{\mathrm{X}}^{m}. \tag{8}$$

It should be noted that the rate of the mixed-phase reaction remains expressed in aqueous-phase concentration units, i.e., in units of moles per liter (of solution) per second. Comparison of (7) and (8) yields the relationship

$$k_{\mathrm{M13}} = \mathrm{H_X^{\mathit{m}}} k_{\mathrm{A13}}. \tag{9}$$

Thus the Henry's law coefficient provides the link between the aqueous- and mixed-phase rate coefficients. Since, as is generally the case in experimental studies of mixed-phase reactions in the phase-mixed limit, it is the partial pressure of the reagent and not its aqueous-phase concentration that is known, it is the mixed-phase k_M that is determined. Thus for a reactive gas, e.g., NO_2, the product $H_X^m k_A$ might be known, but not the individual factors. However, in order to establish that the system under examination satisfies the phase-mixed conditions, it is imperative that these factors be determined separately. Specifically, knowledge of k_A permits evaluation of the time quantity τ_r characteristic of chemical reaction in the aqueous phase. This characteristic time is given by

$$\tau_r = \begin{cases} k_A^{-1}, & m = 1 \\ (H_X p_X k_A)^{-1}, & m = 2 \\ (H_X p_X)^{(m-1)} k_A^{-1}, & m = m \end{cases}$$

where m is the reaction order. Comparison of τ_r with the characteristic time τ_{replen} of replenishment of the aqueous phase reagent is necessary for addressing the assumption of phase mixedness in a system under examination; specifically, the phase-mixed assumption is valid only if $\tau_r \gg \tau_{\text{replen}}$ (Lee and Schwartz, 1981b; Schwartz and Freiberg, 1981).

2.4. Convective-Controlled Uptake

In this limiting situation it is assumed that the rate of uptake of the gas is controlled by the rate of convection of the material present at the surface into the bulk aqueous phase. If the concentration at the surface is denoted [X(s)], the rate of uptake (in molar per second) is described as

$$R_{\text{abs}} = k_{s\to a}[X(s)],$$

where $k_{s\to a}$ is a stochastic first-order "rate coefficient" that characterizes the frequency with which material at the surface is convected into the bulk solution. It is further assumed that Henry's law is satisfied at the surface, i.e., that the surface concentration of the reacting gas is in equilibrium with the gas phase

$$[X(s)] = H_X p_X,$$

and hence

$$R_{\text{abs}} = k_{s\to a} H_X p_X. \tag{10}$$

The rate coefficient $k_{s\to a}$ is not an intrinsic property of the reaction system under consideration but depends on the nature and intensity of convective mixing that pertains to a given physical situation (i.e., is "apparatus dependent"). Under favorable circumstances $k_{s\to a}$ may be determined by appropriate characterization measurements. Under such circumstances the for mass transport by diffusion only:

$$J_X \approx \mathrm{H}_X p_X (D_X k_A)^{1/2}, \qquad k_L \leq 0.7\ (D_X k_A)^{1/2}. \tag{18}$$

At high values of k_L the rate of uptake becomes controlled entirely by the rate of convective mass-transport and independent of the chemical–kinetic rate constant k_A:

$$J_X \approx \mathrm{H}_X p_X k_L, \qquad k_L \geq 1.8\ (D_X k_A)^{1/2}. \tag{19}$$

Equation (19) is seen to exhibit identical dependence on H_X and p_X as that given by (14), differing only insofar as the rate of uptake is expressed per unit area of gas–liquid interface [Eq. (19)] or per unit liquid volume [Eq. (14)]. Introducing the ratio of the interface area to liquid volume a (units: length^{-1}) and observing that $R_{\mathrm{abs}} = aJ$, we see that equations (14) and (19) are identical if we identify k_{as} with $k_L a$; the latter is the nomenclature that is conventionally employed in the chemical engineering literature. For further discussion, the reader is referred to Chapter 6 of the monograph of Danckwerts (1970).

2.8. Gas-Phase Mass Transport

Before concluding this discussion, we wish to emphasize that the preceding review has assumed that the interfacial partial pressure of the reactive gas is equal to the partial pressure in the bulk gas. If this condition is not met, as might be the case for a fast aqueous-phase reaction, the interfacial partial pressure of the reactive gas must be employed in the above expressions. The decrease in partial pressure from the bulk to the interface may be inferred from J for known gas-phase mass-transport coefficient k_G. In this regard it should be noted also that for a situation in which the rate of uptake is controlled by gas-phase mass transport, the rate of uptake again is proportional to the first power of p_X, irrespective of the rate and mechanism of aqueous-phase reaction.

2.9. Apparent Reaction Order

One means of experimentally identifying the situation that governs a particular system under investigation is examination of the power law dependence of the rate of absorption on the partial pressure of the reagent gas, i.e., the apparent reaction order referred to the reagent gas concentration. This dependence is summarized in Table 3 for the several limiting conditions for various aqueous-phase reaction orders. As we have noted, the apparent gas-phase order is equal to the aqueous-phase order in the phase-mixed limit, but the relationship between the two orders becomes weaker as the situation becomes increasingly mass-transport controlled. Also, we would sequence of differing convention in the definition of the rate coefficient. We continue to employ the convention (4) for an mth order reaction, $d[\mathrm{X}]/dt = -mk[\mathrm{X}]^m$, rather than the expression $d[\mathrm{X}]/dt = -k[\mathrm{X}]^m$ commonly employed in kinetic studies by penetration theory.

If the steady-state rate J_{X} is measured for known p_{X}, and if D_{X} is known or, as is generally the case, can be accurately estimated (Wilke and Chang, 1955), such measurements yield the product

$$\begin{aligned} &k_{\mathrm{A}}^{1/2}\mathrm{H}_{\mathrm{X}}, && m = 1 \\ &k_{\mathrm{A}}^{1/2}\mathrm{H}_{\mathrm{X}}^{3/2}, && m = 2 \\ &k_{\mathrm{A}}^{1/2}\mathrm{H}_{\mathrm{X}}^{(m+1)/2}, && m = m. \end{aligned}$$

Thus kinetic studies in this diffusion-controlled limit in conjunction, for example, with kinetic studies in the phase-mixed limit can yield both H_{X} and k_{A}, as is desired.

In the case of a first-order reaction, the expression for the time dependence of Q, the amount of reagent taken up per unit area in a time of contact t, has been given (Danckwerts, 1950) as

$$Q_{\mathrm{X}}(t) = D_{\mathrm{X}}^{1/2}k_{\mathrm{A}}^{1/2}\mathrm{H}_{\mathrm{X}}p_{\mathrm{X}}\left(t + \frac{1}{2k_{\mathrm{A}}}\right), \qquad k_{\mathrm{A}}t > 1. \tag{16}$$

It may be seen that measurement of Q_{X} as a function of contact time permits evaluation of both k_{A} and H_{X}, provided D_{X} is known or can be accurately estimated. Also, k_{A} may be determined without knowledge of D_{X} (or for that matter even p_{X}) from the slope : intercept ratio.

2.7. Fast Reactions

We now treat the situation intermediate between that of convective- and diffusive-controlled uptake. This situation, in which the transport of reagent occurs by mechanically induced convection in addition to diffusion, continues to exhibit a rate of uptake of the reactive gas proportional to the area of the gas–liquid interface, but this rate is enhanced by the convective mass-transport process. An expression for this rate, developed for the so-called film model of the absorption into agitated liquids, is given by Danckwerts (1970, p. 107) for reaction by a first-order or pseudo-first-order mechanism as

$$J_{\mathrm{X}} = \mathrm{H}_{\mathrm{X}}p_{\mathrm{X}}(D_{\mathrm{X}}k_{\mathrm{A}})^{1/2}\coth\left[\frac{(D_{\mathrm{X}}k_{\mathrm{A}})^{1/2}}{k_{\mathrm{L}}}\right] \tag{17}$$

where k_{L}, having units $\mathrm{m\,s^{-1}}$, is the liquid-phase mass-transfer coefficient. For a given system, k_{L} may be determined from measurement of the rate of uptake of a gas of a known Henry's law coefficient. For low values of k_{L}, the rate of uptake given by Eq. (17) approaches that given by Eq. (15)

Henry's law coefficient of the reactive gas may be determined directly from the measured rate of uptake since this rate of uptake depends only on the physical solubility of the gas and is independent of the details of the aqueous-phase reaction.

2.5. Slow Reactions

We now consider the situation intermediate to the two limiting cases just discussed. The model describing this situation again posits a surface layer saturated in the reagent gas. Additionally, a uniform reagent concentration is assumed in the bulk aqueous phase having a steady-state value governed by the rates of convective mass-transport coupling the bulk and surface regions and chemical reaction. Again denoting the surface aqueous-phase concentration [X(s)], we may describe the rates of the aqueous-phase mass-transport process governing the bulk concentration [X(aq)] as

$$\mathrm{X(s)} \xrightarrow{k_{\mathrm{s}\to\mathrm{a}}} \mathrm{X(aq)}$$

and

$$\mathrm{X(aq)} \xrightarrow{k_{\mathrm{a}\to\mathrm{s}}} \mathrm{X(s)}.$$

For a first-order reaction

$$\mathrm{X(aq)} \xrightarrow{k_{\mathrm{A}}} \text{products},$$

the steady-state concentration [X(a)] is given by

$$\frac{d[\mathrm{X(a)}]}{dt} = 0 = k_{\mathrm{s}\to\mathrm{a}}[\mathrm{X(s)}] - k_{\mathrm{a}\to\mathrm{s}}[\mathrm{X(aq)}] - k_{\mathrm{A}}[\mathrm{X(aq)}],$$

whence

$$[\mathrm{X(aq)}] = \frac{k_{\mathrm{s}\to\mathrm{a}}[\mathrm{X(s)}]}{k_{\mathrm{a}\to\mathrm{s}} + k_{\mathrm{A}}} = \frac{\mathrm{H_X} k_{\mathrm{s}\to\mathrm{a}} p_{\mathrm{X}}}{k_{\mathrm{a}\to\mathrm{s}} + k_{\mathrm{A}}}, \tag{11}$$

where Henry's law equilibrium has been assumed at the surface. Finally, we observe that $k_{\mathrm{s}\to\mathrm{a}} = k_{\mathrm{a}\to\mathrm{s}}$, since, in the absence of reaction ($k_{\mathrm{A}} = 0$), X(aq) is in Henry's law equilibrium with the gas,

$$[\mathrm{X(aq)}] = \mathrm{H_X} p_{\mathrm{X}}, \tag{6}$$

whereas by (11), for $k_{\mathrm{A}} = 0$,

$$[\mathrm{X(aq)}] = \mathrm{H_X} \frac{k_{\mathrm{s}\to\mathrm{a}}}{k_{\mathrm{a}\to\mathrm{s}}} p_{\mathrm{X}}.$$

In subsequent discussion we may thus refer to the aqueous-phase mixing coefficient without indication of direction, i.e., $k_{\mathrm{as}} = k_{\mathrm{a}\to\mathrm{s}} = k_{\mathrm{s}\to\mathrm{a}}$.

Returning to the reactive system, we observe that the overall rate of absorption is given by

$$R_{\mathrm{abs}} = k_{\mathrm{A}}[\mathrm{X(aq)}] = \frac{k_{\mathrm{A}}\mathrm{H}_{\mathrm{X}}k_{\mathrm{as}}}{k_{\mathrm{as}} + k_{\mathrm{A}}}p_{\mathrm{X}}. \tag{12}$$

Measurement of R_{abs} as a function of k_{as} permits both H_{X} and k_{A} to be determined. For high values of k_{as}, which promote phase mixing, one obtains the phase-mixed condition as a limit to (12)

$$R_{\mathrm{abs}} = \mathrm{H}_{\mathrm{X}}k_{\mathrm{A}}p_{\mathrm{X}}, \qquad k_{\mathrm{as}} \gg k_{\mathrm{A}} \tag{13}$$

equivalent to (7) for $m = 1$. On the other hand, for lower values of k_{as} such that $k_{\mathrm{as}} \ll k_{\mathrm{A}}$, one obtains the situation described above in which the rate of absorption is controlled entirely by the rate of convective mass transport,

$$R_{\mathrm{abs}} = \mathrm{H}_{\mathrm{X}}k_{\mathrm{as}}p_{\mathrm{X}}, \qquad k_{\mathrm{as}} \ll k_{\mathrm{A}}. \tag{14}$$

Generalization of the slow reaction treatment to reaction of arbitrary order has been given, among others, by Astarita (1967).

2.6. Diffusion-Controlled Uptake (Very Fast Reaction)

Laboratory experiments may also be profitably conducted under conditions in which the characteristic time of reaction is shorter than that of mass transport (by either convection or molecular diffusion). Under such conditions the reaction takes place entirely in a thin region near the surface in which there is a nonuniform reagent concentration profile that is governed by the interworking of reaction and molecular diffusion. The rate of reaction, which is proportional to the surface area of contact between the two phases, has been treated for a variety of chemical mechanisms according to this so-called penetration theory (Danckwerts, 1970). For a reaction that is *m*th order in a single reagent *X*, the steady-state rate of uptake of the reagent species is given (Danckwerts, 1970, p. 49) by

$$J_{\mathrm{X}} = \left(\frac{2m}{m+1}\right)^{1/2} D_{\mathrm{X}}^{1/2}k_{\mathrm{A}}^{1/2}\mathrm{H}_{\mathrm{X}}^{(m+1)/2}p_{\mathrm{X}}^{(m+1)/2} \tag{15}$$

where J_{X} is the flux of gas X into the liquid (kmol $\mathrm{m}^{-2}\ \mathrm{s}^{-1}$), D_{X} is the aqueous-phase diffusion coefficient of the dissolved reagent X ($\mathrm{m}^2\ \mathrm{s}^{-1}$), and k_{A} is the *m*th-order aqueous-phase rate coefficient ($\mathrm{M}^{(1-m)}\ \mathrm{s}^{-1}$).

A further word about units may be pertinent here. We have chosen to employ MKS units, as indicated. Consistent with these units, the appropriate unit for concentration would be kmol m^{-3}. However, since this unit is numerically equal to mol liter^{-1} or molar (M), we may continue to employ molar units for concentrations and for compound quantities, e.g., H and k_{A}. Also, we should point out that the rate expression (15) differs by a factor of $m^{1/2}$ from that frequently employed (e.g., Danckwerts, 1970), as a con-

Table 3. Apparent Reaction Order in Gas-Phase Reagent

Aqueous-Phase Reaction Order	Phase-Mixed Limit	Convective Mass-Transport Controlled	Diffusive Mass-Transport Controlled
0	0	1	$\frac{1}{2}$
$\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{3}{4}$
1	1	1	1
2	2	1	$\frac{3}{2}$
3	3	1	2
m	m	1	$(m + 1)/2$

point out that the several situations identified are idealizations and that intermediate situations would be expected. The criteria that must be satisfied for a gas–liquid reaction to be described by one of the three limiting situations outlined above are summarized in Table 4.

3. RATE EXPRESSIONS FOR NITROGEN OXIDE REACTIONS

As noted in Section 1, the study of the reactive dissolution of nitrogen oxides is complicated by the fact that these oxides undergo rapid interconversion (in both gas and aqueous phases) between the so-called simple oxides (NO and NO_2) and the compound oxides (N_2O_3 and N_2O_4). As is shown in Sections 5.3 and 5.4, the aqueous-phase interconversion equilibria are established rapidly in comparison to the rates of the subsequent hydrolysis reactions (to form nitrous and/or nitric acids). Consequently, it is not possible by studies of the kinetics of the latter reactions to ascertain whether the immediate precursor of reaction is a single molecule of the compound oxide or two molecules of the simple oxides. Therefore, the choice of whether to express the reaction kinetics in terms of the concentration of the compound

Table 4. Mixing Conditions for Limiting Regimes of Gas–Liquid Reactions[a]

Regime	Conditions
Phase mixed	$\tau_r \gtrsim 10\tau_m$ or $\tau_r \gtrsim 10\tau_d$
Convective mass-transport controlled	$\tau_r \lesssim 0.1\tau_m$ and $\tau_r \gtrsim 3\tau_m^2/\tau_d$
Diffusive mass-transport controlled	$\tau_r \lesssim 0.1\tau_d$ and $\tau_r \lesssim 0.38\tau_m^2/\tau_d$

[a] Times τ_r, τ_m, and τ_d are the characteristic time or reaction, convective mixing, and molecular diffusion, as defined by $\tau_r = \{(-d_r[A]/dt)/[A]\}^{-1}$, $\tau_m = (k_L a)^{-1}$, and $\tau_d = (Da^2)^{-1}$, respectively. In these equations k_L is the liquid-side mass-transfer coefficient, a is the interfacial area per unit liquid volume, and D is the aqueous-phase diffusion coefficient of the reagent species. Adapted from Lee and Schwartz (1981b).

oxide or the simple oxides is arbitrary. However, as we have seen in Section 2, under non-phase-mixed conditions the description of the reaction kinetics depends strongly on the reaction order—actually the order in transported species. Thus it is convenient to be able to express the reaction rate in terms of the concentration of either the simple or compound oxides, depending on which form is predominately present. Although such treatment is convenient, one must not lose sight of the relationships between the different kinetic expressions, since they ultimately pertain to the same reactions. These relationships are developed here.

3.1. Reactions [1] and [4]

We first consider the aqueous-phase reaction

$$2NO_2(aq) \overset{w}{\rightarrow} HNO_2 + H^+ + NO_3^- . \qquad [A1']$$

This reaction might occur as an elementary reaction as written, in which case the rate of formation of nitrate ion product would be

$$\frac{d}{dt}[NO_3^-] = \frac{d_{A1'}}{dt}[NO_3^-] \equiv R_{A1'} = k_{A1'}[NO_2(aq)]^2;$$

alternatively, the reaction might occur by way of an intermediate N_2O_4 according to the mechanism

$$2NO_2(aq) \rightarrow N_2O_4(aq) \qquad [A7]$$

$$N_2O_4(aq) \overset{w}{\rightarrow} HNO_2 + H^+ + NO_3^- , \qquad [A4']$$

in which case the rate of formation of nitrate ion would be given by

$$\frac{d}{dt}[NO_3^-] = \frac{d_{A4'}}{dt}[NO_3^-] \equiv R_{A4'} = k_{A4'}[N_2O_4(aq)].$$

As we have noted, the aqueous-phase equilibrium [A7] appears to be established rapidly on a time scale relative to that of the overall reaction. Under the assumption that equilibrium [A7] obtains, then

$$[N_2O_4(aq)] = K_{A7}[NO_2(aq)]^2,$$

and hence the rate of reaction [A4′] can be equally well expressed as a function of the concentration of $NO_2(aq)$, viz.,

$$R_{A4'} \equiv \frac{d_{A4'}}{dt}[NO_3^-] = k_{A4'}K_{A7}[NO_2(aq)]^2.$$

Because of the identical dependence on $[NO_2(aq)]^2$ of the rate of nitrate formation by each of these two mechanisms, it is impossible to distinguish the contributions of the two paths to the total rate under conditions in which equilibrium [A7] obtains (Bray, 1932). Consequently, it becomes notationally convenient to consider the two mechanisms collectively as

$$2NO_2(aq)(N_2O_4(aq)) \overset{w}{\rightarrow} HNO_2 + H^+ + NO_3^- . \qquad [A1'/4']$$

The rate of this "hybrid" reaction is the sum of the rates of the two separate mechanisms,

$$\begin{aligned} R_{A1'/4'} &\equiv R_{A1'} + R_{A4'} \\ &= \frac{d_{A1'}}{dt}[NO_3^-] + \frac{d_{A4'}}{dt}[NO_3^-] \\ &= k_{A1'}[NO_2(aq)]^2 + k_{A4'}K_{A7}[NO_2(aq)]^2 \\ &= k_{A1'/4'}[NO_2(aq)]^2, \end{aligned} \qquad (20)$$

where we have introduced the hybrid rate constant,

$$k_{A1'/4'} \equiv k_{A1'} + k_{A4'}K_{A7}. \qquad (21)$$

For purposes of comparing kinetic measurements by various techniques, it is sometimes convenient to express the rate of reaction [A1′/4′] in terms of N_2O_4 as the reagent. We express this hybrid reaction as

$$N_2O_4(2NO_2) \overset{w}{\rightarrow} HNO_2 + H^+ + NO_3^- \qquad [A4'/1']$$

having rate

$$R_{A4'/1'} = k_{A4'/1'}[N_2O_4(aq)] \qquad (22)$$

where

$$k_{A4'/1'} = \frac{k_{A1'/4'}}{K_{A7}} = \frac{k_{A1'}}{K_{A7}} + k_{A4'}. \qquad (23)$$

3.2. Reverse Reaction

It is useful to extend the treatment of indistinguishable reactions to the reverse reactions

$$HNO_2 + H^+ + NO_3^- \overset{w}{\rightarrow} 2NO_2(aq) \qquad [-A1']$$

and

$$HNO_2 + H^+ + NO_3^- \overset{w}{\rightarrow} N_2O_4(aq). \qquad [-A4']$$

The rates of these reactions are given respectively by

$$R_{-A1'} = k_{-A1'}[HNO_2][H^+][NO_3^-]$$

and

$$R_{-A4'} = k_{-A4'}[HNO_2][H^+][NO_3^-].$$

Hence the total rate of the reverse reaction may be expressed as

$$R_{-A1'/4'} \equiv R_{-A1'} + R_{-A4'} = (k_{-A1'} + k_{-A4'})[HNO_2][H^+][NO_3^-]$$

where $R_{-A1'/4'}$ is the rate of the hybrid reaction

$$HNO_2 + H^+ + NO_3^- \rightarrow 2NO_2(N_2O_4). \qquad [-A1'/4']$$

The rate coefficient for the hybrid reaction is seen to be equal to the sum of the rate coefficients for the two individual reactions

$$k_{-A1'/4'} = k_{-A1'} + k_{-A4'}. \qquad (24)$$

At equilibrium the forward and reverse rates for each reaction are equal (principle of detailed balance):

$$k_{A1'}[NO_2(aq)]^2 = k_{-A1'}[HNO_2][H^+][NO_3^-]$$

$$k_{A4'}[N_2O_4(aq)]^2 = k_{A4'}K_{A7}[NO_2(aq)]^2 = k_{-A4'}[HNO_2][H^+][NO_3^-]$$

whence

$$k_{A1'/4'}[NO_2(aq)]^2 = k_{-A1'/4'}[HNO_2][H^+][NO_3^-]$$

whence

$$\frac{k_{A1'/4'}}{k_{-A1'/4'}} = \frac{[HNO_2][H^+][NO_3^-]}{[NO_2(aq)]^2} = K_{A1'}. \qquad (25)$$

Thus it is seen that the forward and reverse hybrid reactions [A1′/4′] and [−A1′/4′], although not elementary reactions, exhibit the properties of elementary reactions that the rates are expressed in terms of the molecularity of the reaction, that the forward: reverse rate constant ratio is equal to the equilibrium constant, and that the rate constant is independent of composition.

3.3. Phase-Mixed System

The above considerations may be directly extended to the mixed-phase reaction in the phase-mixed limit. By (7) we obtain for the rate of the mixed-phase reaction [M1′]

$$R_{M1'} = k_{A1'}H^2_{NO_2}p^2_{NO_2}$$

and similarly for [M4′],

$$R_{M4'} = k_{A4'}H_{N_2O_4}p_{N_2O_4}.$$

However, under the assumption of gas-phase equilibrium [G7], it follows that

$$p_{N_2O_4} = K_{G7}p^2_{NO_2},$$

and thus the rate of reaction [M4′] can be expressed as a function of the partial pressure of NO_2,

$$R_{M4'} = K_{G7} k_{A4'} H_{N_2O_4} p^2_{NO_2}.$$

Hence we may define the hybrid mixed-phase reaction

$$2NO_2(g)(N_2O_4(g)) \rightarrow HNO_2 + H^+ + NO_3^- \qquad [M1'/4']$$

having rate

$$\begin{aligned} R_{M1'/4'} &\equiv R_{M1'} + R_{M4'} \\ &= k_{A1'} H^2_{NO_2} p^2_{NO_2} + K_{G7} k_{A4'} H_{N_2O_4} p^2_{NO_2} \\ &= k_{M1'/4'} p^2_{NO_2}, \end{aligned}$$

where we introduce the hybrid mixed-phase rate constant

$$k_{M1'/4'} \equiv k_{A1'} H^2_{NO_2} + K_{G7} k_{A4'} H_{N_2O_4}. \qquad (26)$$

From examination of thermochemical cycles (Schwartz and White, 1981) it is readily established that the Henry's law coefficients of NO_2 and N_2O_4 are related by

$$H_{N_2O_4} = \frac{K_{A7}}{K_{G7}} H^2_{NO_2}; \qquad (27)$$

hence one obtains the relationship between the mixed- and aqueous-phase rate constants,

$$k_{M1'/4'} = H^2_{NO_2}(k_{A1'} + K_{A7} k_{A4'}) = H^2_{NO_2} k_{A1'/4'}. \qquad (28)$$

In consideration of reactions under phase-mixed conditions, $k_{A1'/4'}$ may thus be treated as if it were the rate constant of an elementary reaction second-order in $NO_2(aq)$ [see Eq. (9)].

Analogously to the previous discussion, the rate constant for the hybrid reverse mixed-phase reaction

$$HNO_2 + H^+ + NO_3^- \xrightarrow{w} 2NO_2(g)(N_2O_4(g)) \qquad [-M1'/4']$$

is given by

$$k_{-M1'/4'} = k_{-M1'} + k_{-M4'}, \qquad (29)$$

and the relationship to the equilibrium constant is

$$K_{M1'} = \frac{k_{M1'/4'}}{k_{-M1'/4'}}.$$

3.4. Reactions [2] and [5]

The concept of indistinguishable reactions applies also to formation of nitrous acid from NO and NO_2 by the reaction

$$NO(aq) + NO_2(aq) \xrightarrow{w} 2HNO_2 \qquad [A2']$$

or by the sequence

$$\mathrm{NO(aq)} + \mathrm{NO_2(aq)} = \mathrm{N_2O_3(aq)} \qquad [\mathrm{A8}]$$

$$\mathrm{N_2O_3(aq)} \xrightarrow{w} \mathrm{2HNO_2}. \qquad [\mathrm{A5'}]$$

This leads to definition of the hybrid aqueous-phase reactions

$$\mathrm{NO(aq)} + \mathrm{NO_2(aq)(N_2O_3(aq))} \xrightarrow{w} \mathrm{2HNO_2} \qquad [\mathrm{A2'/5'}]$$

and

$$\mathrm{2HNO_2} \xrightarrow{w} \mathrm{NO(aq)} + \mathrm{NO_2(aq)(N_2O_3(aq))} \qquad [-\mathrm{A2'/5'}]$$

having rate constants

$$k_{\mathrm{A2'/5'}} = k_{\mathrm{A2'}} + k_{\mathrm{A5'}} K_{\mathrm{A8}} \tag{30}$$

and

$$k_{-\mathrm{A2'/5'}} = k_{-\mathrm{A2'}} + k_{-\mathrm{A5'}}, \tag{31}$$

such that the rates of the hybrid reactions may be evaluated as

$$R_{\mathrm{A2'/5'}} = k_{\mathrm{A2'/5'}}[\mathrm{NO(aq)}][\mathrm{NO_2(aq)}] \tag{32}$$

and

$$R_{-\mathrm{A1'/5'}} = k_{-\mathrm{A2'/5'}}[\mathrm{HNO_2}]^2. \tag{33}$$

Similarly, we define the hybrid mixed-phase reactions

$$\mathrm{NO(g)} + \mathrm{NO_2(g)(N_2O_3(g))} \xrightarrow{w} \mathrm{2HNO_2(aq)} \qquad [\mathrm{M2'/5'}]$$

and

$$\mathrm{2HNO_2(aq)} \xrightarrow{w} \mathrm{NO(g)} + \mathrm{NO_2(g)(N_2O_3(g))} \qquad [-\mathrm{M2'/5'}]$$

having rate constants

$$k_{\mathrm{M2'/5'}} = k_{\mathrm{A2'}} \mathrm{H_{NO}} \mathrm{H_{NO_2}} + K_{\mathrm{G8}} k_{\mathrm{A5'}} \mathrm{H_{N_2O_3}} \tag{34}$$

and

$$k_{-\mathrm{M2'/5'}} = k_{-\mathrm{M2'}} + k_{-\mathrm{M5'}}. \tag{35}$$

3.5. Reactions Involving Nitrous Acid and/or Nitrite

One further notational consideration addresses the relationship between the kinetics of reactions involving nitrous acid and the corresponding reactions involving nitrite (as distinguished here by the presence or absence, respectively, of primes in the reaction numbers). Consider the reactions

$$\mathrm{2NO_2(aq)} \xrightarrow{w} \mathrm{H^+} + \mathrm{NO_3^-} + \mathrm{HNO_2} \qquad [\mathrm{A1'}]$$

and

$$\mathrm{2NO_2(aq)} \xrightarrow{w} \mathrm{2H^+} + \mathrm{NO_3^-} + \mathrm{NO_2^-}. \qquad [\mathrm{A1}]$$

Kinetically the nitrous acid dissociation equilibrium (as any protonation equilibrium) may be expected to be established quite fast (Eigen et al., 1964), and thus under ordinary circumstances we are unable to distinguish, say, between direct reaction by [A1] or reaction [A1′] followed by ionization of the HNO_2 product. The rate of reaction by the sum of both paths is

$$R_{\mathrm{A1}} + R_{\mathrm{A1'}} = -\frac{1}{2}\frac{d[\mathrm{NO_2(aq)}]}{dt} = (k_{\mathrm{A1}} + k_{\mathrm{A1'}})[\mathrm{NO_2(aq)}]^2. \qquad (36)$$

For simplicity, and without confusion, we choose not to retain the distinction between the two paths and simply denote the sum as

$$R_{\mathrm{A1*}} \equiv R_{\mathrm{A1}} + R_{\mathrm{A1'}} = k_{\mathrm{A1*}}[\mathrm{NO_2(aq)}]^2, \qquad (37)$$

where we introduce

$$k_{\mathrm{A1*}} \equiv k_{\mathrm{A1}} + k_{\mathrm{A1'}}.$$

Similar considerations apply regarding the reverse reaction, which may occur as

$$\mathrm{H^+ + NO_3^- + HNO_2 \xrightarrow{w} 2NO_2(aq)} \qquad [-\mathrm{A1'}]$$

and/or

$$\mathrm{2H^+ + NO_3^- + NO_2^- \xrightarrow{w} 2NO_2(aq)} \qquad [-\mathrm{A1}]$$

with rates

$$R_{-\mathrm{A1'}} = k_{-\mathrm{A1'}}[\mathrm{H^+}][\mathrm{NO_3^-}][\mathrm{HNO_2}] \qquad (38)$$

and

$$R_{-\mathrm{A1}} = k_{-\mathrm{A1}}[\mathrm{H^+}]^2[\mathrm{NO_3^-}][\mathrm{NO_2^-}]. \qquad (39)$$

Assuming that the nitrous acid dissociation equilibrium [I2] obtains, i.e., $K_{\mathrm{I2}} = [\mathrm{H^+}][\mathrm{NO_2^-}]/[\mathrm{HNO_2}]$, we may write $R_{-\mathrm{A1}}$ in terms of the associated species as

$$R_{-\mathrm{A1}} = k_{-\mathrm{A1}}K_{\mathrm{I2}}[\mathrm{H^+}][\mathrm{NO_3^+}][\mathrm{HNO_2}] \qquad (40)$$

and in turn may write the total reaction rate by both paths as

$$\begin{aligned} R_{-\mathrm{A1}} + R_{-\mathrm{A1'}} &= (k_{-\mathrm{A1'}} + k_{-\mathrm{A1}}K_{\mathrm{I2}})[\mathrm{H^+}][\mathrm{NO_3^-}][\mathrm{HNO_2}] \\ &= k_{-\mathrm{A1*}}[\mathrm{H^+}][\mathrm{NO_3^-}][\mathrm{HNO_2}] \end{aligned} \qquad (41)$$

where we have introduced $k_{-\mathrm{A1*}} \equiv k_{-\mathrm{A1'}} + K_{-\mathrm{A1}}K_{\mathrm{I2}}$. From detailed balance considerations it is seen that $k_{\mathrm{A1*}}$ and $k_{-\mathrm{A1*}}$ are related as

$$\frac{k_{\mathrm{A1*}}}{k_{-\mathrm{A1*}}} = K_{\mathrm{A1'}},$$

and thus that the hybrid reaction [A1*]

$$\mathrm{2NO_2(aq) \overset{w}{\rightleftharpoons} H^+ + NO_3^- + HNO_2(H^+ + NO_2^-)} \qquad [\mathrm{A1*}]$$

may be treated as an elementary reaction. We utilize this hybrid notation as well to avoid being burdened with retaining the distinction between the two separate paths. Furthermore, the preceding discussion concerning the hybrid reactions [A1′/4′], [M1′/4′], etc. may be extended to encompass this further hybridization by replacing the primes with asterisks.

These hybrid reactions and the corresponding rate expression will be useful in the discussion of laboratory studies of the rates of the aqueous-phase and mixed-phase reactions of the nitrogen oxides and oxyacids. In particular, for the discussion of experimental studies of reactions [1/4] and [2/5], we establish the convention of expressing the kinetics of these reactions in the hybrid notation regardless of the formulation employed by the original investigators. The validity of this treatment, which depends on equilibria [A7] and [A8] being rapidly established relative to the time scale of reactions [A1*/4*] and [A2*/5*], respectively, is addressed in Sections 5.3 and 5.4.

4. INDIRECT MEASUREMENTS OF PHASE-MIXED KINETICS

Although there is a large body of work directly bearing on the aqueous and mixed-phase kinetics of the reactions of the nitrogen oxides with water (Sections 5 and 6), there is also considerable literature that pertains indirectly to the kinetics of these reactions. Specifically, there are a number of studies of aqueous-phase reactions of the nitrogen oxides and oxyacids that can be interpreted in terms of a sequence of elementary reactions whose rate-determining step is one of the elementary reactions of interest here. From the measured kinetics of the overall reactions, it is possible to infer the kinetics of the reactions of interest. These studies are reviewed in this section.

4.1. Reaction [M1*/4′]

The kinetics of the mixed-phase reaction

$$2NO_2(g)(N_2O_4(g) \overset{w}{\rightarrow} H^+ + NO_3^- + HNO_2(aq)(H^+ + NO_2^-) \qquad [M1^*/4^*]$$

may be inferred from studies of the kinetics of nitrous acid decomposition and formation, isotope exchange, and electrochemical reduction. These studies are reviewed here.

4.1.1. Nitrous Acid Decomposition

The earliest reliable measurement of the kinetics of reaction [M1*/4*] resulted from a remarkable study of the kinetics of nitrous acid decomposition

$$3HNO_2(aq) \overset{w}{\rightarrow} H^+ + NO_3^- + 2NO(g) \qquad [M10^*]$$

and formation

$$H^+ + NO_3^- + 2NO(g) \overset{w}{\rightarrow} 3HNO_2(aq) \qquad [-M10^*]$$

by E. Abel and H. Schmid (1928a–f). A major advance in the understanding of these reactions was achieved by the recognition of the need for a well-defined NO partial pressure and for sufficient interphase mixing to assure that the Henry's law equilibrium for NO was maintained. Under these conditions the stoichiometry of nitrous acid decomposition was established as that of reaction [M10*], and the initial rate law was found to be

$$R_{\mathrm{M10^*}} \equiv \frac{1}{3}\frac{d_{\mathrm{M10^*}}}{dt}[\mathrm{HNO_2}] = k_{\mathrm{fwd}}\frac{[\mathrm{HNO_2}]^4}{p_{\mathrm{NO}}^2}, \tag{42}$$

where k_{fwd} denotes an empirical rate coefficient for reaction [M10*] in the forward direction. (We point out that we have expressed $R_{\mathrm{M10^*}}$ consistent with the modern convention [Eq. (2)]. This convention differs by a factor of 3 from that employed by the original investigators, who reported $R_{\mathrm{M10^*}}$ as $-d_{\mathrm{M10^*}}[\mathrm{HNO_2}]/dt$). The observed rate law, which excited considerable theoretical interest because of the unusual order in reagents (differing markedly from the reaction stoichiometry), was interpreted in terms of the following mechanism:

$$4\mathrm{HNO_2(aq)} \overset{\mathrm{w}}{=} 2\mathrm{NO_2(aq)(N_2O_4(aq))} + 2\mathrm{NO(aq)} \qquad [-2\mathrm{A2'}]$$

$$2\mathrm{NO_2(aq)(N_2O_4(aq))} \xrightarrow{\mathrm{w}} \mathrm{H^+} + \mathrm{NO_3^-} + \mathrm{HNO_2(H^+} + \mathrm{NO_2^-)} \qquad [\mathrm{A1^*/4^*}]$$

$$2\mathrm{NO(aq)} = 2\mathrm{NO(g)} \qquad [-2\mathrm{H_{NO}}]$$

where reactions [A2′] and [$\mathrm{H_{NO}}$] are assumed to be in equilibrium and [A1*/4*] is the rate-determining step. Assumption of equilibrium [A7] permits the rate of reaction [A1*/4*] (and hence of the overall reaction) to be expressed in terms of the unknown concentration of the intermediate $\mathrm{NO_2(aq)}$ [see Eq. (20)] as

$$R_{\mathrm{M10^*}} = R_{\mathrm{A1^*/4^*}} = k_{\mathrm{A1^*/4^*}}[\mathrm{NO_2(aq)}]^2$$

Assumption of equilibrium [A2′] permits [$\mathrm{NO_2(aq)}$] to be expressed in terms of [NO(aq)],

$$[\mathrm{NO_2(aq)}] = K_{\mathrm{A2'}}^{-1}\frac{[\mathrm{HNO_2}]^2}{[\mathrm{NO(aq)}]}, \tag{44}$$

and the further assumption of the Henry's law equilibrium for NO (phase-mixed limit) allows [$\mathrm{NO_2(aq)}$] to be expressed in terms of p_{NO},

$$[\mathrm{NO_2(aq)}] = \mathrm{H_{NO}^{-1}}K_{\mathrm{A2'}}^{-1}\frac{[\mathrm{HNO_2}]^2}{p_{\mathrm{NO}}}.$$

Hence for the rate of the overall reaction [M10*], one obtains

$$R_{\mathrm{M10^*}} = k_{\mathrm{A1^*/4^*}}\mathrm{H_{NO}^{-2}}K_{\mathrm{A2'}}^{-2}\frac{[\mathrm{HNO_2}]^4}{p_{\mathrm{NO}}^2}. \tag{45}$$

Comparison of equations (42) and (45) shows that the hybrid rate constant

$k_{\mathrm{A1^*/4^*}}$ is related to the measured rate coefficient k_{fwd} as

$$k_{\mathrm{A1^*/4^*}} = \mathrm{H}_{\mathrm{NO}}^{2} K_{\mathrm{A2'}}^{2} k_{\mathrm{fwd}}. \tag{46}$$

Equation (46) is not directly applicable since the aqueous-phase equilibrium constant $K_{\mathrm{A2'}}$ is not firmly established (Schwartz and White, 1981). However, we observe [see Eq. (28)] that

$$k_{\mathrm{M1^*/4^*}} = \mathrm{H}_{\mathrm{NO_2}}^{2} k_{\mathrm{A1^*/4^*}} \tag{47}$$

and hence

$$k_{\mathrm{M1^*/4^*}} = \mathrm{H}_{\mathrm{NO_2}}^{2} \mathrm{H}_{\mathrm{NO}}^{2} K_{\mathrm{A2'}}^{2} k_{\mathrm{fwd}}.$$

Observing (see Tables 1 and 2) that the expressions for the mixed- and aqueous-phase equilibria [M2′] and [A2′] are related by the Henry's law coefficients for NO and $\mathrm{NO_2}$ as

$$K_{\mathrm{A2'}} = \frac{K_{\mathrm{M2'}}}{\mathrm{H}_{\mathrm{NO}} \mathrm{H}_{\mathrm{NO_2}}}, \tag{48}$$

one obtains as the rate coefficient for the hybrid mixed-phase reaction

$$k_{\mathrm{M1^*/4^*}} = K_{\mathrm{M2'}}^{2} k_{\mathrm{fwd}}. \tag{49}$$

Abel and H. Schmid (1928c) obtained the value $k_{\mathrm{fwd}} = 2.6 \times 10^{-1}\ \mathrm{atm^2\ M^{-3}\ s^{-1}}$ at 25°C and zero ionic strength; following those authors (see also H. Schmid, 1940), but employing the value $K_{\mathrm{M2'}} = 1.26 \times 10^{2}\ \mathrm{M^2\ atm^{-2}}$ from Table 2, we obtain the value of $k_{\mathrm{M1^*/4^*}}$ given in Table 5, $4.06 \times 10^{3}\ \mathrm{M\ atm^{-2}\ s^{-1}}$.

4.1.2. Temperature Dependence

The temperature dependence of the empirical rate coefficient k_{fwd} was studied by Abel et al. (1930), who found an activation energy of 28.6 kcal mol^{-1}. This may be combined with $\Delta H^\circ[\mathrm{M2'}] = -18.2$ kcal mol^{-1} (Table 2) to yield an activation energy associated with $k_{\mathrm{M1^*/4^*}}$ of -7.8 kcal mol^{-1}. This negative activation energy, which indicates a decrease in the reaction rate with increasing temperature, undoubtedly reflects a negative enthalpy of solution of $\mathrm{NO_2}$ (decrease in the Henry's law coefficient for $\mathrm{NO_2}$ with increasing temperature) that outweighs the presumably positive activation energy associated with $k_{\mathrm{A1^*/4^*}}$.

4.1.3. Reverse Reaction

In their study of the reverse of [M10′], i.e., the formation of nitrous acid from NO(g) and nitric acid, Abel and H. Schmid (1928d) obtained the rate law

$$R_{-\mathrm{M10^*}} \equiv \frac{1}{3}\frac{d_{-\mathrm{M10^*}}}{dt}[\mathrm{HNO_2}] = k_{\mathrm{rev}}[\mathrm{H^+}][\mathrm{NO_3^-}][\mathrm{HNO_2}]. \tag{50}$$

Table 5. Experimental Determinations of $k_{-\mathrm{A}1^*/4^*}$ and $k_{\mathrm{M}1^*/4^*}$ at 25°C

Reference	$k_{-\mathrm{A}1^*/4^*}$ ($\mathrm{M}^{-2}\,\mathrm{s}^{-1}$)	$k_{\mathrm{M}1^*/4^*}$ ($\mathrm{M\,atm}^{-2}\,\mathrm{s}^{-1}$)	$k_{\mathrm{M}4^*/1^*}$ ($\mathrm{M\,atm}^{-1}\,\mathrm{s}^{-1}$)
Abel and H. Schmid (1928c)		4.06(3)	5.92(2)
Abel and H. Schmid (1928d)	8.9(−3)	4.25(3)[a]	6.20(2)
G. Schmid and Bähr (1964)	9.3(−3)[b]	4.42(3)[a,b]	6.44(2)
Komiyama and Inoue (1978)		8.63(3)	12.6 (2)
Komiyama and Inoue (1978)		11.4 (3)[c]	7.45(2)[c]
Jordan and Bonner (1973)	7.2(−3)	3.4 (3)[d]	5.0 (2)
Heckner (1973)		12.9 (3)	18.8 (2)

[a] Computed from $k_{-\mathrm{A}1^*/4^*}$ by (52).

[b] Measurements at 20°C corrected to 25°C.

[c] Measurements at 15°C, not temperature corrected.

(Again we note that the rate convention employed here differs by a factor of 3 from that employed by the original investigators.) The rate law (50) exhibits the interesting feature that it is autocatalytic, i.e., that the rate of formation of the product HNO_2 is proportional to the HNO_2 concentration. This rate law also differs from the reaction stoichiometry, but it is seen that the equilibrium constant expression, obtained by equating $R_{\mathrm{M}10^*}$ and $R_{-\mathrm{M}10^*}$, nonetheless exhibits the appropriate dependence on reagent concentrations [see Eq. (5)]. This rate law was interpreted in terms of the reverse of the decomposition mechanism:

$$\mathrm{HNO_2 + H^+ + NO_3^- \xrightarrow{w} 2NO_2(aq)(N_2O_4(aq))} \qquad [-\mathrm{A}1^*/4^*]$$

$$\mathrm{2NO_2(aq)(N_2O_4(aq)) + 2NO(aq) \overset{w}{=} 4HNO_2(aq)} \qquad [2\mathrm{A}2^*]$$

$$\mathrm{2NO(g) = 2NO(aq).} \qquad [2\mathrm{H_{NO}}]$$

For reaction $[-\mathrm{A}1^*/4^*]$ rate limiting,

$$R_{-\mathrm{M}10^*} = R_{-\mathrm{A}1^*/4^*} = k_{-\mathrm{A}1^*/4^*}[\mathrm{HNO_2}][\mathrm{H^+}][\mathrm{NO_3^-}]; \qquad (51)$$

i.e., $k_{-\mathrm{A}1^*/4^*}$ is equal to the empirically observed rate coefficient k_{rev}. We have noted [Eq. (25)] that the ratio of the forward and reverse hybrid rate coefficients is equal to the equilibrium constant $K_{\mathrm{A}1'}$ and hence

$$k_{\mathrm{A}1^*/4^*} = K_{\mathrm{A}1'} k_{-\mathrm{A}1^*/4^*} = K_{\mathrm{A}1'} k_{\mathrm{rev}},$$

and in turn [Eq. (28)] we obtain for the mixed-phase rate coefficient

$$k_{\mathrm{M}1^*/4^*} = \mathrm{H}^2_{\mathrm{NO_2}} K_{\mathrm{A}1'} k_{\mathrm{rev}},$$

We further observe (see Tables 1 and 2) that $K_{\mathrm{A}1'} = K_{\mathrm{M}1'}/\mathrm{H}^2_{\mathrm{NO_2}}$, and hence

$$k_{\mathrm{M}1^*/4^*} = k_{\mathrm{M}1'} k_{\mathrm{rev}}. \qquad (52)$$

Using the value of k_{rev} ($8.9 \times 10^{-3}\ \mathrm{M}^{-2}\ \mathrm{s}^{-1}$) determined by Abel and

H. Schmid (1928d) at 25°C and zero ionic strength and the value $K_{\mathrm{M1'}} = 4.78 \times 10^5$ M^3 atm^{-2} given in Table 2, we obtain $k_{\mathrm{M1^*/4^*}} = 4.25 \times 10^3$ M atm^{-2} s^{-1}, in substantial agreement with that obtained from measurement of the forward reaction rate.

A similar study, but at higher ionic strength, was carried out by G. Schmid and Bähr (1964). Those authors obtained the value for k_{rev} at 20°C, extrapolated to zero ionic strength, 5.56×10^{-3} M^{-2} s^{-1}. Employing the value $K_{\mathrm{M1'}} = 9.91 \times 10^5$ M^3 atm^{-2} obtained from Table 2 for 20°C, we obtain $k_{\mathrm{M1^*/4^*}} = 5.51 \times 10^3$ M atm^{-2} s^{-1} at 20°C. Correcting this value to 25°C by means of the activation energy obtained by Abel et al. (1930), we obtain $k_{\mathrm{M1^*/4^*}} = 4.42 \times 10^3$ M atm^{-2} s^{-1}, in close agreement with the earlier determinations.

4.1.4. *Non-Phase-Mixed Study*

A study of nitrous acid decomposition similar to that of Abel and H. Schmid was carried out by Komiyama and Inoue (1978). In this study, however, the aqueous-phase concentration of NO was not maintained equal to a value in Henry's law equilibrium with the gas phase but was maintained, rather, in steady state, as controlled by the formation reaction

$$3\mathrm{HNO_2(aq)} \rightarrow \mathrm{H^+} + \mathrm{NO_3^-} + 2\mathrm{NO(aq)} \qquad [\mathrm{A10^*}]$$

and mass transfer of the NO from the solution into a flowing sparge gas,

$$\mathrm{NO(aq)} \xrightarrow{k_{\mathrm{as}}} \mathrm{NO(g)},$$

[see Eq. (11) describing steady-state reagent concentrations in the slow-reaction regime]. The mass-transfer rate, which was controlled by the physical characteristics of the reactor and the flow rate of helium used as a sparge gas, was determined in separate experiments employing CO_2. Under these conditions the rate law observed for reaction [A10*] was

$$R_{\mathrm{A10^*}} = k'_{\mathrm{fwd}} k_{\mathrm{as}}^{2/3} [\mathrm{HNO_2}]^{4/3}. \qquad (53)$$

This rate law was shown to be consistent with the Abel–Schmid mechanism as given above, except that NO(aq) is interpreted not as being in Henry's law equilibrium, but in steady state, as controlled by the net rate of [− A2*] and the mass-transfer rate. Under this assumption the steady-state equations for NO(aq) and NO_2(aq) are

$$\frac{d[\mathrm{NO(aq)}]}{dt} = 0 = k_{-\mathrm{A2^*}}[\mathrm{HNO_2}]^2 - k_{\mathrm{A2^*}}[\mathrm{NO(aq)}][\mathrm{NO_2(aq)}] - k_{\mathrm{as}}[\mathrm{NO(aq)}] \qquad (54)$$

and

$$\frac{d[\mathrm{NO_2(aq)}]}{dt} = 0 = k_{-\mathrm{A2^*}}[\mathrm{HNO_2}]^2 - k_{\mathrm{A2^*}}[\mathrm{NO(aq)}][\mathrm{NO_2(aq)}] - 2k_{\mathrm{A1^*/4^*}}[\mathrm{NO_2(aq)}]^2. \qquad (55)$$

From (54) and (55) we obtain

$$[\mathrm{NO(aq)}] = \frac{2k_{\mathrm{A1^*/4^*}}}{k_{\mathrm{as}}}[\mathrm{NO_2(aq)}]^2.$$

Assumption of equilibrium [A2′] permits $[\mathrm{NO_2(aq)}]$ to be evaluated by (44) as

$$[\mathrm{NO_2(aq)}] = 2^{-1/3}K_{\mathrm{A2'}}^{-1/3}k_{\mathrm{A1^*/4^*}}^{-1/3}k_{\mathrm{as}}^{1/3}[\mathrm{HNO_2}]^{2/3}.$$

Hence, by (43) we obtain

$$R_{\mathrm{A10^*}} = 2^{-2/3}K_{\mathrm{A2'}}^{-2/3}k_{\mathrm{A1^*/4^*}}^{1/3}k_{\mathrm{as}}^{2/3}[\mathrm{HNO_2}]^{4/3}. \tag{56}$$

Comparison of (56) with (53) gives

$$k_{\mathrm{A1^*/4^*}} = 4K_{\mathrm{A2'}}^2 k_{\mathrm{fwd}}'^3.$$

Finally, from (45) and (49) we obtain

$$k_{\mathrm{M1^*/4^*}} = 4k_{\mathrm{fwd}}'^3\frac{K_{\mathrm{M2'}}^2}{\mathrm{H}_{\mathrm{NO}}^2}. \tag{57}$$

From the value $k'_{\mathrm{fwd}} = 7.97 \times 10^{-3}\ \mathrm{M}^{-1/3}\ \mathrm{s}^{-1/3}$ determined by Komiyama and Inoue for 25°C and $K_{\mathrm{M2'}}$ and $\mathrm{H_{NO}}$ as given in Table 2, we obtain $k_{\mathrm{M1^*/4^*}} = 8.63 \times 10^3\ \mathrm{M\ atm^{-2}\ s^{-1}}$, a factor of roughly 2 greater than the values obtained in the studies (Abel and H. Schmid, 1928d; G. Schmid and Bähr, 1964) in which NO was maintained at its Henry's law concentration. The authors suggest that in those studies the Henry's law equilibrium may not have been maintained; alternatively, the question may be raised as to whether Komiyama and Inoue's model, which assumes a uniform NO concentration and in turn a uniform NO_2 concentration, correctly describes their experimental situation, in which [NO(aq)] is maintained by competition between formation by chemical reaction and removal by mass transport from the aqueous phase into the gas phase. The existence of a nonuniform concentration profile for NO_2(aq) over a significant portion of the liquid volume would result in an average rate different from that computed by using the mean NO_2(aq) concentration, since this rate is quadratic in $[\mathrm{NO_2(aq)}$ [Eq. (43)]. In turn, the resulting value of $k_{\mathrm{A1^*/4^*}}$ would exhibit a corresponding departure from the true value. Because of the uncertainty raised by the possibility of nonuniform concentration profiles, we question the numerical accuracy of the value of $k_{\mathrm{M1^*/4^*}}$. Nonetheless, the observed reaction-rate law, in expectation with that based on the Abel–Schmid mechanism, and the proximity of the rate constant with that obtained in the earlier studies, lends support to the mechanistic interpretation by Abel and H. Schmid.

4.1.5. Isotope Exchange Study

The rate of reaction [$-$A10*] may be determined also from measurement of the rate of nitrogen exchange between NO and nitric acid in aqueous solution, which has been shown to be limited by NO_3^-–HNO_2 exchange (Jordan and Bonner, 1973). In that study isotopically labeled NO was brought into contact with aqueous HNO_3 solution. Initially the exchange rate was quite slow. However, after an induction period that was attributed to formation of an equilibrium concentration of HNO_2, a faster linear exchange rate was observed. (In separate experiments the buildup of HNO_2, monitored spectrophotometrically, was shown to take place on a time scale corresponding to the induction period of the exchange reaction.) The rate law for nitrogen exchange, derived from the measured rate of isotopic equilibration, was $R_N = k_{ex}[H^+][NO_3^-][HNO_2]$, where $[HNO_2]$ was evaluated as the equilibrium concentration as determined by the NO and HNO_3 concentrations. This rate law is identical to that observed by Abel and H. Schmid (1928d) for reaction [$-$A10*] [Eq. (51)]. Although it was not appreciated by the original authors, their data are represented by a rate constant that also exhibits close quantitative agreement with the rate constant of Abel and H. Schmid. The concentration and rate data for the several runs reported by Jordan and Bonner as well as the activity data for nitric acid at these concentrations as obtained by interpolation from the data of Davis and DeBruin (1964) are presented in Table 6. The data in the last column represent the rate constant for reaction [$-$A10*] under the assumption that this reaction is the rate-limiting step in the nitrogen exchange. The mean rate constant $(7.15 \pm 6\%) \times 10^{-3}$ $M^{-2}\ s^{-1}$ lies within some 20% of the values determined by Abel and H. Schmid (1928d) and G. Schmid and Bähr (1964) as shown in Table 5.

4.1.6. *Electrochemical Kinetic Studies*

The rate of reaction [$-$A10*] has been measured indirectly also in studies of the time dependence of the electrochemical reduction of nitric acid to

Table 6. Determination of $k_{-A1^*/4^*}$ from Isotopic Exchange Data of Jordan and Bonner (1973)[a]

$[HNO_3]$ (M)	$[HNO_2]$ (M)	p_{NO} (atm)	R_N ($M\ s^{-1}$)	$y_\pm$[b] (—)	α[b] (—)	$a_\pm$ (M)	$\frac{R_N}{[HNO_2]a_\pm^2}$ ($M^{-2}\ s^{-1}$)
0.914	8.2(−2)	0.218	2.8(−4)	0.76	0.98	0.68	7.5(−3)
0.609	7.1(−2)	0.189	1.1(−4)	0.74	0.98	0.45	7.8(−3)
0.499	6.4(−2)	0.259	6.7(−5)	0.74	0.98	0.37	7.8(−3)
0.450	6.1(−2)	0.228	3.7(−5)	0.74	0.99	0.33	5.5(−3)
0.440	6.0(−2)	0.203	4.3(−5)	0.74	0.99	0.32	6.9(−3)
0.308	5.2(−2)	0.228	2.3(−5)	0.74	0.99	0.23	8.8(−3)
0.301	5.0(−2)	0.226	1.4(−5)	0.74	0.99	0.22	5.7(−3)
							(7.2 ± 6%[c])(−3)

[a] 25°C.

[b] Activity coefficient $y_\pm$ and fractional dissociation α obtained by interpolation from data of Davis and DeBruin (1964).

[c] Standard deviation of the mean.

nitrous acid following sudden application of a constant electrode potential (Heckner, 1973; G. Schmid and Krichel, 1964). The reaction mixture consisted of a dilute solution of nitrous acid in rather concentrated nitric or mixed nitric and perchloric acids (≥3 M total acid concentration). After application of the constant electrode potential, the current was found to exhibit a well-defined maximum (20–400 ms depending on conditions) followed by a slow decrease. G. Schmid (1961) has interpreted such current–time observations in terms of concurrent diffusion and homogeneous reaction of a species (HNO_2) undergoing autocatalytic decomposition. The differential equation describing the species concentration C is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + k_{\mathrm{auto}}C, \tag{58}$$

where k_{auto} is the rate coefficient for the autocatalytic reaction. The solution of (58) yields the time dependence of the current i,

$$i = FC_0\left(\frac{D}{\pi t}\right)^{1/2}\exp(k_{\mathrm{auto}}t),$$

where F is the Faraday constant, D is the diffusion coefficient of the species, and C_0 is the initial (uniform) concentration of the species. It is seen that the current exhibits a maximum at time $t_m = (2k_{\mathrm{auto}})^{-1}$, whence

$$k_{\mathrm{auto}} = (2t_m)^{-1}. \tag{59}$$

The observations were interpreted in terms of the following mechanism for the cathode half-reaction:

$$2(\mathrm{HNO_2} + \mathrm{H^+} + e^- \xrightarrow{\mathrm{w}} \mathrm{NO}) \qquad [\mathrm{A14}]$$

$$\mathrm{H^+} + \mathrm{NO_3^-} + 2\mathrm{NO} \xrightarrow{\mathrm{w}} 3\mathrm{HNO_2} \qquad [-\mathrm{A10}^*]$$

$$\overline{\mathrm{3H^+} + \mathrm{NO_3^-} + 2e^- \xrightarrow{\mathrm{w}} \mathrm{HNO_2}.} \qquad [\mathrm{A15}]$$

Here [A14] represents the heterogeneous electrode reaction, which is posited to be fast, and the homogeneous reaction [−A10*] is assumed to be the rate-determining step. We have seen [Eq. (51)] that reaction [−A10*] has the rate

$$R_{-\mathrm{A10}^*} = k_{-\mathrm{A1}^*/4^*}a_{\mathrm{HNO_2}}a_{\mathrm{H^+}}a_{\mathrm{NO_3^-}}, \tag{60}$$

which is taken to be the rate of the overall reaction [15]. Here we have utilized activities in place of concentrations because of the rather high acid concentrations employed. Introducing activity coefficients into (60), we obtain

$$\begin{aligned}\frac{d[\mathrm{HNO_2}]}{dt} &= R_{\mathrm{A15}}\\ &= k_{-\mathrm{A1}^*/4^*}y_{\mathrm{H^+}}y_{\mathrm{NO_3^-}}y_{\mathrm{HNO_2}}[\mathrm{H^+}][\mathrm{NO_3^-}][\mathrm{HNO_2}].\end{aligned}$$

For fixed $[H^+]$ and $[NO_3^-]$, we see that reaction [A15] is autocatalytic in $[HNO_2]$; i.e., that

$$\frac{d[HNO_2]}{dt} = k_{auto}[HNO_2]$$

where

$$k_{auto} = k_{-A1^*/4^*}[H^+][NO_3^-]y_{H^+}y_{NO_3^-}y_{HNO_2},$$

thus permitting k_{auto} and, in turn $k_{-A1^*/4^*}$ to be determined [Eq. (59)] from the measured time to maximum current t_m.

Measurements of t_m and, in turn, $k_{-A1^*/4^*}$ were presented as a function of nitric acid concentration by G. Schmid and Krichel (1964); values of $k_{-A1^*/4^*}$ ranged from $4.2 \times 10^{-2}\,M^{-2}\,s^{-1}$ upward, increasing with increasing acid concentration. These values were indicated by the authors as being entirely consistent with the values of the empirical rate coefficient k_{rev} [Eq. (50)] for reaction [−M10*], as determined by G. Schmid and Bähr (1964). Similarly, in the work of Heckner (1973) measurements of t_m extrapolated to zero ionic strength led to a value of $k_{-A1^*/4^*}$ of $(2.7 \pm 20\%) \times 10^{-2}\,M^{-2}\,s^{-1}$. In this case also quantitative agreement was indicated between the value of the rate constant $k_{-A1^*/4^*}$ inferred from electrochemical measurements and the empirical coefficient k_{rev} (Abel and H. Schmid, 1928d; G. Schmid and Bähr, 1964).

Unfortunately, the close quantitative agreement between the chemical–kinetic and electrochemical experiments appears to be fortuitous. We have noted in conjunction with Eq. (50) that the expression for R_{-M10^*} adopted by Abel and H. Schmid (as well as by G. Schmid and Bähr) differs by a factor of 3 from modern convention. The value of $k_{-A1^*/4^*}$ obtained from the electrochemical measurements must be identified not with the rate constant given by Abel and H. Schmid (denoted k_2 by those authors), but rather with their rate constant *divided by 3*, i.e., the quantity k_{rev} as defined here. In view of the apparently close agreement found between $k_{-A1^*/4^*}$ determined by chemical kinetics and in the electrochemical studies, we are somewhat disappointed to have discovered this discrepancy. On the other hand, we take some solace in the qualitative agreement between the predicted dependence of the electrochemical transients on species concentrations that supports the mechanism of reaction [A10*] initially proposed by Abel and H. Schmid.

4.1.7. Summary

Rate constants $k_{-A1^*/4^*}$ and $k_{M1^*/4^*}$ determined by the several studies that were conducted at low ionic strength or that can be extrapolated to zero ionic strength are given in Table 5. Comparison of these results shows quite close agreement (8% spread) for the studies by Abel and H. Schmid (1928c,d) and G. Schmid and Bähr (1964). Since these studies represent independent investigations by two different methods (decomposition and formation of nitrous acid) characterized by a large number of individual determinations, including examination of dependence on ionic strength and temperature, we place the greatest confidence in these results.

To facilitate subsequent comparison of these measurements to measurements by other techniques, it is convenient to express the rate constant in terms of the compound oxide N_2O_4 as the reagent. In this notation the forward reaction is written as

$$N_2O_4(g)(2NO_2(g)) \overset{w}{\rightarrow} H^+ + NO_3^- + HNO_2(H^+ + NO_2^-) \qquad [M4^*/1^*]$$

having rate

$$R_{M4^*/1^*} = k_{M4^*/1^*} p_{N_2O_4},$$

where

$$k_{M4^*/1^*} = \frac{k_{M1^*/4^*}}{K_{G7}}.$$

Values of $k_{M4^*/1^*}$, obtained with $K_{G7} = 6.86\ \mathrm{atm}^{-1}$ at 25°C (Table 2), are also given in Table 5.

The temperature dependence of $k_{M4^*/1^*}$ may be expressed as an activation energy evaluated as

$$E_a[M4^*/1^*] = E_a[M1^*/4^*] - \Delta H°[G7].$$

From the value $E_a[M1^*/4^*] = -7.8\ \mathrm{kcal\ mol}^{-1}$ given above and $\Delta H°[G7]$ given in Table 2, we obtain $E_a[M4^*/1^*] = +5.9\ \mathrm{kcal\ mol}^{-1}$.

4.1.8. Examination of Assumptions

Before concluding the discussion of reaction [A1*/4*], it is of interest to examine more closely the mechanistic interpretation of the nitrous acid decomposition kinetics as initially set forth by Abel and H. Schmid, to address the assumptions of that mechanism. In particular, it was assumed that the reaction

$$2HNO_2(aq) \overset{w}{=} NO_2(aq) + NO(aq) \qquad [-A2']$$

could be considered to be at equilibrium. A necessary condition that must be satisfied for this equilibrium to obtain is that the rate of formation of $NO_2(aq)$ by reaction [−A2′] greatly exceed the rate of its depletion by reaction [A1*/4*],

$$2NO_2(aq)(N_2O_4(aq)) \overset{w}{\rightarrow} HNO_2 + H^+ + NO_3^-, \qquad [A1^*/4^*]$$

i.e., that

$$k_{-A2'}[HNO_2]^2 \gg 2k_{A1^*/4^*}[NO_2(aq)]^2. \qquad (61)$$

For evaluation of these rates, it is necessary to anticipate values of the two rate constants; based on the discussion presented below, we take $k_{-A2'} =$

5.6 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k_{\mathrm{A1^*/4^*}}$ as $6 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. Also, to evaluate $[\mathrm{NO_2(aq)}]$, we take $K_{\mathrm{A2'}} = 8 \times 10^6$, consistent with $H_{\mathrm{NO_2}} = 1 \times 10^{-2}\ \mathrm{M\ atm}^{-1}$. With these quantities we evaluate the rates of reactions [−A2′] and [A1*/4*] for the concentrations employed by Abel and H. Schmid (1928c, p. 293), as shown in Table 7. It is seen that the rate of reaction [A2′] greatly exceeds (three to four orders of magnitude) that of reaction [A1*/4*] for the concentrations employed, thus satisfying condition (61). Also shown is the rate of the overall reaction [A10′] evaluated by Eq. (42); this rate is seen to coincide with that of the rate-determining step [A1*/4*]. It is thus established that the Abel–Schmid mechanism is entirely consistent with values of the several constants of the magnitude assumed.

Similar examination has been made of the data of Komiyama and Inoue (1978) shown in Table 8 for representative conditions of that study. In most cases $R_{-\mathrm{A2'}}$ sufficiently exceeds $2R_{\mathrm{A1^*/4^*}}$ that the assumption of equilibrium [A2′] appears justified. However, at low $[\mathrm{HNO_2}]$ and high k_{as}, $2R_{\mathrm{A1^*/4^*}}$ becomes appreciable in comparison to $R_{-\mathrm{A2'}}$ (as great as 40%), suggesting that this assumption may not be appropriate under these conditions.

4.2. Reaction [M2*/5*]

The rate coefficient $k_{\mathrm{M2^*/5^*}}$ of the mixed-phase reaction

$$\mathrm{NO(g)} + \mathrm{NO_2(g)(N_2O_3(g))} \overset{\mathrm{w}}{\rightarrow} \mathrm{2HNO_2(2H^+ + 2NO_2^-)} \qquad [\mathrm{M2^*/5^*}]$$

may be inferred indirectly from measurement of the kinetics of the reverse reaction, i.e., from measurement of the kinetics of formation of $\mathrm{N_2O_3(aq)}$ from $\mathrm{HNO_2(aq)}$,

$$\mathrm{2HNO_2(aq)} \rightarrow \mathrm{N_2O_3(aq)}, \qquad [-\mathrm{A5'}]$$

Table 7. Rates of Elementary Reactions in $\mathrm{HNO_2}$ Decomposition Study by Abel and H. Schmid

Run Number	$[\mathrm{HNO_2}]^a$ (M)	$p_{\mathrm{NO}}{}^a$ (atm)	[NO(aq)] (M)	$[\mathrm{NO_2(aq)}]^b$ (M)	$R_{-\mathrm{A2'}}{}^b$ ($\mathrm{M\ s^{-1}}$)	$R_{\mathrm{A1^*/4^*}}{}^b$ ($\mathrm{M\ s^{-1}}$)	$R_{\mathrm{A10',\ meas}}{}^a$ ($\mathrm{M\ s^{-1}}$)
17	0.025	0.47	9.1(−4)	8.6(−8)	3.5(−3)	4.5(−7)	4.6(−7)
18	0.040	0.47	9.1(−4)	2.2(−7)	9.0(−3)	2.9(−6)	3.0(−6)
19	0.025	0.286	5.5(−4)	1.4(−7)	3.5(−3)	1.2(−6)	1.2(−6)
2	0.075	0.98	1.9(−3)	3.7(−7)	3.2(−2)	8.3(−6)	8.6(−6)
7	0.050	0.965	1.9(−3)	1.7(−7)	1.4(−2)	1.7(−6)	1.7(−6)
20	0.040	0.495	9.6(−4)	2.1(−7)	9.0(−3)	2.5(−6)	2.8(−6)

[a] Concentrations and rates given by Abel and H. Schmid (1928c, p. 293).

[b] Constants employed: $K_{\mathrm{A2'}} = 8 \times 10^6$; $k_{-\mathrm{A2'}} = 5.6\ \mathrm{M^{-1}\ s^{-1}}$; $k_{\mathrm{A1^*/4^*}} = 6 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$; k_{fwd} [Eq. (42)] $= 2.6 \times 10^{-1}\ \mathrm{atm^2\ M^{-3}\ s^{-1}}$.

Table 8. Rates of Elementary Reactions in HNO_2 Decomposition Study by Komiyama and Inoue

k_{as}[a] (s^{-1})	$[HNO_2]$[a] (M)	[NO(aq)][b] (M)	$[NO_2(aq)]$[b] (M)	$R_{-A2'}$[b] ($M\ s^{-1}$)	$R_{A1^*/4^*}$[b] ($M\ s^{-1}$)	$R_{A10',meas}$[a] ($M\ s^{-1}$)
2.4(−1)	5(−2)	3.7(−4)	8.5(−7)	1.4(−2)	4.3(−5)	7.2(−5)
2.4(−1)	1(−2)	4.3(−5)	2.9(−7)	5.6(−4)	5.1(−6)	
2.4(−1)	1(−3)	2.0(−6)	6.3(−8)	5.6(−6)	2.4(−7)	
2.4(−1)	1(−4)	9.2(−8)	1.4(−8)	5.6(−8)	1.1(−8)	
1.2(−1)	5(−2)	4.6(−4)	6.7(−7)	1.4(−2)	2.7(−5)	3.9(−5)
1.2(−1)	1(−2)	5.4(−5)	2.3(−7)	5.6(−4)	3.2(−6)	
1.2(−1)	1(−3)	2.5(−6)	5.0(−8)	5.6(−6)	1.5(−7)	
1.2(−1)	5(−4)	1.0(−6)	3.1(−8)	1.4(−6)	5.9(−8)	
4.5(−2)	5(−2)	6.4(−4)	4.9(−7)	1.4(−2)	1.4(−5)	2.1(−5)
4.5(−2)	1(−2)	7.5(−5)	1.7(−7)	5.6(−4)	1.7(−6)	
4.5(−2)	1(−3)	3.5(−6)	3.6(−8)	5.6(−6)	7.8(−8)	
4.5(−2)	5(−4)	1.4(−6)	2.3(−8)	1.4(−6)	3.1(−8)	
7.7(−3)	5(−2)	1.2(−3)	2.7(−7)	1.4(−2)	4.4(−6)	5.8(−6)
7.7(−3)	1(−2)	1.3(−4)	9.3(−8)	5.6(−4)	5.2(−7)	
7.7(−3)	1(−3)	6.3(−6)	2.0(−8)	5.6(−6)	2.4(−8)	
7.7(−3)	5(−4)	2.5(−6)	1.3(−8)	1.4(−6)	9.5(−9)	

[a] Concentrations and rates from Komiyama and Inoue (1978), Figures 4 and 5.

[b] Evaluated by using $K_{A2'} = 8 \times 10^6$, $k_{-A2'} = 5.6\ M^{-1}\ s^{-1}$, $k_{A1^*/4^*} = 6 \times 10^7\ M^{-1}\ s^{-1}$.

as

$$k_{M2^*/5^*} = k_{-A5'} K_{M2'}. \tag{62}$$

The rate coefficient $k_{-A5'}$ has not been measured directly but has been inferred from the rate of diazotization, nitrosation, and isotope exchange reactions that are interpreted as proceeding through N_2O_3 intermediate. If the rate-limiting step of those reactions is [−A5′], the rate constant $k_{-A5'}$ may be determined from the rate of the overall reaction.

4.2.1. Diazotization Studies

The rate and mechanism of diazotization reactions by N_2O_3 in aqueous solution has been of interest for some time (Ridd, 1961). Of importance in the present context is the observation (Bunton et al., 1961; Hughes and Ridd, 1958; Kalatzis and Ridd, 1966) that the diazotization or nitrosation of amines under certain conditions exhibits a rate law of the form

$$R_d = k_{obs}[HNO_2]^2 \tag{63}$$

independent of the concentration of the amine. Moreover, over a limited range of basicity, the observed rate constant is independent of the nature of the amine. This rate law has been interpreted in terms of the mechanism

$$2HNO_2 \xrightarrow{k_{-A5'}} N_2O_3$$

$$N_2O_3 \xrightarrow{k_{A5'}} 2HNO_2$$

$$N_2O_3 + ArNH_2 \xrightarrow{k_d} ArN_2^+ + NO_2^-.$$

Making the steady-state assumption for $[N_2O_3]$, one obtains

$$R_d = k_d[N_2O_3][ArNH_2]$$

$$= \frac{k_{-A5'}k_d[ArNH_2][HNO_2]^2}{k_{A5'} + k_d[ArNH_2]}.$$

For $k_d[ArNH_2] \gg k_{A5'}$,

$$R_d = k_{-A5'}[HNO_2]^2,$$

establishing identification of the observed rate constant k_{obs} [Eq. (63)] with $k_{-A5'}$.

Values of k_{obs} have been reported by Hughes and Ridd (1958) and Kalatzis and Ridd (1966), respectively, for diazotization of aniline and for nitrosation of *N*-methyl aniline at 0°C. Evaluation of k_{obs} from the experimental measurements is somewhat sensitive to the value of the acid dissociation constant of nitrous acid, K_{12}, employed. For $K_{12} = 3.5 \times 10^{-4}$ M at 0°C (as calculated from Table 2), we obtain $k_{obs} = 0.78$ M^{-1} s^{-1} at 0°C for both reactions. By the identification above, this value may be taken for $k_{-A5'}$ at this temperature.

Recently a value of 12.4 kcal mol^{-1} has been reported for the activation energy of $k_{-A5'}$ based on the temperature dependence of the rate of aniline diazotization (Ford, 1980). This value, in conjunction with the above value of $k_{-A5'}$ at 0°C, yields the value 5.3 M^{-1} s^{-1} at 25°C.

4.2.2. *Isotope Exchange Studies*

The rate and mechanism of oxygen–isotope exchange between nitrous acid and water has been examined by Bunton et al. (1959; 1961). The isotopic equilibration was found to exhibit the rate law

$$R_{ex} = k_{ex}[HNO_2]^2.$$

The exchange reaction also was interpreted as proceeding by means of N_2O_3 as an intermediate:

$$HONO + HONO^* \xrightarrow{\text{slow}} N_2O_3 + H_2O^*$$

$$H_2O + N_2O_3 \xrightarrow{\text{fast}} 2HONO,$$

leading to identification of k_{ex} with $k_{-A5'}$.

For k_{ex} at 0°C, Bunton et al. (1959) give 0.51 M^{-1} s^{-1}, in reasonably good agreement with the value given for $k_{A5'}$ based on diazotization kinetics, 0.78 $M^{-1}\,s^{-1}$. Subsequently (Bunton et al., 1961), the diazotization and exchange reactions were studied under "identical conditions," and "almost identical" reaction rates were reported, although, unfortunately, no details of that study have been given.

Bunton et al. (1959) also examined the isotope exchange kinetics at 25°C, from which a value of $k_{ex} = 5.8 \pm 15\%\ M^{-1}\,s^{-1}$ may be inferred, based on two measurements, in close agreement with the 25°C value for $k_{-A5'}$ obtained from diazotization kinetics. We thus take the value $k_{-A5'} = (5.6 \pm 15\%)\ M^{-1}\,s^{-1}$ representing the mean of these two determinations. This value of $k_{-A5'}$, in conjunction with $K_{M2'} = 126\ M^2\,atm^{-2}$ at 25°C (Table 2), permits $k_{M2^*/5^*}$ to be evaluated by Eq. (63). The resulting value, $7.0 \times 10^2\ M\,atm^{-2}\,s^{-1}$, is given in Table 9. Also given is $k_{M5^*/2^*}$, evaluated as $K_{M2^*/5^*}/K_{G8}$.

4.2.3. *Temperature Dependence*

As noted above, the activation energy of $k_{-A5'}$ inferred from diazotization kinetics (Ford, 1980) was 12.4 kcal mol^{-1}. The value inferred from the isotope exchange kinetics (Bunton et al., 1959) is 15.8 kcal mol^{-1}, yielding an average value and range of 14.1 ± 1.7 kcal mol^{-1}. From (63) it is seen that the activation energy associated with $k_{M2^*/5^*}$ may be evaluated as

$$E_a[M2^*/5^*] = E_a[-A5'] + \Delta H^\circ[M2'].$$

From the value $\Delta H^\circ[M2'] = -18.2$ kcal mol^{-1} (Table 2) we obtain $E_a[M2^*/5^*] = -(4.1 \pm 1.7)$ kcal mol^{-1}. The overall negative activation energy (increasing rate with decreasing temperature) would appear to reflect an increased solubility at lower temperatures outweighing a presumably decreasing rate of reaction [A2*/5*]. We note (Table 2) the negative enthalpy of solution of NO, $\Delta H^\circ(H_{NO}) = -2.9$ kcal mol^{-1}.

The activation energy associated with $k_{M5^*/2^*}$ evaluated as

$$E_a[M5^*/2^*] = E_a[M2^*/5^*] - \Delta H^\circ[G8]$$

Table 9. Experimental Determination of $k_{-A5'}$ and $k_{M2^*/5^*}$ at 25°C[a]

Rate Constant	Diazotization	Isotope Exchange	Mean	Units
$k_{-A5'}$	5.3[a]	5.8[b]	5.6 ± 15%	$M^{-1}\,s^{-1}$
$k_{M2^*/5^*}$[c]	6.7(2)	7.3(2)	7.0(2)	$M\,atm^{-2}\,s^{-1}$
$k_{M5^*/2^*}$[d]	1.25(3)	1.37(3)	1.3(3)	$M\,atm^{-1}\,s^{-1}$

[a] From measurements of Hughes and Ridd (1958) and Kalatzis and Ridd (1966) at 0°C, as corrected to 25°C by employing the activation energy reported by Ford (1980).

[b] Measurements by Bunton et al. (1959).

[c] Evaluated as $k_{M2^*/5^*} = k_{-A5'}K_{M2'}$ for $K_{M2'} = 126\ M^2\,atm^{-2}$.

[d] Evaluated as $k_{M5^*/2^*} = k_{M2^*/5^*}/K_{G8}$ for $K_{G8} = 0.535\ atm^{-1}$.

is $+5.4 \pm 1.7$ kcal mol^{-1}, where we have employed the value of $\Delta H°$[G8] in Table 2.

4.3. Reaction [M11′]

In a recent study Epstein et al. (1980) have examined the kinetics of the oxidation of ferrous ion by nitric acid,

$$3Fe^{2+} + 4H^{+} + NO_3^{-} \overset{w}{=} 3Fe^{3+} + NO.$$

The kinetics of this system are complex and, as the authors point out, have yet to be entirely elucidated. The approach taken by Epstein et al. was to describe the evolution of the concentrations of the several species in terms of a set of coupled ordinary differential equations in these concentrations. The computed time profiles of various observables (extinction, redox potential) were compared to observation as a function of parameters (rate constants, H_{NO_2}, initial HNO_2 concentration), and values of these parameters were inferred from the best fit to observation. By this approach the authors deduced inter alia the rate of the reaction

$$H^{+} + NO_3^{-} + NO(aq) = HNO_2 + NO_2(aq). \qquad [-A11']$$

The rate expression given was

$$R_{-A11'} = k_{(64)}[H^{+}]^2[NO_3^{-}][NO(aq)]; \qquad (64)$$

we choose to write this as

$$R_{-A11'} = k_{-A11'}[H^{+}][NO_3^{-}][NO(aq)], \qquad (65)$$

where $k_{-A11'}$, the effective rate constant for reaction [−A11′] as written, incorporates the additional hydrogen-ion dependence, i.e., $k_{-A11'} = k_{(64)}[H^{+}]$. From the numerical value given by Epstein et al. for $k_{(64)}$, we obtain $k_{-A11'} = 7.5\ [H^{+}]\ M^{-2}\ s^{-1}$ at 23°C. The uncertainty in the value of the rate constant given by Epstein et al. was claimed to be "factor-of-two"; however, ionic strength corrections, which were estimated only by means of the Debye–Hückel formula, which would break down at concentrations well below the ionic strength of 2.1 M employed, led the authors to state that the values of the rate constants obtained were "probably accurate to no better than an order of magnitude."

Knowledge of the value of the effective rate constant $k_{-A11'}$ permits evaluation of the rate constant of the reverse reaction

$$NO_2(g) + HNO_2(aq) \rightarrow H^{+} + NO_3^{-} + NO \qquad [M11']$$

by means of the equilibrium constant of the reaction

$$NO_2(g) + HNO_2 = NO(aq) + H^{+} + NO_3^{-} \qquad [M11†]$$

as

$$k_{\mathrm{M11'}} = K_{\mathrm{M11\dagger}} k_{-\mathrm{A11'}}.$$

The equilibrium constant $K_{\mathrm{M11\dagger}}$ may be evaluated as $K_{\mathrm{M11'}} H_{\mathrm{NO}}$ and has the value 7.58 $\mathrm{M^2\ atm^{-1}}$ at 25°C (data from Table 2). The resulting value of $k_{\mathrm{M11'}}$ is $5.7 \times 10^1[\mathrm{H^+}]\ \mathrm{atm^{-1}\ s^{-1}}$.

In view of the indirect means by which Epstein et al. inferred the rate of reaction [−A11′] in their system, it is of interest to address the consistency of this rate with other experimental studies. We first consider studies of reaction

$$2\mathrm{NO(aq)} + \mathrm{H^+} + \mathrm{NO_3^-} \xrightarrow{\mathrm{w}} 3\mathrm{HNO_2(aq)}. \qquad [-\mathrm{A10'}]$$

Assuming that reaction (−A11′) occurs (as claimed by Epstein et al.), the overall reaction [−M10′] may proceed by way of not only the sequence discussed in Section 4.1, but also the sequence

$$2\mathrm{NO(g)} = 2\mathrm{NO(aq)} \qquad [2\mathrm{H_{NO}}]$$

$$\mathrm{NO(aq)} + \mathrm{H^+} + \mathrm{NO_3^-} \rightarrow \mathrm{HNO_2} + \mathrm{NO_2(aq)} \qquad [-\mathrm{A11'}]$$

$$\mathrm{NO(aq)} + \mathrm{NO_2(aq)} \overset{\mathrm{w}}{=} 2\mathrm{HNO_2} \qquad [\mathrm{A2'}]$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$2\mathrm{NO(g)} + \mathrm{H^+} + \mathrm{NO_3^-} \xrightarrow{\mathrm{w}} 3\mathrm{HNO_2} \qquad [-\mathrm{M10'}]$$

For reaction [A2′] fast, reaction [−A11′] is rate determining, and the rate of [−A10′] may be evaluated as

$$R_{-\mathrm{A10'}} = k_{-\mathrm{A11'}}[\mathrm{NO(aq)}][\mathrm{H^+}][\mathrm{NO_3^-}]. \qquad (66)$$

For NO at Henry's law equilibrium (phase-mixed limit), this rate is

$$R_{-\mathrm{M10'}} = k_{-\mathrm{A11'}} \mathrm{H_{NO}} p_{\mathrm{NO}} [\mathrm{H^+}][\mathrm{NO_3^-}]. \qquad (67)$$

This predicted rate law stands at variance with the observed rate law for this reaction discussed above (Section 4.1),

$$R_{-\mathrm{M10'}} = k_{\mathrm{rev}}[\mathrm{H^+}][\mathrm{NO_3^-}][\mathrm{HNO_2}]. \qquad (50)$$

This inconsistency may be addressed further by comparing the rates given by (67) and (50) with experimental data. This is done in Table 10, without correction for ionic strength. It is seen that the rate of reaction [−M10′] predicted by the mechanism incorporating the reaction proposed by Epstein et al. exceeds the measured rate by one to two orders of magnitude. Furthermore, this rate law predicts neither the observed dependence on $[\mathrm{HNO_2}]$ (cf. runs 5 and 6) nor the observed independence on p_{NO} (cf. runs 19 and Table 9). It is thus established that this rate law is inconsistent with the measured rates.

It is of interest also to explore the consequences of the rate of reaction [A11′] proposed by Epstein et al. (1980) on the kinetics of nitrous acid

Table 10. Comparison of Measured[a] and Calculated Rates of Reaction [−M10′]

Run Number	$[H^+]$ (M)	$[NO_3^-]$ (M)	$[HNO_2]$ 10^{-3} M	p_{NO} (atm)	$R_{-M10'}$ ($M\ s^{-1}$) Measured	Eq. (50)	Eq. (67)
19	0.050	0.060	10.0	1	1.9(−7)	2.7(−7)	2.2(−6)
20	0.050	0.120	10.0	1	3.9(−7)	5.3(−7)	4.3(−6)
13–15	0.197	0.206	8.8	1	1.8(−6)	3.2(−6)	1.2(−4)
5	0.203	0.162	9.8	1	1.5(−6)	2.9(−6)	9.8(−5)
6	0.203	0.162	2.4	1	3.8(−7)	7.0(−7)	9.7(−5)
Table 9	0.050	0.060	10.0	0.514	2.1(−7)	2.7(−7)	1.1(−6)

[a] Data of Abel and H. Schmid (1928d, pp. 141–142).

decomposition. If, as was assumed in the Abel–Schmid mechanism treated above, it is assumed that reaction [−A2′] is in equilibrium, the subsequent occurrence of reaction [A11′] would yield the following mechanism:

$$2HNO_2 \overset{w}{=} NO_2(aq) + NO(aq) \qquad [-A2']$$

$$NO_2(aq) + HNO_2 \rightarrow H^+ + NO_3^- + NO(aq) \qquad [A11']$$

$$2NO(aq) = 2NO(g) \qquad [-2H_{NO}]$$

$$3HNO_2 \overset{w}{\rightarrow} H^+ + NO_3^- + 2NO(g) \qquad [M10']$$

i.e., the overall stoichiometry that is observed. This mechanism yields the kinetic rate law

$$R_{M10'} = k_{A11'}K_{-A2'}\frac{[HNO_2]^3}{[NO(aq)]} = k_{M11'}K_{M2'}^{-1}\frac{[HNO_2]^3}{p_{NO}} \qquad (68)$$

The form of (68) is seen to be inconsistent with the observed rate law (Abel and H. Schmid, 1928c),

$$R_{M10'} = k_{fwd}\frac{[HNO_2]^4}{p_{NO}^2}, \qquad (42)$$

raising further concern about the validity of the rate law (64) for reaction [−A11′] proposed by Epstein et al. This inconsistency is addressed quantitatively in Table 11, in which the rate of reaction [M10′] evaluated by (68) is compared to the measured rates. Again the rate law inferred from (64) is entirely at variance with the measurements. In particular, those runs (5, 6, 14–16) for which the calculated rate exceeds the measured rate (by a factor of as much as 4) would appear to exclude a rate law of the form proposed by Epstein et al.

Table 11. Comparison of Measured[a] and Calculated Rates of HNO_2 Decomposition

Run Number	$[HNO_2]$ 10^{-3} M	$[H^+]$ 10^{-3} M	$R_{-M10'}$ $(M\ s^{-1})$ Measured	Eq. (68)
5	75	99	8.6(−6)	1.9(−5)
6	100	105	3.0(−5)	4.8(−5)
10	25	0.6	9.1(−8)	4.2(−9)
11	50	1.2	1.9(−6)	6.8(−8)
12	50	0.6	1.6(−6)	3.4(−8)
13	50	0.6	1.8(−6)	3.4(−8)
14	50	60.0	2.1(−6)	3.4(−6)
15	50	52.5	1.7(−6)	6.6(−6)
16	50	150	1.8(−6)	8.5(−6)

[a] Concentrations and measurements from Abel and H. Schmid (1928c, pp. 288, 292); $p_{NO} \approx 1$ atm.

Further evidence against the rate law proposed by Epstein et al. may be adduced from the observation of an induction period in the autocatalytic reaction

$$H^+ + NO_3^- + 2NO(g) \xrightarrow{w} 3HNO_2. \qquad [-M10']$$

An example is given by Jordan and Bonner (1973). For 0.46 M HNO_3 and $p_{NO} = 0.20$ atm, the time taken to reach equilibrium HNO_2 concentration (0.06 M) was 20–60 min. This may be compared to that calculated for the mechanism $[2H_{NO}]$–$[-A11']$–$[A2']$ with rate law (67). The time required to reach equilibrium by this rate may be approximated as

$$\tau_e \approx \frac{[HNO_2]_e}{d[HNO_2]/dt} \approx \frac{[HNO_2]_e}{3R_{-M10'}}.$$

Evaluation of this quantity for the concentrations given yields $\tau_e \approx 1$ min, much shorter than that observed.

In conclusion of this section it would appear that little case can be made for the rate expression (64) advanced by Epstein et al. (1980). The evidence in favor of this expression is indirect, and as the authors themselves point out, one must be extremely cautious in drawing quantitative inferences about rate constants from simulations of such complex systems. There is, moreover, strong evidence against the rate expression (64) from several studies. We thus conclude that the rate of the elementary reaction $[-A11']$ is substantially less than that postulated by Epstein et al. and hence that evidence in support of this reaction must be discounted.

5. DIRECT MEASUREMENT OF AQUEOUS-PHASE KINETICS

In view of the difficulties of interpreting indirect studies and in view also of the difficulty of direct measurement of mixed-phase reaction rates in the nitrogen oxide–water system, an attractive alternative approach to these quantities is by means of direct measurement of the aqueous-phase rate constants. Measurement of these rate constants is based on the concept of rapidly preparing an aqueous solution of the nitrogen oxide(s) of interest and monitoring the subsequent evolution of the dissolved species. If this can be done on a time scale short compared to coupling to the gas phase (e.g., "outgassing"), the possibility exists of determining the aqueous-phase rate constant of the reaction under examination. We address in this section studies of this sort where the aqueous nitrogen oxide(s) are produced by pulse radiolysis or flash photolysis or are directly injected into water under high pressure.

5.1. Reaction [A7]

In the study by Grätzel et al. (1969), $NO_2(aq)$ was produced by pulse radiolysis of an aqueous solution of nitrite in the presence of N_2O [the experiment is outlined more completely in the discussion of equilibrium [A7] given by Schwartz and White (1981)]. The concentration of NO_2 initially formed was determined absolutely by pulse dosimetry. The decay of $[NO_2]$, which was monitored by optical absorption at 400 nm, took place initially on a microsecond time scale and subsequently on a millisecond time scale.

The initial rapid decrease in $[NO_2(aq)]$ is ascribed to the reaction

$$2NO_2(aq) \xrightarrow{k_{A7}} N_2O_4(aq).$$

A second-order initial rate law was observed

$$\frac{d[NO_2]}{dt} = -2k_{A7}[NO_2]^2 \tag{69}$$

for initial $[NO_2]$ ranging from 8×10^{-6} to 30×10^{-6} M. The authors derived k_{A7} from the initial rate data only (i.e., neglecting the back reaction). From the integrated form of (69), one obtains for $\tau_{3/4}$, the time for the absorbance of NO_2 to decrease to three-fourths of its initial value,

$$\tau_{3/4} = \frac{1}{3[NO_2]_0}\frac{1}{2k_{A7}}$$

From a graph of $\tau_{3/4}$ versus $[NO_2]_0^{-1}$ (as determined from the measured absorbance at 400 nm, making use of the extinction coefficient also derived in that study), Grätzel et al. (1969) obtained the value $k_{A7} = (4.5 \pm 1.0) \times 10^8\ M^{-1}\ s^{-1}$.

5.2. Reaction [A8]

In the presence of excess NO (2×10^{-5} to 1×10^{-4} M), NO_2 formed in the pulse radiolysis was found to react according to

$$NO(aq) + NO_2(aq) \underset{k_{-A8}}{\overset{k_{A8}}{\rightleftharpoons}} N_2O_3(aq);$$

the kinetics of approach to equilibrium [A8] was monitored (Grätzel et al., 1970) by the rate of increase of absorption at 260 nm (N_2O_3) or by the rate of decrease of absorption at 400 nm (NO_2). The N_2O_3 concentration was observed to exhibit the time dependence

$$[N_2O_3] = [N_2O_3]_f(1 - e^{-t/\tau}),$$

where $[N_2O_3]_f$ represents the final value of $[N_2O_3]$. From consideration of reversible pseudo-first-order kinetics ([NO(aq)] is in excess and effectively constant), the time constant τ is given (Eigen and DeMaeyer, 1963) as

$$\tau^{-1} = k_{A8}[NO] + k_{-A8'},$$

and hence, by (5),

$$\tau^{-1} = k_{A8}([NO] + K_{A8}^{-1}).$$

From a graph of τ^{-1} versus [NO], k_{A8} was determined as 1.1×10^9 M^{-1} s^{-1} (20°C).

5.3. Reaction [A1*/4*]

As discussed in Section 3.1, $NO_2(aq)$ and/or $N_2O_4(aq)$ react with water according to the stoichiometry

$$2NO_2(aq)(N_2O_4(aq)) \overset{w}{\rightarrow} H^+ + NO_3^- + HNO_2(H^+ + NO_2^-). \quad [A1^*/4^*]$$

If, as is the case even in the pulse radiolysis experiments, equilibrium [A7] is established more rapidly than is [A1*/4*], one cannot distinguish between the two paths. We have chosen [see Eq. (20)] to express the rate of reaction referred to two NO_2 molecules as reagents, i.e.,

$$R_{A1^*/4^*} = k_{A1^*/4^*}[NO_2]^2. \tag{70}$$

5.3.1. Pulse Radiolysis and Flash Photolysis Studies

In the pulse radiolysis experiment by Grätzel et al. (1969), which was conducted in slightly basic solution, the rate of [A1*/4*] was monitored as a decrease in $[OH^-]$, itself monitored by electrical conductivity. Under these conditions

$$R_{A1^*/4^*} = -\frac{1}{2}\frac{d[OH^-]}{dt} = -\frac{1}{2}\frac{d[N(IV)]}{dt}, \tag{71}$$

where $[\mathrm{N(IV)}] \equiv [\mathrm{NO_2}] + 2[\mathrm{N_2O_4}]$. Assuming equilibrium [A7] to be established, i.e., $[\mathrm{N_2O_4}] = K_{\mathrm{A7}}[\mathrm{NO_2}]^2$, one may express $[\mathrm{NO_2}]$ in terms of $[\mathrm{N(IV)}]$ as

$$[\mathrm{NO_2}] = \frac{(8K_{\mathrm{A7}}[\mathrm{N(IV)}] + 1)^{1/2} - 1}{4K_{\mathrm{A7}}}. \tag{72}$$

Observing that $-d[\mathrm{N(IV)}]/dt = 2k_{\mathrm{A1^*/4^*}}[\mathrm{NO_2}]^2$, one obtains a differential equation in $[\mathrm{N(IV)}]$,

$$-\frac{d[\mathrm{N(IV)}]}{dt} = k_{\mathrm{A1^*/4^*}}K_{\mathrm{A7}}\left\{[\mathrm{N(IV)}] - \frac{K_{\mathrm{A7}}}{4}\left[\left(\frac{8[\mathrm{N(IV)}]}{K_{\mathrm{A7}}} + 1\right)^{1/2} - 1\right]\right\}. \tag{73}$$

Equation (73) may exhibit apparent first- or second-order kinetics in the limit as N(IV) is present predominantly as $\mathrm{N_2O_4}$ or $\mathrm{NO_2}$, respectively, as governed by equilibrium [A7]. The distribution of N(IV) between $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ is shown in Figure 1 as a function of total N(IV) concentration. From inspection of this diagram we may place the bounds on the N(IV) concen-

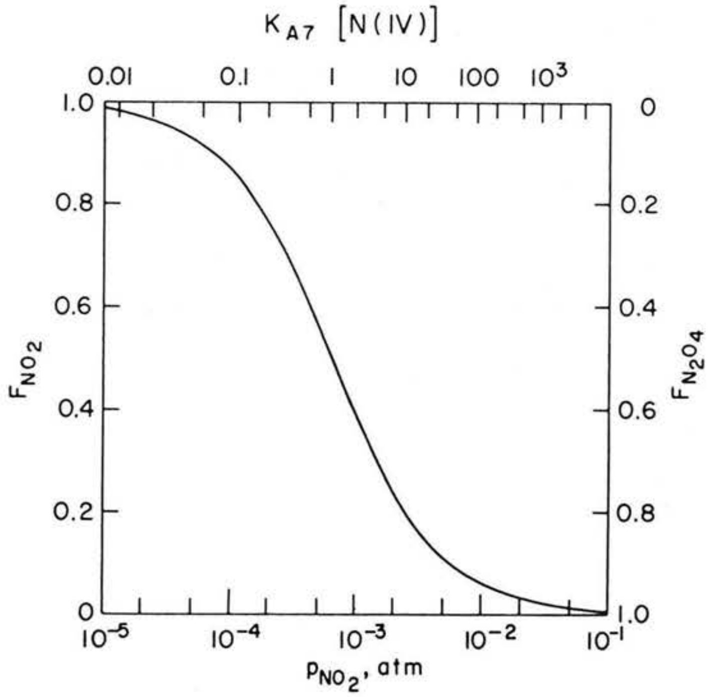

Figure 1. Equilibrium distribution of aqueous N(IV) between monomeric and dimeric forms as a function of K_{A7} [N(IV)] (top scale) and of $p_{\mathrm{NO_2}}$ (bottom scale); $F_{\mathrm{NO_2}}$ and $F_{\mathrm{N_2O_4}}$ represent fraction of N(IV) present as $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$, respectively. In evaluation as function of $p_{\mathrm{NO_2}}$, $\mathrm{H_{NO_2}}$ was taken as 1.2 M atm^{-1} and K_{A7} as 6.5×10^4 M^{-1}.

tration regime for first- or second-order kinetics as

$$-\frac{d[\mathrm{N(IV)}]}{dt} = \begin{cases} \dfrac{k_{\mathrm{A1^*/4^*}}}{K_{\mathrm{A7}}}[\mathrm{N(IV)}], & [\mathrm{N(IV)}] \gtrsim 50K_{\mathrm{A7}}^{-1} \quad (74) \\ \\ 2k_{\mathrm{A1^*/4^*}}[\mathrm{N(IV)}]^2, & [\mathrm{N(IV)}] \lesssim 0.06K_{\mathrm{A7}}^{-1} \quad (75) \end{cases}$$

Experimentally it was found that the half-life for reaction [A1*/4*] increased from 3 to 14 ms with decreasing $[\mathrm{N(IV)}]_0$ in the range $(0.46\text{–}6) \times 10^{-6}$ M (cf. $K_{\mathrm{A7}}^{-1} = 15.3 \times 10^{-6}$ M). Grätzel et al. interpreted these data according to mixed-order kinetics [Eq. (73)], making use of their value of K_{A7}. The value of the rate constant determined in this way, expressed as $k_{\mathrm{A1^*/4^*}}$, is $k_{\mathrm{A1^*/4^*}} = (6.5 \pm 10\%) \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$.

Reaction [A1*/4*] was studied also (by pulse radiolysis and flash photolysis) by Treinin and Hayon (1970). In this study $\mathrm{NO_2(aq)}$ in the absence of NO(aq) was produced by pulse radiolysis of nitrite solution in the presence of $\mathrm{N_2O}$ [the same method as employed by Grätzel et al. (1969)] or by flash photolysis of nitrate in the presence of nitrite:

$$\mathrm{NO_3^-} + h\nu \rightarrow \mathrm{NO_2} + \mathrm{O^-}$$

followed by

$$\mathrm{O^-} + \mathrm{NO_2^-} \overset{\mathrm{w}}{\rightarrow} \mathrm{NO_2} + 2\mathrm{OH^-}. \qquad [\mathrm{A16}]$$

The extent of reaction was followed by monitoring $\mathrm{NO_2}$ or $\mathrm{N_2O_4}$ spectrophotometrically. Treinin and Hayon obtained essentially the same value of K_{A7} as was obtained by Grätzel et al. However, in the kinetic study, in contrast to the findings of Grätzel et al., Treinin and Hayon observed an apparent first-order decay of $[\mathrm{NO_2}]$ that was independent of $[\mathrm{NO_2}]$ throughout the range studied $[(0.25\text{–}22) \times 10^{-6}$ M, corresponding to [N(IV)] in the range $(0.26\text{–}100) \times 10^{-6}$ M]. The value of the observed first-order rate constant was $k_{\mathrm{obs}} \approx 300\ \mathrm{s^{-1}}$ at 25°C, with the reaction half-life in no case greater than 3.6 ms (cf. 3–14 ms observed by Grätzel et al.). These authors also addressed the possible dependence of k_{obs} on nitrite and nitrate concentrations (≤ 0.1 M) and pH (5.0–11.4) and found k_{obs} to be independent of these variables.

The observations by Treinin and Hayon may be interpreted as follows, bearing in mind that in this study the observed reactant was $\mathrm{NO_2}$. We note that

$$2[\mathrm{NO_2}]\frac{d[\mathrm{NO_2}]}{dt} = K_{\mathrm{A7}}^{-1}\frac{d[\mathrm{N_2O_4}]}{dt},$$

and hence

$$\frac{d[\mathrm{N(IV)}]}{dt} \equiv \frac{d[\mathrm{NO_2}]}{dt} + 2\frac{d[\mathrm{N_2O_4}]}{dt} = (1 + 4K_{\mathrm{A7}}[\mathrm{NO_2}])\frac{d[\mathrm{NO_2}]}{dt}.$$

From Eq. (70) we thus obtain

$$-\frac{d[\mathrm{NO_2}]}{dt} = \frac{2k_{\mathrm{A1^*/4^*}}[\mathrm{NO_2}]^2}{1 + 4K_{\mathrm{A7}}[\mathrm{NO_2}]}. \tag{76}$$

At high $[\mathrm{NO_2}]$ this reduces to

$$-\frac{d[\mathrm{NO_2}]}{dt} = \frac{k_{\mathrm{A1^*/4^*}}}{2K_{\mathrm{A7}}}[\mathrm{NO_2}], \qquad [\mathrm{NO_2}] \gtrsim 2.5\ K_{\mathrm{A7}}^{-1}. \tag{77}$$

Setting (77) equal to the observed first-order rate constant, we obtain $k_{\mathrm{A1^*/4^*}} = (4.7 \pm 22\%) \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$, which is in reasonable agreement with the value determined by Grätzel et al. Unfortunately for this interpretation, it is seen that the condition (77) is scarcely fulfilled at the highest initial $\mathrm{NO_2}$ concentrations employed by Treinin and Hayon ($4K_{\mathrm{A7}}[\mathrm{NO_2}]_{\mathrm{max}} = 7$). Thus, to account for the observed first-order kinetics, Treinin and Hayon proposed an additional reaction sequence

$$\mathrm{NO_2(aq)} + \mathrm{X} \rightarrow \mathrm{NO_2} \cdot \mathrm{X} \tag{A17}$$

$$\mathrm{NO_2} \cdot \mathrm{X} + \mathrm{NO_2(aq)} \xrightarrow{\mathrm{w}} 2\mathrm{H^+} + \mathrm{NO_2^-} + \mathrm{NO_3^-}(+\mathrm{X}) \tag{A18}$$

where X (which may be water itself) is present at constant composition. For [A17] fast, the sequence [A17]–[A18] has rate

$$R_{\mathrm{A17-A18}} = k_{\mathrm{A17}}[\mathrm{NO_2}],$$

and hence (70) becomes

$$-\frac{d[\mathrm{N(IV)}]}{dt} = 2k_{\mathrm{A1^*/4^*}}[\mathrm{NO_2}]^2 + 2k_{\mathrm{A17}}[\mathrm{NO_2}]$$

leading to

$$-\frac{d[\mathrm{NO_2}]}{dt} = 2k_{\mathrm{A17}}[\mathrm{NO_2}]\left\{\frac{1 + (k_{\mathrm{A1^*/4^*}}/k_{\mathrm{A17}})[\mathrm{NO_2}]}{1 + 4K_{\mathrm{A7}}[\mathrm{NO_2}]}\right\}. \tag{78}$$

Equation (78) is seen to explain the first-order decay of $[\mathrm{NO_2}]$ with $k_{\mathrm{obs}} = 2k_{\mathrm{A17}}$, provided the quantity in braces remains approximately constant over the range of $[\mathrm{NO_2}]$ investigated. The latter condition is satisfied for $k_{\mathrm{A1^*/4^*}} = 4K_{\mathrm{A7}}k_{\mathrm{A17}} = 2K_{\mathrm{A7}}k_{\mathrm{obs}}$ and is seen to be equivalent to the high-$[\mathrm{NO_2}]$ limit to (76); i.e., $k_{\mathrm{A1^*/4^*}} = 4.7 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$, which agrees with $k_{\mathrm{A1^*/4^*}}$ determined by Grätzel et al. The apparent first-order rate constant was determined as $k_{\mathrm{A17}} = k_{\mathrm{obs}}/2 = (1.5 \pm 22\%) \times 10^2\ \mathrm{s^{-1}}$ at 25°C. The temperature dependence of the hydrolysis rate was examined as well. For temperatures of up to 76°C, $\mathrm{NO_2}$ continued to react with apparent first-order kinetics, with an apparent activation energy of 4.7 kcal $\mathrm{mol^{-1}}$.

The experimental results of Treinin and Hayon disagree with those of Grätzel et al., which showed an increase in the characteristic lifetime of aqueous N(IV) well beyond the value given by the first-order mechanism proposed by Treinin and Hayon. We are unable to explain this inconsistency.

However, we are somewhat uneasy with Treinin and Hayon's explanation for the constancy of k_{obs} in terms of the coincidence of $k_{\mathrm{A1^*/4^*}}$ and $4K_{\mathrm{A7}}k_{\mathrm{A17}}$, especially as this coincidence is required to obtain over the temperature range 25–76°C.

Reaction [A1*/4*] was investigated by Ottolenghi and Rabani (1968) in the ferrocyanide-sensitized flash photolysis of nitrate. On ultraviolet excitation, ferrocyanide efficiently ejects an electron, which, the authors argued, reacts with nitrate to form NO_2:

$$e(\mathrm{aq})^- + \mathrm{NO_3^-} \overset{\mathrm{w}}{\rightarrow} \mathrm{NO_2} + 2\mathrm{OH^-}.$$

The NO_2 thus formed reacted either with ferrocyanide

$$\mathrm{NO_2} + \mathrm{Fe(CN)_6^{4-}} \rightarrow \mathrm{Fe(CN)_6^{3-}} + \mathrm{NO_2^-} \qquad [\mathrm{A19}]$$

or by reaction [A1*/4*]; the competition between these reactions was varied by varying $[NO_2]_0$ and/or $[\mathrm{Fe(CN)_6^{4-}}]$. The time-dependent concentrations (over some tens of milliseconds) of NO_2, $\mathrm{Fe(CN)_6^{4-}}$, and $\mathrm{Fe(CN)_6^{3-}}$ were inferred from the optical extinction measured at 420 nm. At low $[NO_2]_0$, NO_2 reacted exclusively by reaction [A19], permitting determination of k_{A19}. With increasing $[NO_2]_0$, $1.6–7.3 \times 10^{-6}$ M, an increasing proportion of NO_2 reacted by [A1*/4*]; $k_{\mathrm{A1^*/4^*}}$ was determined by fit to the time-dependent absorption measurements as $(3.8 \pm 1.4) \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$ (temperature unspecified but presumably 20–25°C).

In our judgment this experiment should be taken as yielding only semiquantitative information on the rate and mechanism of reaction [A1*/4*]. First, we note that Ottolenghi and Rabani's estimated error bars on the extinction coefficient of NO_2 [obtained by difference in the presence of the much more intensely absorbing $\mathrm{Fe(CN)_6^{4-}}$] are ±50%. Second, reaction [A1*/4*] was apparently interpreted entirely as a second-order reaction in NO_2,

$$-\frac{d[\mathrm{NO_2}]}{dt} = 2k_{\mathrm{A1^*/4^*}}[\mathrm{NO_2}]^2$$

rather than by mixed-order kinetics [Eq. (76)], although mixed-order kinetic analysis is mandatory at the apparent NO_2 concentrations employed ($4K_{\mathrm{A7}}[\mathrm{NO_2}]_0 = 0.4–1.9$). The failure to use a mixed-order analysis would result in a value of $k_{\mathrm{A1^*/4^*}}$ that is too low; compare this with the value of $6.5 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$ determined by Grätzel et al. More important, however, is the fact that there was no indication of a process (e.g., reaction [17] giving rise to a first-order rate law for reaction [A1*/4*], although this process would dominate at low $[NO_2]$ if the rate law advanced by Treinin and Hayon were correct. Thus this experiment may be taken as evidence against the first-order rate law advanced by Treinin and Hayon.

5.3.2. Flow-Tube Study

Reaction [A1*/4*] was studied also by Moll (1966) by a rapid-mixing flow technique. Liquid N_2O_4 was injected under pressure into a rapidly flowing turbulent water stream. The rate of reaction as a function of distance downstream was determined by monitoring the longitudinal temperature profile, under the assumption that the heat evolution and hence the local temperature rise was proportional to the local rate of reaction. Rather high initial N_2O_4 concentrations were employed (8×10^{-2} M), corresponding to $[\mathrm{N(IV)}]_0 K_{A7} \approx 5000$, justifying the interpretation of the data in terms of first-order kinetics as treated by Moll. For the studies at 20°C Moll obtained a $1/e$ lifetime $\tau_{obs} = 3.77 \times 10^{-3}$ s, corresponding to $k_{A1^*/4^*} = 1.73 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$, a factor of roughly 4 and 2.3 lower than the values obtained by Grätzel et al. (1969) and Treinin and Hayon (1970), respectively.

A possible source of systematic error in Moll's experiment is that of a transition from first- to second-order kinetics as N(IV) is no longer predominately present as N_2O_4. Reexamination of Moll's data suggests the possibility of a somewhat greater initial rate, consistent with this interpretation. Utilizing only the initial data points from Moll's run ($x < 7$ cm), we obtain an upward revision of the rate coefficient ($\tau_{obs} = 2.56 \times 10^{-3}$ s; $k_{A1/4^*} = 2.6 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$), which nonetheless remains a factor of 2.5 and 1.6 lower than the values given by Grätzel et al. and Treinin and Hayon, respectively.

5.3.3. Comparison of Rates of Reactions [*A7*] *and* [*A1*/4**]

Before concluding the discussion of reaction [A1*/4*], we observe that it is possible to address the relative rates of reactions [A7] and [A1*/4*] and thereby to address the assumption inherent throughout this discussion that equilibrium [A7] is achieved rapidly compared to the time scale of reaction [A1*/4*]. A quantitative test of this assumption is achieved by comparison of the relaxation time of reaction [A7], $\tau^{(7)}$, with the characteristic time of reaction [A1*/4*], $\tau^{(1/4)}$; a necessary and sufficient condition for equilibrium [A7] to be maintained is that $\tau^{(1/4)} \gg \tau^{(7)}$. The characteristic time $\tau^{(1/4)}$ may be evaluated as

$$\tau^{(1/4)} = (k_{A1^*/4^*}[\mathrm{NO_2(aq)}])^{-1}.$$

The relaxation time $\tau^{(7)}$ may be evaluated (Eigen and De Maeyer, 1963) as

$$\tau^{(7)} = (4k_{A7}[\mathrm{NO_2(aq)}] + k_{-A7})^{-1}.$$

By (5) $k_{-A7} = k_{A7}/K_{A7}$, and hence

$$\frac{\tau^{(1/4)}}{\tau^{(7)}} = \frac{k_{A7}}{k_{A1^*/4^*}}\left(4 + \frac{K_{A7}^{-1}}{[\mathrm{NO_2(aq)}]}\right).$$

From the data of Grätzel et al. (1969) $k_{A7} = 4.5 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$, $k_{A1^*/4^*} = 6 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$, and $K_{A7}^{-1} = 1.4 \times 10^{-5}$ M (see also Section 7.1). Thus it is seen that $\tau^{(1/4)}/\tau^{(7)}$ is at least as great as 30 and correspondingly greater for $[\mathrm{NO_2(aq)}]$ less than 10^{-5} M. This agreement thus establishes the appropriateness of the hybrid reaction treatment that has been adopted.

5.4. Reaction [A2*/5*]

In the study by Grätzel et al. (1970) the rate of hydrolysis of the equilibrium mixture of $NO-NO_2-N_2O_3$,

$$NO(aq) + NO_2(aq)(N_2O_3(aq)) \xrightarrow{w} 2HNO_2(2H^+ + 2NO_2^-), \quad [A2^*/5^*]$$

was monitored as the rate of decrease in $[N_2O_3(aq)]$, as measured by absorption spectrophotometry at 260 nm. Under conditions of excess [NO(aq)], $[N_2O_3(aq)]$ was observed to decrease according to first-order kinetics, i.e.,

$$-\frac{1}{[N_2O_3(aq)]}\frac{d[N_2O_3(aq)]}{dt} = \tau_{obs}^{-1}. \tag{79}$$

The observed time constant τ_{obs} may be related to the hybrid rate constant $k_{A2^*/5^*}$ as follows. First, we note that at fixed [NO(aq)]—as is the case for $[NO(aq)] \gg [NO_2(aq)] + [N_2O_3(aq)]$—the ratio of $[N_2O_3]$ to the sum of $[N_2O_3] + [NO_2]$ is given by

$$\frac{[N_2O_3(aq)]}{[N_2O_3(aq)] + [NO_2(aq)]} = \frac{K_{A8}[NO(aq)]}{K_{A8}[NO(aq)] + 1} \tag{80}$$

a quantity that remains constant, independent of the extent of hydrolysis. Consequently, $[N_2O_3(aq)]$ will decrease in proportion to the sum of $[NO_2(aq)] + [N_2O_3(aq)]$,

$$\begin{aligned} -\frac{d[N_2O_3(aq)]}{dt} &= R_{A2^*/5^*}\frac{[N_2O_3(aq)]}{[N_2O_3(aq)] + [NO_2(aq)]} \\ &= R_{A2^*/5^*}\frac{K_{A8}[NO(aq)]}{K_{A8}[NO(aq)] + 1}. \end{aligned} \tag{81}$$

Since [see Eq. (32)]

$$R_{A2^*/5^*} = k_{A2^*/5^*}[NO(aq)][NO_2(aq)] \tag{82}$$

we obtain

$$\tau_{obs} = k_{A2^*/5^*}^{-1}([NO(aq)]^{-1} + K_{A8}). \tag{83}$$

Grätzel et al. (1970) obtained $\tau_{obs} = 3.2 \times 10^{-3}$ s for $[NO(aq)] = 1.04 \times 10^{-4}$ M at 20°C. Unfortunately, the dependence of τ_{obs} on [NO(aq)] was not examined. Such measurements would enhance our confidence in the interpretation of the measurements as well as provide an independent measurement of K_{A8}. Using the measurement of τ_{obs} at the single NO(aq) concentration employed and Grätzel et al.'s value of K_{A8} (1.37×10^4 M^{-1}), we obtain $k_{A2^*/5^*} = 7.4 \times 10^6$ M^{-1} s^{-1}.

The possible interference of $NO_2(N_2O_4)$ hydrolysis (reaction [A1*/4*]) must be considered, since if this reaction were occurring in parallel to [A2*/5*], part of the decrease in $[NO_2]$ (and, in turn, of the observed $[N_2O_3]$) would be misascribed to [A2*/5*]. The ratio of rates of NO_2 loss by these two reactions is

$$\frac{R_{A1^*/4^*}}{R_{A2^*/5^*}} = \frac{k_{A1^*/4^*}[NO_2]}{k_{A2^*/5^*}[NO]} . \tag{84}$$

For Grätzel et al.'s conditions of $[NO] = 1.04 \times 10^{-4}$ M and initial $[NO_2] = 2 \times 10^{-6}$ M, this quantity is initially 0.17, decreasing as $[NO_2]$ decreases during the course of the reaction. (Here we have used the values of $k_{A1^*/4^*}$ and $k_{A2^*/5^*}$ given above.) Thus the value of $k_{A2^*/5^*}$ may be somewhat too great, reflecting a slight contribution of reaction [A1*/4*]. For this reason also it would seem advisable to study reaction [A2*/5*] as a function of [NO(aq)] since the relative contribution of reaction [A1*/4*] would be lessened at higher [NO(aq)].

Reaction [A2*/5*] was studied also by Treinin and Hayon. Under the condition of high excess NO(aq) ($[NO(aq)] = 1.9 \times 10^{-3}$ M), N_2O_3(aq) (in equilibrium with NO_2(aq), prepared by flash photolysis of nitrite solution and monitored by ultraviolet (UV) absorption spectrophotometry, presumably at 280 nm) decayed by pseudo-first-order kinetics [Eq. (79)]. The value of τ_{obs} was observed to decrease with increasing $[OH^-]$ in the pH range 7–10, as given by

$$\tau_{obs}^{-1} = (2 \times 10^3 + 10^8[OH^-])\ s^{-1},$$

indicating a hydroxide-ion-dependent mechanism in addition to reaction directly by [A2*/5*]. For pH $\lesssim 8$, reaction [A2*/5*] is seen to dominate the hydrolysis mechanism with $\tau_{obs} = 0.5 \times 10^{-3}$ s. This value of τ_{obs} may be combined with K_{A8} [Eq. (83)] to yield $k_{A2^*/5^*}$. Again, unfortunately, the dependence of τ_{obs} on [NO(aq)] was not examined. Using Treinin and Hayon's value K_{A8} ($5 \times 10^4\ M^{-1}$), we obtain $k_{A2^*/5^*} = 1.0 \times 10^8\ M^{-1}\ s^{-1}$, more than an order of magnitude greater than that derived from the data of Grätzel et al. Alternatively, if we use Grätzel et al.'s value of K_{A8}, we obtain $k_{A2^*/5^*} = 2.8 \times 10^7\ M^{-1}\ s^{-1}$, still a factor of 4 greater than the value derived from the measurements by Grätzel et al.

The rate of decrease of $[N_2O_3(aq)]$ was monitored also in the flash photolysis of nitrite solutions in the absence of added NO. Under these conditions, equal initial concentrations are expected for NO(aq) and NO_2(aq) since, according to the interpretation of this system advanced by Treinin and Hayon, the initial photolysis

$$NO_2^- + h\nu \rightarrow NO + O^- \tag*{[A20]}$$

is followed by

$$O^- + NO_2^- \xrightarrow{w} NO_2 + 2\,OH^- . \tag*{[A16]}$$

For reaction of NO and NO_2 entirely by [A2*/5*], it is seen that there is no net reaction, whereas for reaction of $2NO_2$ by [A1*/4*], one has the overall reaction stoichiometry

$$3NO_2^- \xrightarrow{w} 2NO + NO_3^- + 2OH^- .$$

Under conditions of low intensity, steady illumination of 2.7×10^{-4} M NO_2^- solution at 229 nm, Treinin and Hayon found a quantum yield for NO_2^- depletion of less than 10^{-3}. In the flash photolysis reactions also there was "no" net reaction of NO_2^-, as measured in the final NO_2^- absorbance, despite a "high" yield for the primary photolytic reaction [A20].

In the studies of the flash photolysis of nitrite in the absence of added NO, N_2O_3 (as monitored at 280 nm) was found to exhibit apparent first-order kinetics with $k_{obs} = (510 \pm 60)\ s^{-1}$; NO_2, monitored at 400 nm, also exhibited apparent first-order kinetics with $k_{obs} = (293 \pm 47)\ s^{-1}$. The measurements were interpreted as if the hydrolysis took place entirely by reaction [A2*/5*], in conformity with the observation of no net reaction. For hydrolysis by reaction [A2*/5*] only, the concentrations of NO and NO_2 would decrease at the same rate and thus remain equal throughout the course of the hydrolysis. Thus $[N_2O_3]$ would be proportional to $[NO_2]^2$; the approximate factor of 2 between the observed rate constants for N_2O_3 and NO_2 was taken to reflect this proportionality. However, for $[N_2O_3] \propto [NO_2]^2$, N_2O_3 would be expected to exhibit mixed-order kinetics, as was anticipated also for NO_2 in the study of reaction [A1*/4*] [Eq. (76)]. The failure to observe the transition from first- to second-order kinetics raises uncertainty with this study and indicates the need for further systematic investigation of this reaction system.

An additional serious concern with the photolysis mechanism proposed by Treinin and Hayon and/or with our understanding of both reactions [A1*/4*] and [A2*/5*] is raised by the absence of net reaction in the photolysis of nitrite solution. If, as Treinin and Hayon propose, NO(aq) and NO_2(aq) are formed in equal concentrations and hence by (84), the ratio of $R_{A1^*/4^*}$ (which leads to net reaction) to $R_{A2^*/5^*}$ (which does not) should be equal to the ratio of the rate constants $k_{A1^*/4^*}/k_{A2^*/5^*}$. The latter ratio is equal to 8.8 (as evaluated from the data due to Grätzel et al.) or 0.5–1.7 (as evaluated from the data of Treinin and Hayon). Such values are entirely inconsistent with the observation of a net yield for loss of NO_2^- of 10^{-3}, despite a high primary photolytic yield.

The validity of treating reaction [A2*/5*] as a hybrid reaction may be examined (as was done above for reaction [A1*/4*]) by comparing the characteristic time for reaction [A2*/5*], $\tau^{(2/5)}$, with the relaxation time for equilibrium [A8], $\tau^{(8)}$. The characteristic time $\tau^{(2/5)}$ is given by

$$\tau^{(2/5)} = \{k_{A2^*/5^*}([NO(aq)] + [NO_2(aq)])\}^{-1},$$

and the relaxation time $\tau^{(8)}$ is given by

$$\begin{aligned}\tau^{(8)} &= \{k_{A8}([NO(aq)] + [NO_2(aq)]) + k_{-A8}\}^{-1} \\ &= \{k_{A8}([NO(aq)] + [NO_2(aq)]) + K_{A8}^{-1})\}^{-1}.\end{aligned}$$

The ratio

$$\frac{\tau^{(2/5)}}{\tau^{(8)}} = \frac{k_{A8}}{k_{A2^*/5^*}}\left(1 + \frac{K_{A8}}{[NO(aq)] + [NO_2(aq)]}\right)$$

may be evaluated for known k_{A8}, $k_{A2^*/5^*}$, and K_{A8}. Although there is some spread in the values of these constants as determined by Grätzel et al. (1970) and Treinin and Hayon (1970), it appears that the ratio $\tau^{(2/5)}/\tau^{(8)}$ exceeds an order of magnitude, supporting the hybrid reaction treatment.

5.5. Summary

The directly measured rate constants given above for the several reactions studied are summarized in Table 12. For reactions [A7] and [A8], only the measurements by Grätzel et al. (1969, 1970) are available. These, however, derive from measurements over a rather wide range of reagent concentration that conform well with mechanistic expectation, so we feel rather confident in the mechanism and the numerical values of the rate constants.

With respect to reactions [A1*/4*] and [A2*/5*], there is substantial divergence in the observations and the mechanistic interpretation as well as in the numerical values of the rate constants. With respect to reaction [A1*/4*] based on our review we place highest confidence in the work of Grätzel et al. (1969), although we are somewhat unsettled by Treinin and Hayon's failure to observe a transition from first- to second-order kinetics in their study. With respect to reaction [A2*/5*], the situation is worse still. Neither Grätzel et al.'s nor Treinin and Hayon's measurements were taken over an appropriately wide range of reagent concentrations. Still more unsettling are the quantum yield studies by Treinin and Hayon, which if their photolytic mechanism is correct, reopen the entire question of mechanism of these two reactions.

To facilitate comparison of these measurements of the rate constants for reaction [A1*/4*] to measurements by other techniques, it is convenient to express the rate constant in terms of the compound oxide N_2O_4 as the reagent. In this notation the reaction is expressed as

$$N_2O_4(aq)(2NO_2(aq)) \xrightarrow{w} H^+ + NO_3^- + HNO_2(H^+ + NO_2^-) \qquad [A4^*/1^*]$$

having rate

$$R_{A4^*/1^*} = k_{A4^*/1^*}[N_2O_4(aq)]$$

where

$$k_{A4^*/1^*} = k_{A1^*/4^*}/K_{A7}.$$

Similarly, for reaction [A2*/5*], we express the reaction alternatively as

$$N_2O_3(aq)(NO(aq) + NO_2(aq)) \xrightarrow{w} 2HNO_2(2H^+ + 2NO_2^-) \qquad [A5^*/2^*]$$

with rate

$$R_{A5^*/2^*} = k_{A5^*/2^*}[N_2O_3(aq)]$$

where

$$k_{A5^*/2^*} = k_{A2^*/5^*}/K_{A8}.$$

Values of $k_{A4^*/1^*}$ and $k_{A5^*/2^*}$ are given in Table 13.

Table 12. Directly Measured Aqueous-Phase Rate Constants

	Reaction	k ($M^{-1}\ s^{-1}$)	T (°C)	Reference
[A7]	$2NO_2(aq) \rightarrow N_2O_4(aq)$	4.5 ± 1.0(8)	20	Grätzel et al. (1969)
[A8]	$NO(aq) + NO_2(aq) \rightarrow N_2O_3(aq)$	1.1 (9)	20	Grätzel et al. (1970)
[A1*/4*]	$2NO_2(aq)(N_2O_4(aq)) \xrightarrow{w} H^+ + NO_3^- + HNO_2(H^+ + NO_2^-)$	6.5 ± 0.7(7)	20	Grätzel et al. (1969)
		4.7 ± 1.0(7)[a]	25	Treinin and Hayon (1970)
		2.6 (7)[b]	20	Moll (1966)
[A2*/5*]	$NO(aq) + NO_2(aq)(N_2O_3(aq)) \xrightarrow{w} 2HNO_2(2H^+ + 2NO_2^-)$	7.4 (6)	20	Grätzel et al. (1970)
		1.0 (8)	25	Treinin and Hayon (1970)
		2.8 (7)[c]	25	Treinin and Hayon (1970)

[a] Plus an additional pseudo-first-order component: $R_{A1^*/4^*} = k_{A17}[NO_2(aq)]$, with $k_{A17} = (1.5 \pm 0.3) \times 10^2\ s^{-1}$.

[b] As recalculated; see text.

[c] As recalculated by using K_{A8} from Grätzel et al. (1970); see text.

Table 13. Directly Measured Aqueous-Phase Rate Constants, Referred to Compound Oxides

	Reaction	k (s^{-1})	T (°C)	Reference
[A4*/1*]	$N_2O_4(aq)(2NO_2(aq)) \xrightarrow{w} H^+ + NO_3^- + HNO_2(H^+ + NO_2^-)$	1.0(3)	20	Grätzel et al. (1969)
		6.0(2)	25	Treinin and Hayon (1970)
		4.0(2)	20	Moll (1966)
[A5*/2*]	$N_2O_3(aq)(NO(aq) + NO_2(aq)) \xrightarrow{w} 2HNO_2(2H^+ + 2NO_2^-)$	5.3(2)	20	Grätzel et al. (1970)
		2.0(3)	25	Treinin and Hayon (1970)

6. MIXED-PHASE STUDIES OF REACTIVE DISSOLUTION OF NITROGEN OXIDES BY LIQUID WATER

As has been indicated in the preceding discussion, the reactive uptake of the nitrogen oxides into aqueous solution under non-phase-mixed conditions is a complex process that is fraught with interpretational uncertainty. Nevertheless, a number of studies have been carried out under conditions that are sufficiently well characterized to permit interpretation in terms of the elementary processes (equilibrium constants and rate constants) of the present concern. We review these studies here insofar as they lead, in our judgment, to such interpretations. If the results of these studies are correctly interpreted, they should, of course, be consistent with studies by other methods described.

A major difficulty in interpretation of non-phase-mixed studies of the absorption of the nitrogen oxides has been that of inferring the reaction mechanism. The difficulty of these studies is due not only to the usual ambiguities of such studies [i.e., the mechanism of mass transport and the phase(s) in which mass transport is controlled and in which reaction takes place] but also, in the case of the nitrogen oxides, to the multiplicity of possible reaction mechanisms. Here the peculiar property of the nitrogen oxides to form compound oxides (N_2O_3, N_2O_4) comes into play, since interpretation of the competition between mass transport and reaction depends on knowledge of the order of reaction in diffusing species. Thus in the case of reaction [A1*/4*],

$$2NO_2(aq)(N_2O_4(aq)) \overset{w}{\rightarrow} H^+ + NO_3^- + HNO_2(H^+ + NO_2^-), \quad [A1^*/4^*]$$

the order in diffusing species will be 2 or 1, respectively, as NO_2 or N_2O_4 is the predominant aqueous N(IV) species as dictated by equilibrium [A7]. For N_2O_4 predominant, the reaction is first order in the diffusing species and consequently exhibits a first-power dependence on $p_{N_2O_4}$, irrespective of the mechanism and extent of aqueous-phase mass transport, as indicated in Table 3. This first-power dependence on $p_{N_2O_4}$, in turn, through equilibrium [G7], results in a second-power dependence on p_{NO_2}. In contrast, for NO_2 the predominant aqueous phase species, the rate of reaction will exhibit a dependence on p_{NO_2} to the second, first, or three-halves power as the phase mixing in the system is in the phase-mixed, convective-mass-transport, or molecular-diffusion regimes, respectively. The apparent reaction orders with respect to gas-phase NO_2 are summarized in Table 14 for the several regimes and for various aqueous-phase reaction orders [referred to NO_2(aq)] for the dimer N_2O_4 being the predominant N(IV) species present in and diffusing in the aqueous solution. These apparent reaction orders may be compared with those given in Table 3 for the monomer being the transported species. This comparison is facilitated by examination of Figure 2, which summarizes the apparent reaction orders for the various regimes.

One point that must again be emphasized is that the power dependences

Table 14. Apparent Reaction Order in Gas-Phase NO_2 for Principal Aqueous-Phase Species Being N_2O_4

Reaction Order in $NO_2(aq)$	Phase-Mixed Limit	Convective Mass-Transport Controlled	Diffusive Mass-Transport Controlled
0	0	2	1
$\frac{1}{2}$	$\frac{1}{2}$	2	$\frac{5}{4}$
1	1	2	$\frac{3}{2}$
2	2	2	2
3	3	2	$\frac{5}{2}$
m	m	2	$m/2 + 1$

on p_{NO_2} must be considered to be limiting cases and that intermediate cases may be expected as a consequence both of the transition between mass-transport regimes and of the transition between N_2O_4 and NO_2 as the predominant aqueous N(IV) species. In the case of reaction [A1*/4*] both of these "dimensions" may be expected to be affected as the partial pressure of the reagent gas is varied. Consequently, one must be highly cautious in accepting any determination of Henry's law coefficient or of kinetic rate constant from direct measurement of the rate of uptake of NO_2 in a mixed-phase system. In particular, one test that may be readily applied is that the

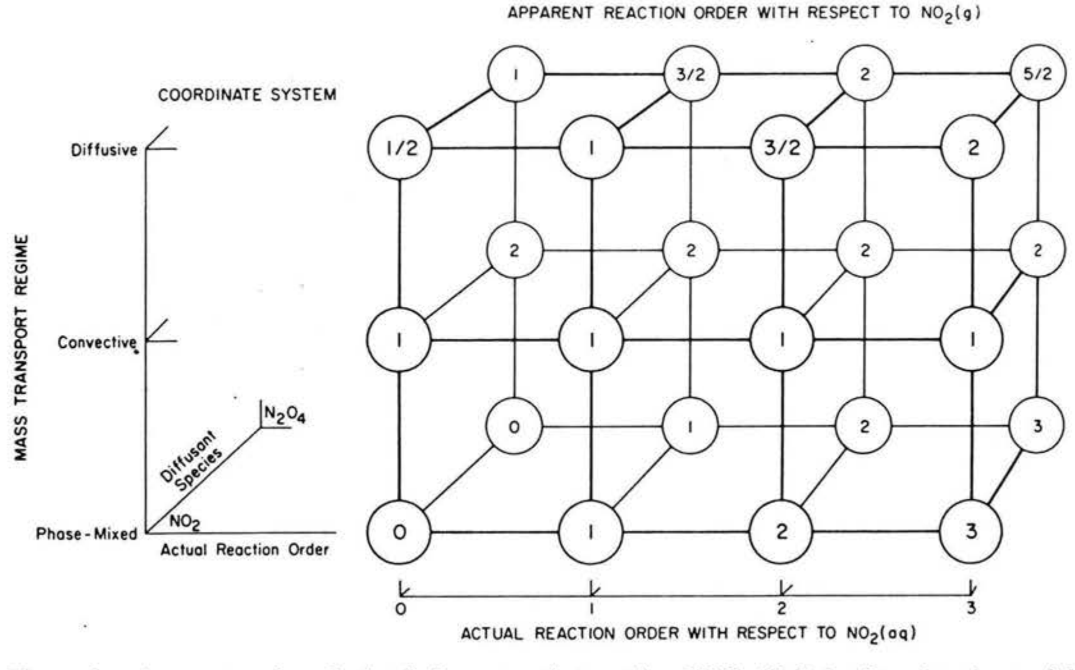

Figure 2. Apparent order of mixed-phase reactive uptake of NO_2 (N_2O_4) referred to the partial pressure of NO_2, displayed for limiting cases of reaction order, phase-mixing regime, and diffusing species (NO_2 or N_2O_4). Apparent reaction order is indicated by the numerical value displayed at the appropriate coordinate location.

predominant N(IV) species present be consistent with the model employed in the interpretation. Unfortunately, this test has not previously been applied, even in studies subsequent to the determination of K_{A7} by Grätzel et al. (1969).

This review of direct measurements of the rate of uptake of nitrogen oxides into aqueous solution is organized about the dependence of this rate on the partial pressures of the oxides (apparent reaction order referred to the gaseous reagents). We first consider studies of the uptake of NO_2 (N_2O_4) and then consider studies of the simultaneous uptake of NO and NO_2 (N_2O_3).

6.1. Second-Order Uptake of NO_2

As noted in Section 1, there has been a deep and continuing interest in the mechanism and rate of reaction of $NO_2(g)$ [and/or $N_2O_4(g)$] at high partial pressures (10^{-3}–10^{-1} atm) with liquid water because of the role of this process in the industrially important manufacture of nitric acid. Much of the early work (e.g., Chambers and Sherwood, 1937) suggested that the rate of uptake was controlled by gas-phase mass transport. Subsequent investigators (e.g., Denbigh and Prince, 1947) carried out experiments such that gas-phase mass transport was not controlling, permitting investigation of chemical–kinetic influences on the rate of reactive dissolution.

A second persistent question has been the phase (gas or aqueous) in which the reaction takes place. Peters and colleagues (Peters and Holman, 1955; Peters et al., 1955) have argued that at least some of the reaction taking place under laboratory conditions must be occurring in the gas phase, as evidence by mist formation when gaseous NO_2 and N_2O_4 are mixed with water vapor. Carberry (1959), on the other hand, argues against significant gas-phase reaction, pointing out that mist formation is found only when a condensed phase is present. Subsequent work (England and Corcoran, 1974; Kaiser and Wu, 1977a) has provided a rate constant for the gas-phase reaction [G1]—in fact an upper limit, because of the possibility of heterogeneous contribution to the reaction rate—that establishes that the gas-phase reaction is slow in comparison to measured aqueous-phase rates. It now seems generally accepted (e.g., Sherwood et al., 1975) that the mixed-phase reactions under examination can be accounted for entirely by reactions taking place in the aqueous phase.

A significant advance in the understanding of this system was made by Wendel and Pigford (1958), who quantitatively addressed both the mass transport of NO_2 (N_2O_4) in the gas phase (which leads to a reduction in partial pressure at the gas-liquid interface, compared to that in the bulk gas) and the rate of aqueous-phase reaction. In that study it was found that the rate of uptake expressed as amount of N_2O_4 taken up in unit time per unit area of interface was given by

$$J_{N_2O_4} = q p_{N_2O_4(i)} \tag{85}$$

where $p_{N_2O_4(i)}$ refers to the interfacial partial pressure, and q is a constant. (This proportionality to $p_{N_2O_4}$ is, of course, equivalent to a proportionality to $p_{NO_2}^2$, i.e., an apparent reaction order of 2 referred to $NO_2(g)$.) This first-order dependence on $p_{N_2O_4}$ (or second-order dependence on p_{NO_2}) has been confirmed in subsequent investigations, which have somewhat refined the value of q from that given by Wendel and Pigford, as listed in Table 15.

The studies of Wendel and Pigford and subsequent investigators have been interpreted by means of "penetration theory" (see Section 2) for a pseudo-first-order aqueous-phase reaction of N_2O_4, i.e., dissolution and diffusion of N_2O_4 and reaction by

$$N_2O_4 \xrightarrow{w} H^+ + NO_3^- + HNO_2(H^+ + NO_2^-); \qquad [A4^*]$$

such a pseudo-first-order reaction ($m = 1$) would give rise to the observed dependence of $J_{N_2O_4}$ on the first power of the interfacial partial pressure of N_2O_4 [see Eq. (15)]. If this interpretation is correct, which we believe it to be, we may identify the observed q [Eq. (85)] with the product $H_{N_2O_4}(k_{A4^*}D_{N_2O_4})^{1/2}$, where $D_{N_2O_4}$ is the diffusion coefficient of N_2O_4 in aqueous solution. Since this diffusion coefficient may be accurately estimated [e.g., by the semiempirical correlation of Wilke and Chang (1955)], it is seen that measurement of q leads to the product $H_{N_2O_4}k_{A4^*}^{1/2}$. As has been recognized by numerous investigators, the product $H_{N_2O_4}k_{A4^*}^{1/2}$ may be resolved as is desired into its component factors using additional information from other experiments; we defer that discussion for the present.

An alternative interpretation of the observation of a first-power dependence on $p_{N_2O_4}$ might be formulated as follows. As noted above, this pressure dependence is equivalently expressed as a second-order dependence on p_{NO_2}. If NO_2 rather than N_2O_4 were the principal form of the dissolved reagent, such a power-law dependence would be predicted [Eq. (15) or Table 3] for a third-order reaction in $NO_2(aq)$,

$$3NO_2(aq) \rightarrow \text{products}.$$

The choice between these two interpretations may be addressed by considering the distribution of dissolved N(IV) between the two species NO_2 and N_2O_4, since it is the order of the reaction *in diffusing species* that determines the exponent m in Eq. (15) (e.g., Brian, 1964). Expressed as a function of NO_2 partial pressure, the fraction of dissolved N(IV) that is present as NO_2 is

$$F_{NO_2} = \frac{[NO_2(aq)]}{[NO_2(aq)] + 2[N_2O_4(aq)]} = \frac{1}{1 + 2H_{NO_2}K_{A7}p_{NO_2}} \qquad (86)$$

The partial pressure corresponding to a given value of F_{NO_2} is

$$p_{NO_2} = (2H_{NO_2}K_{A7})^{-1}\frac{1 - F_{NO_2}}{F_{NO_2}} \qquad (87)$$

and may be evaluated for assumed equilibrium constants and specified

Table 15. Measurements of the Area Rate Constant for Uptake of N_2O_4 by Aqueous Solution in Diffusion-Controlled Regime

Study	Method[a]	p_{NO_2} (10^{-2} atm)	q[b] (10^{-3} kmol m^{-2} s^{-1} atm^{-1})	$H_{N_2O_4}k^{1/2}_{A4^*/1^*}$[c] (M atm^{-1} $s^{-1/2}$)
Denbigh and Prince (1947)	WWC	3–19	0.37 ± 16%[d,e]	
Caudle and Denbigh (1953)	WWC	0.6–5	0.4–1.6[d]	
Wendel and Pigford (1958)	WWC	3–9	0.26–0.34[d]; 0.58	16
Dekker et al. (1959)	WWC	1.6–7	1.1 ± 13%	29
Kramers et al. (1961)	LWJ	4–14	0.83 ± 3%[f]	22
Gerstacker (1961)	LWJ	9–21	1.05 ± 5%	28
Bartholomé and Gerstacker (1961)	LWJ	10	0.82 ± 5%	22
Corriveau and Pigford (1971)	WS	1.0–2.1	0.47	13
Chilton and Knell (1972)	WWC	1.4–3.6	1.4	37
Hoftyzer and Kwanten (1972)	LWJ	4–40	0.93	25
Kameoka and Pigford (1977)	WS	0.7–1.3	0.69	18
Komiyama and Inoue (1980)[g]	B	0.06–0.08	1.5(1.7)[h]	45(45)[h]
"	F	0.04–0.10	2.4 (2.7)[h]	72(72)[h]

[a] Methods: WWC, wetted wall column; LWJ, laminar water jet; WS, wetted sphere; B, bubbler; F, flat-surface contactor.

[b] Defining equation $J_{N_2O_4} = qp_{N_2O_4}$; all values referred to $p_{N_2O_4}$ at gas–aqueous interace and are for 25°C unless otherwise indicated.

[c] For $D_{N_2O_4} = 1.40 \times 10^{-9}$ m^{-2} s^{-1} at 25°C and 1.10×10^{-9} m^{-2} s^{-1} at 15°C.

[d] Referred to bulk pressure.

[e] NO present, 0.06–0.2 atm.

[f] Derived by interpolation from measurements at 20 and 30°C.

[g] Measurements at 15°C; 0.01 M NaOH.

[h] Corrected to 25°C by using temperature data of Kramers et al. (1961).

F_{NO_2}. Here we have used the values of $H_{NO_2} = 1.2 \times 10^{-2}$ M atm^{-1} and $K_{A7} = 6.5 \times 10^4$ M^{-1} recommended by Schwartz and White (1981) from analysis of thermochemical cycles. However, it should be emphasized that the subsequent discussion does not rely quantitatively on these values—they are introduced here only for the purpose of ascertaining the predominant aqueous-phase N(IV) species. The quantities F_{NO_2} and $F_{N_2O_4}(= 1 - F_{NO_2})$ are shown as function of p_{NO_2} in Figure 1. It is seen that for partial pressures of NO_2 in excess of 6×10^{-3} atm the equilibrium fraction of dissolved N(IV) present as N_2O_4 exceeds 90%. Since this condition is satisfied by essentially all the experiments summarized in Table 15, we may rule out the possibility that the observed pressure dependence of $J_{N_2O_4}$ (as $p_{N_2O_4}$ or as $p^2_{NO_2}$) results from a third-order reaction in NO_2(aq) and thus may confirm the interpretation of a pseudo-first-order reaction in N_2O_4(aq).

The preceding discussion serves to illustrate another point. Because of the distinction in order between reactions [A1*] and [A4*], examination of this reaction in penetration theory might be considered a potential means of distinguishing between these two mechanisms. However, as we have noted, the penetration theory distinguishes the order in diffusing species, not the order of the reaction. Thus, provided any departure from the equilibrium [A7] relaxes fast in comparison to the characteristic time of reaction [A1*/4*], the two mechanisms cannot be distinguished by this type of study. Consequently, the observed quantity q must be identified with $H_{N_2O_4}(k_{A4*/1*}D_{N_2O_4})^{1/2}$ rather than with $H_{N_2O_4}(k_{A4*}D_{N_2O_4})^{1/2}$.

The interpretation of the several experiments presented in Table 15 by penetration theory also requires demonstration, other than by the first-order dependence on $p_{N_2O_4}$, that the reaction occurs in the diffusion-controlled regime since, as may be seen by reference to Table 3, such a first-order dependence is expected for the several mass-transport regimes. The penetration theory is applicable provided the liquid-phase mass-transfer coefficient k_L is sufficiently small [Eq. (18)] and also provided the characteristic depth of reagent penetration is much less than the physical extent of the liquid. First, with respect to the depth of reagent penetration, this may be estimated as $\delta = (D/k\text{A})^{1/2}$. For $D \sim 1 \times 10^{-9}$ m^2 s^{-1} and $k_A \sim 10^3$ s^{-1} (see Table 13 as well as Section 7.1), the penetration depth is estimated as ~ 1 μm, well less than the thickness of the films, jets, etc. employed. Turning to convective mixing, we note that this represents a potential source of error that must be controlled by experimental design or otherwise excluded. In the case of experiments by wetted-wall or laminar-jet absorbers, this condition would appear to be at least closely approached. In the case of the experiments employing bubbler and flat surface absorbers (Komiyama and Inoue, 1980) this condition may be addressed by means of criterion (18); if the apparatus parameters given by the authors and the estimate $k_A \sim 10^3$ s^{-1} are used, the condition of a diffusive-controlled reaction would again appear to be satisfied.

Examination of the data in Table 15 shows a reasonable consistency in the values of q obtained in the several studies Wendel and Pigford (1958) through Kameoka and Pigford (1977). These studies lead to a recommended value of q of $0.9 \pm 0.3 \times 10^{-3}$ kmol m^{-2} s^{-1} atm^{-1}, where the uncertainty is based on the spread in the values reported. The values of Komiyama and Inoue (1980), which were obtained at 15°C, differ significantly (even when corrected for temperature) from the remaining determinations and even from each other. An error with the bubbler contactor might arise from error in the interfacial area, which was determined from photographs; it is difficult to account for a potential source of error with the flat-surface contactor. It is unfortunate that these authors did not address the discrepancy between their results obtained with the two different contactors. Evidently the authors used the data obtained with the bubbler contactor in their evaluation of elementary quantities ($\mathrm{H}_{\mathrm{N_2O_4}}$, $k_{\mathrm{A4^*/1^*}}$, etc.).

As noted in Section 2, the aqueous-phase diffusion coefficient of a dissolved gas may be estimated fairly confidently by using a semiempirical correlation such as that given by Wilke and Chang (1955). This procedure gives $D_{\mathrm{N_2O_4}} = 1.4 \times 10^{-9}$ m^2 s^{-1} at 25°C. Consequently, we obtain $\mathrm{H}_{\mathrm{N_2O_4}} k^{1/2}_{\mathrm{A4^*/1^*}} = (2.3 \pm 0.8) \times 10^1$ M atm^{-1} s$^{-1/2}$ at 25°C. This value is compared below to other experimental measures of $\mathrm{H}_{\mathrm{N_2O_4}}$ and $k_{\mathrm{A4^*/1^*}}$.

As outlined in Section 2, measurement of the amount of gaseous reagent $Q_{\mathrm{X}}(\mathrm{t})$ taken up by the liquid as a function of contact time t under conditions of diffusive mass transport provides further information concerning the elementary constants of the system. As may be seen from Eq. (16), a plot of the quantity $Q_{\mathrm{X}}(t)/t$ versus t^{-1} is expected to be linear with slope $q' p_{\mathrm{X}}/2$, where $q' = \mathrm{H_X} D_{\mathrm{X}}^{1/2} k_{\mathrm{X}}^{-1/2}$. Such studies as a function of contact time have been carried out by varying the length of jet exposed to the gaseous reagent; the results are shown in Table 16. On the basis of the spread in the data, we present a recommended value of $q' = (2.6 \pm 1.2) \times 10^{-6}$ kmol m^{-2} atm^{-1} at 25°C. Again using $D_{\mathrm{N_2O_4}} = 1.4 \times 10^{-9}$ m^2 s^{-1}, we obtain $\mathrm{H}_{\mathrm{N_2O_4}} k^{-1/2}_{\mathrm{A4^*/1^*}} = (6.9 \pm 3.2) \times 10^{-2}$ M atm^{-1} s$^{1/2}$ at 25°C.

The values q and q' may be combined to yield $k_{\mathrm{A4^*/1^*}}$ and $\mathrm{H}_{\mathrm{N_2O_4}}$ as

$$k_{\mathrm{A4^*/1^*}} = \frac{q}{q'}$$

$$\mathrm{H}_{\mathrm{N_2O_4}} = \left(\frac{qq'}{D_{\mathrm{N_2O_4}}}\right)^{1/2}.$$

The values of these quantities obtained from the several studies in which q' was determined are also given in Table 16. We defer further discussion to Section 7.1.

The temperature dependence of the rate of uptake of N_2O_4 has been examined by several investigators, as noted in Table 17. The temperature dependence of q may be interpreted as yielding an overall activation energy associated with the quantity $\mathrm{H}_{\mathrm{N_2O_4}} D^{1/2}_{\mathrm{N_2O_4}} k^{1/2}_{\mathrm{A4^*/1^*}}$, which is equal to the sum

Table 16. Measurements of the Time Dependence of the Amount of Uptake of N_2O_4 by Aqueous Solution

Study	q'^{a} (10^{-6} kmol m^{-2} atm^{-1})	$H_{N_2O_4}k_{A4^*/1^*}^{-1/2}$ (M atm^{-1} $s^{1/2}$)	$k_{A4^*/1^*}$ (s^{-1})	$H_{N_2O_4}{}^{d}$ (M atm^{-1})
Kramers et al. (1961)	2.88^{b}	7.7(−2)	2.9(2)	1.31
Gerstacker (1961)	≤ 1.19			
Bartholomé and Gerstacker (1961)	3.58	9.6(−2)	2.3(2)	1.45
Hoftyzer and Kwanten (1972)	1.39^{c}	3.7(−2)	6.7(2)	0.96

[a] Defining equation: $d[Q_{N_2O_4}(t)/t]/dt = q'p_{N_2O_4}$; all values are referred to $p_{N_2O_4}$ at the gas–aqueous interface and are for 25°C.

[b] Derived by interpolation from measurements at 20 and 30°C.

[c] Original data not presented; deduced from reported derived quantities.

[d] For $D_{N_2O_4} = 1.40 \times 10^{-9}\ m^2\ s^{-1}$.

of the activation energies associated with the several factors, i.e.,

$$E_a(H_{N_2O_4}D_{N_2O_4}^{1/2}k_{A4^*/1^*}^{1/2}) = \Delta H^\circ(H_{N_2O_4}) + \tfrac{1}{2}E_a(D_{N_2O_4}) + \tfrac{1}{2}E_a[A4^*/1^*].$$

The value of $E_a(D_{N_2O_4})$, which represents the activation energy associated with diffusion in aqueous solution, may be inferred from Wilke and Chang (1955) to be 4.45 kcal mol^{-1}, as governed principally by the temperature dependence of the solvent viscosity. The term $\Delta H^\circ(H_{N_2O_4})$ represents the heat of (nonreactive) solution of N_2O_4 and would be expected to be negative, of magnitude several kilocalories per mole, corresponding to a decreasing solubility with increasing temperature. The term $E_a[A4^*/1^*]$, representing the activation energy of reaction, would be expected to be positive. Thus the overall activation enthalpy might be either positive or negative, depending on the relative magnitude of the several terms.

Examination of the data in Table 17 indicates that $E_a(H_{N_2O_4}k_{A4^*/1^*}^{1/2})$ is in the range -4 to $+1.3$ kcal mol^{-1}. Looking more closely at these studies, we would hazard the guess that this quantity lies in the range 0.5 ± 0.7 kcal mol^{-1}, since the value given by Dekker et al. (1959) is superceded by the later, higher value from the same group (Kramers et al., 1961). The value reported by Hoftyzer and Kwanten (1972) represents by far the widest temperature range and hence would be expected to have the greatest accuracy. Unfortunately, this quantity is given only in a review article, which neither describes the experiment nor reports the original data, which do not appear to have been published.

With respect to $E_a(H_{N_2O_4}k_{A4^*/1^*}^{-1/2})$, there are substantially fewer data available and little consistency in those. In particular, there appears to be an

Table 17. Temperature Dependence of $H_{N_2O_4}k^{1/2}_{A4^*/1^*}$ and $H_{N_2O_4}k^{-1/2}_{A4^*/1^*}$[a]

Study	Temperature Range (°C)	E_a (kcal mol^{-1})			
		$H_{N_2O_4}D^{1/2}_{N_2O_4}k^{1/2}_{A4^*/1^*}$	$H_{N_2O_4}k^{1/2}_{A4^*/1^*}$	$H_{N_2O_4}D^{1/2}_{N_2O_4}k^{-1/2}_{A4^*/1^*}$	$H_{N_2O_4}k^{-1/2}_{A4^*/1^*}$
Denbigh and Prince (1947)	25–40	1.61	−0.62		
Wendel and Pigford (1958)	25–40	−0.88	−3.11		
Dekker et al. (1959)	25–35	−1.74	−3.96		
Kramers et al. (1961)	20–30	2.56	0.33	−2.34	−4.57
Bartholomé and Gerstacker (1961)	5–25	2.13	−0.09 (5–15°C) (15–25°C)	−1.80 −17.43	−4.08 −19.67
Hoftyzer and Kwanten (1972)	3–75	3.48	1.25		

[a] The values of $E_a(H_{N_2O_4}k^{1/2}_{A4^*/1^*})$ and $E_a(H_{N_2O_4}k^{-1/2}_{A4^*/1^*})$ were evaluated by using $E_a(D_{N_2O_4})$ = 4.45 kcal mol^{-1}.

anomaly in the measurements by Bartholomé and Gerstacker (1961). Consequently, little inference can be drawn about this quantity.

These studies of the temperature dependence of reaction [4*/1*] is related to other temperature-dependence studies in Section 7.3.

6.2. $\frac{3}{2}$-Order Uptake of NO_2

Several investigators (Komiyama and Inoue, 1980; Sada et al., 1979; Takeuchi et al., 1977) have reported, at NO_2 partial pressures lower than those for which a second-order rate law is observed, a rate of uptake of NO_2 proportional to the $\frac{3}{2}$ power of p_{NO_2},

$$J_{NO_2} = qp_{NO_2}^{3/2}.$$

The results of these studies are summarized in Table 18. The interpretation that has been advanced by all of these investigators to account for this observed rate law is that of a second-order reaction of dissolved NO_2 in the fast-reaction limit, NO_2 being the diffusant species, for which J_{NO_2} is given by Eq. (15) with $m = 2$, viz.,

$$J_{NO_2} = (\tfrac{4}{3})^{1/2} D_{NO_2}^{1/2} k_{A1^*/4^*}^{1/2} \mathrm{H}_{NO_2}^{3/2} p_{NO_2}^{3/2}. \tag{88}$$

According to this interpretation, the following identification can be made:

$$q = (\tfrac{4}{3})^{1/2} D_{NO_2}^{1/2} k_{A1^*/4^*}^{1/2} \mathrm{H}_{NO_2}^{3/2}. \tag{89}$$

Again the diffusion coefficient may be estimated rather closely, based on the correlation by Wilke and Chang (1955). In the case of NO_2 there is some uncertainty in application of the Wilke–Chang formula because of the unknown molar volume V of the liquid at its normal boiling point. Taking $V = 35.1\ \mathrm{cm^3\ mol^{-1}}$ [cf. 36.4 and 34.0 $\mathrm{cm^3\ mol^{-1}}$ for N_2O and CO_2, respectively (Himmelblau, 1964)] we obtain the values of D_{NO_2} presented in Table 18. The resulting values of $\mathrm{H}_{NO_2}^{3/2} k_{A1^*/4^*}^{1/2}$, evaluated by Eq. (89), are also shown. However, on the basis of the discussion below, we consider the interpretation of these data by means of equations (88) and (89) not to be entirely justified and thus would expect some inaccuracy in the values of $\mathrm{H}_{NO_2}^{3/2} k_{A1^*/4^*}^{1/2}$ thus evaluated.

Fundamentally, the argument against interpretation of the $\frac{3}{2}$-order data by Eq. (88) is that NO_2 is not the sole aqueous phase N(IV) species as is assumed in the derivation of that equation. That this is the case may be seen by inspection of Figure 1, which indicates a substantial proportion of N(IV) present as N_2O_4 at the partial pressures employed in all of the studies listed in Table 18. Thus, unless the values of H_{NO_2} and/or K_{A7} utilized in preparing Figure 1 are greatly in error, the condition that NO_2 be the predominant diffusing species is not satisfied, and the interpretation of the rate of uptake by means of equation (88) is not quantitatively correct. The value of

Table 18. $\frac{3}{2}$-Order Uptake of NO_2

Study	Method[a]	T (°C)	p_{NO_2} (10^{-4} atm)	q[b] (10^{-3} kmol m^{-2} s^{-1} $atm^{-3/2}$)	D_{NO_2} (10^{-9} m^2 s^{-1})	$H^{3/2}_{NO_2}k^{1/2}_{A1^*/4^*}$[c] (M $atm^{-3/2}$ $s^{-1/2}$)	$F_{N_2O_4}$[d] (%)
Takeuchi et al. (1977)	F	25	1.0–4.7	2.6	2.00	50	13–42
		15	0.9–3.8	3.8	1.57	83	
		10	0.4–3.7	5.7	1.30	137	
Sada et al. (1979)	F	25	2.9–8.1	1.74	2.00	34	29–56
Komiyama and Inoue (1980)[e]	F	15	1.0–2.9	1.16	1.57	25	13–29
"	B	15	0.34–1.8	0.79	1.57	17	5–22

[a] Methods: F, flat-surface contactor; B, bubbler.

[b] Defining equation: $J_{NO_2} = q p^{3/2}_{NO_2}$.

[c] Defining equation: $H^{3/2}_{NO_2} k_{A1^*/4^*} = q/(4/3)^{1/2} D^{1/2}_{NO_2}$.

[d] Evaluated from Figure 1 for $H_{NO_2} = 1.2 \times 10^{-2}$ M atm^{-1} and $K_{A7} = 6.5 \times 10^4$ M atm^{-1}.

[e] 0.01 M NaOH.

$H^{3/2}_{NO_2}k^{1/2}_{A1^*/4^*}$ determined from the data of the several studies is seen to decrease with decreasing p_{NO_2} and resulting decrease of $F_{N_2O_4}$. Of the several studies, those by Komiyama and Inoue (1980) would appear to exhibit the least influence from diffusion and reaction of N_2O_4 occurring in parallel with diffusion and reaction of NO_2.

6.3. First-Order Uptake of NO_2

A rate of uptake of NO_2 into aqueous solution proportional to the first power of p_{NO_2} has been reported by Andrew and Hanson (1961) and Komiyama and Inoue (1980). The former study was interpreted as convective mass-transport-controlled reactive uptake of NO_2 according to the overall reaction

$$4NO_2(g) + 2H_2O(l) \rightarrow 2H^+ + 2NO_3^- + 2HNO_2(g).$$

The rate of uptake of NO_2 per unit interfacial area J_{NO_2} was determined from the measured efficiency of removal of NO_2 from a flowing gas stream by a sieve-plate reactor of known mass-transfer characteristics. At the lowest NO_2 partial pressures employed, $(1.8\text{–}6.1) \times 10^{-4}$ atm, the authors reported a constant efficiency of removal of NO_2 from the gas stream flowing through their reactor, i.e., a removal rate proportional to the first power of the partial pressure of the gas.

For convective mass-transport-controlled uptake, the rate of uptake would be related to the Henry's law coefficient of the gas as

$$J_{NO_2} = k_L H_{NO_2} p_{NO_2} \tag{90}$$

[see Eqs. (14) and (19)]. However, since by the analytical method employed, the evolved nitrous acid was equivalent to nitrogen dioxide by the equilibrium

$$2HNO_2(g) = NO(g) + NO_2(g) + H_2O(g), \qquad [-G2]$$

the authors interpreted the measured net rate of uptake of NO_2 as three-fourths the rate of uptake of physically dissolved NO_2; i.e., $J_{\text{meas}} = \frac{3}{4}k_L H_{NO_2} p_{NO_2}$. The value of H_{NO_2} thus obtained was 4.1×10^{-2} M atm^{-1}.

The problem of evolution of HNO_2 was obviated by Komiyama and Inoue (1980), who employed alkaline solution (0.01 M NaOH). These authors also extended the range of measurement to a partial pressure lower than that employed by Andrew and Hanson (1.2×10^{-5} atm). In contrast to those authors, Komiyama and Inoue found that the ratio of the rate of uptake of NO_2 to the partial pressure of the gas continued to decrease with decreasing partial pressure of NO_2 to partial pressure as low as 2×10^{-5} atm. Using the limiting low-pressure rate of uptake and interpreting their measured rate of uptake according to Eq. (90), Komiyama and Inoue reported a value of $H_{NO_2} = 2.35 \times 10^{-2}$ M atm^{-1} at 15°C, somewhat lower than the value reported by Andrew and Hanson. The results of these experiments are summarized in Table 19.

For comparison of the values of H_{NO_2} obtained by Komiyama and Inoue (1980) to other values at higher temperature, it is desirable to estimate the temperature dependence of this quantity on the basis of an estimated enthalpy of solution. Such an estimate was given by Schwartz and White (1981) by use of the second-law heat of solution of O_3 to estimate that for NO_2; the resulting corrected value for H_{NO_2} at 25°C was given as 1.9×10^{-2} M atm^{-1}.

It is necessary also to address the assumption, inherent in interpretation of these studies, that the dissolved N(IV) species is present as NO_2, not N_2O_4. The equilibrium fraction of dissolved N(IV) present as N_2O_4, $F_{N_2O_4}$ may be evaluated [Eq. (86)] for specified values of K_{A7}, H_{NO_2} and p_{NO_2}. Using the value of K_{A7} given by Grätzel et al. (1969) and H_{NO_2} given by Andrew and Hanson, we find $F_{N_2O_4}$ to range from 49 to 76% for the range partial pressures that appeared to indicate a constant efficiency of uptake. This high a fraction of N_2O_4 would appear to invalidate Andrew and Hanson's interpretation of their study (unless the value of K_{A7} determined by Grätzel et al. is greatly in error) and indeed raises questions regarding the accuracy of their measurement method. We are thus inclined to reject Andrew and Hanson's value for H_{NO_2}.

Similar examination applied to the results of Komiyama and Inoue (1980) indicates that the fraction of N(IV) present as N_2O_4 was 4–7% at the partial pressures employed in that study, and thus it would appear that N_2O_4 would be making only a slight contribution to the rate of uptake attributed to NO_2. On this basis we are inclined to decrease the reported value of H_{NO_2} slightly (6%) to account for this contribution. The resulting value of H_{NO_2} is 2.2×10^{-2} M atm^{-1} at 15°C or, using the temperature coefficient estimate given above, 1.8×10^{-2} M atm^{-1} at 25°C.

The values of H_{NO_2} obtained by Komiyama and Inoue (1980) are compared below to the results of other studies. However, it is useful at this point to note that these authors' value of H_{NO_2} may be combined with their value of $H_{NO_2}^{3/2} k_{A1^*/4^*}^{1/2}$ obtained with the same apparatus (bubbler contactor) to yield $k_{A1^*/4^*} = 2.12 \times 10^7$ M^{-1} s^{-1}. These quantities may also be combined with

Table 19. First-Order Uptake of NO_2

Study	Method[a]	T (°C)	p_{NO_2} (10^{-5} atm)	H_{NO_2} (M atm^{-1})
Andrew and Hanson (1961)	SP	25	18–61	4.1 (−2)[b]
Komiyama and Inoue (1980)	B	15	1.2–2.4	2.35(−2)[c]

[a] Methods: SP, sieve plate; B, bubbler.

[b] Defining equation: $J_{NO_2} = \frac{3}{4} H_{NO_2} k_L p_{NO_2}$.

[c] Defining equation: $J_{NO_2} = H_{NO_2} k_L p_{NO_2}$.

Table 20. Evaluation of Equilibrium and Rate Constants from Komiyama and Inoue (1980)

Quantity	Value	Units
$H_{NO_2}{}^{a}$	2.35(−2)	M atm^{-1}
$H^{3/2}_{NO_2}k^{1/2}_{A1^*/4^*}{}^{a}$	17	M atm$^{-3/2}$ s$^{-1/2}$
$H_{N_2O_4}k^{1/2}_{A4^*/1^*}{}^{a}$	46	M atm^{-1} s$^{-1/2}$
$k_{A1^*/4^*}$	2.1 (7)	M^{-1} s^{-1}
$H_{N_2O_4}$	2.7	M atm^{-1}
K_{A7}	7.5 (4)	M^{-1}
$k_{A4^*/1^*}$	2.8 (2)	s^{-1}

[a] Data from experiments with bubbler contactor at 15°C. Other data employed: $D_{NO_2} = 1.57 \times 10^{-9}$ m^2 s^{-1}; $D_{N_2O_4} = 1.08 \times 10^{-9}$ m^2 s^{-1}; $K_{G7} = 15.3$ atm^{-1}.

their value of $H_{N_2O_4}k^{1/2}_{A4^*/1^*}$ to yield $H_{N_2O_4}$ and K_{A7} since the latter quantities are related to the measured quantities by

$$H_{N_2O_4} = H^2_{NO_2}K_{A7}K^{-1}_{G7} \tag{91}$$

and

$$k_{A1^*/4^*} = k_{A4^*/1^*}K_{A7}. \tag{92}$$

The values of $H_{N_2O_4}$ and K_{A7} may thus be evaluated in terms of the primary measured quantities as

$$H_{N_2O_4} = \frac{(H_{N_2O_4}k^{1/2}_{A4^*/1^*})^2 H_{NO_2}K_{G7}}{(H^{3/2}_{NO_2}k^{1/2}_{A1^*/4^*})^2} \tag{93}$$

and

$$K_{A7} = \frac{(H_{N_2O_4}k^{1/2}_{A4^*/1^*})^2 K^2_{G7}}{(H^{3/2}_{NO_2}k^{1/2}_{A1^*/4^*})^2 H_{NO_2}} \tag{94}$$

Finally, $k_{A4^*/1^*}$ may be evaluated by use of (92). The quantities employed in the calculation and the resulting derived quantities are summarized in Table 20. These results permit further examination of the identity of the transported aqueous-phase N(IV) species. In particular, for the pressures leading to the observed $\frac{3}{2}$-order uptake, $(0.34\text{–}1.8) \times 10^{-4}$ atm, $F_{N_2O_4}$ is calculated to range from 11 to 39%, again indicating the possibility of inaccuracy in the value of $H^{3/2}_{NO_2}k_{A1^*/4^*}$ derived in this pressure range.

The experimental parameters furnished by Komiyama and Inoue also permit the evaluation of the characteristic times of their mixed-phase reaction system to allow determination of whether the criteria of the several limiting regimes are fulfilled, as listed in Table 4. These characteristic times are given in Table 21. The criteria for diffusive mass-transport-controlled

Table 21. Characteristic Times in Study of Reaction [A1*/4*] by Komiyama and Inoue (1980)

Process	Characteristic Time	Value (s)
Convective mixing[a]	τ_m	4.3(1)
Diffusion (N_2O_4)[b]	$\tau_d(N_2O_4)$	5.5(4)
Diffusion (NO_2)[b]	$\tau_d(NO_2)$	3.8(4)
	$\tau_m^2/\tau_d(N_2O_4)$	3.3(−2)
	$\tau_m^2/\tau_d(NO_2)$	4.8(−2)
Reaction (N_2O_4)[c]	$\tau_r(N_2O_4)$	3.6(−3)
Reaction (NO_2)[d]	$\tau_r(NO_2)$	
p_{NO_2} (atm)		
1.8(−4)		5.6(−3)
5.3(−5)		1.9(−2)
3.4(−5)		3.0(−2)
2.4(−5)		4.2(−2)
1.2(−5)		8.4(−2)

[a] Evaluated as $\tau_m = (k_L a)^{-1}$ for $k_L = 1.8 \times 10^{-4}$ m s^{-1} and $a = 1.3 \times 10^2$ m^{-1} for the bubbler contactor.

[b] Evaluated as $\tau_d = (Da^2)^{-1}$ for $D_{NO_2} = 1.57 \times 10^{-9}$ m^2 s^{-1} and $D_{N_2O_4} = 1.08 \times 10^{-9}$ m^2 s^{-1}.

[c] Evaluated as $\tau_r(N_2O_4) = k_{A4^*/1^*}^{-1}$, for value of $k_{A4^*/1^*}$ given in Table 19.

[d] Evaluated as $\tau_r(NO_2) = (2H_{NO_2}k_{A1^*/4^*}p_{NO_2})^{-1}$, for values of H_{NO_2} and $k_{A1^*/4^*}$ given in Table 20.

reaction are

$$\tau_r \lesssim 0.1\tau_d \tag{95}$$

and

$$\tau_r \lesssim 0.38\,\frac{\tau_m^2}{\tau_d}\,. \tag{96}$$

Comparison of $\tau_r(N_2O_4)$ with $\tau_d(N_2O_4)$ and with $\tau_m^2/\tau_d(N_2O_4)$ shows that these criteria are fulfilled, i.e., that the interpretation of the second-order uptake of NO_2 (i.e., first order in N_2O_4) as diffusive mass-transport controlled leads to no inconsistency.

A similar examination may be made for the $\frac{3}{2}$-order uptake of NO_2 (1.8×10^{-4} atm $\geq p_{NO_2} \geq 3.4 \times 10^{-5}$ atm), but for a second-order reaction it must be noted that τ_r is a function of p_{NO_2}. Condition (95) is readily met for both extremes of p_{NO_2}. However, at the lower end of the partial pressure range for which the $\frac{3}{2}$-power law was observed, τ_r considerably exceeds the bound $0.38\ \tau_m^2/\tau_d$ (1.8×10^{-2} s) that represents the onset of significant (>10%) enhancement to the rate of uptake of NO_2 above that given by diffusion alone, as a consequence of convective mass transport. Alternatively, condition (96) may be used to set the lower bound to NO_2 partial pressures for which one may analyze the rate of uptake according to diffusive mass-transport-controlled reaction (5.3×10^{-5} atm). However, although this has the effect of satisfying the mass-transport condition, the range of contribution of N_2O_4 to dissolved N(IV) over the $\frac{3}{2}$-power regime increases to 16–39%.

The criteria for convective mass-transport-controlled uptake (Table 4) are

$$\tau_r \lesssim 0.1\tau_m \tag{97}$$

and

$$\tau_r \gtrsim 3\,\frac{\tau_m^2}{\tau_d}\,. \tag{98}$$

Condition (97) is readily met for both extremes of partial pressure [$(1.2\text{–}2.4) \times 10^{-5}$ atm] that gave rise to a first-order power law for the dependence of the rate of uptake on p_{NO_2}. However, condition (98) is seen not to be met (or even closely approached) for either extreme of p_{NO_2} ($3\tau_m^2/\tau_d = 1.5 \times 10^{-1}$ s). This finding contradicts the assumption that the rate of uptake of NO_2 in this pressure range was controlled by convective mass transport. This inconsistency forces us to conclude that the interpretation of the data of Komiyama and Inoue (1980) leading to the values of the equilibrium and rate constants given in Table 21 cannot be correct. In particular, the value of H_{NO_2} and/or $H_{NO_2}^{3/2}k_{A1^*/4^*}^{1/2}$ must be significantly in error. These considerations are addressed further in Section 7.1.

6.4. Mixed-Order Uptake of NO_2 at Very Low Partial Pressures

The reactive dissolution of NO_2 by water at low partial pressures was recently reëxamined by Lee and Schwartz (1981b). The gas was brought into contact with the liquid as finely dispersed bubbles produced by flowing through a disk-frit. The concentration of dissolved product species was monitored by electrical conductivity, permitting high sensitivity. The mass-transfer time constant of the reactor, which was varied, was determined from the rate of approach to saturation following introduction of CO_2 into the flowing gas, also monitored by electrical conductivity. Nitrogen dioxide partial pressures ranged from 1×10^{-7} to 8×10^{-4} atm. The stoichiometry of the reaction was established by analysis of the aqueous-phase products to be that of reaction [M1], i.e., $2NO_2(g) \xrightarrow{w} 2H^+ + NO_2^- + NO_3^-$. The power dependence of the reaction rate on p_{NO_2} was approximately $\frac{3}{2}$; however, systematic variations about this value were observed. The rate of uptake at the low end of the partial pressure range (1×10^{-7}–1×10^{-5} atm) was interpreted in terms of a model of a second-order reaction in the slow-reaction limit [see Eq. (12) for a first-order reaction]. This model is briefly summarized here (cf. Astarita, 1967). Henry's law equilibrium is assumed for the surface concentration of dissolved NO_2,

$$[NO_2(s)] = H_{NO_2} p_{NO_2}.$$

The aqueous-phase NO_2 concentration is assumed to be governed by convective mass transport and second-order reaction:

$$NO_2(s) \underset{k_{as}}{\overset{k_{as}}{\rightleftharpoons}} NO_2(aq)$$

$$2NO_2(aq) \xrightarrow{k_{A1^*/4^*}} 2H^+ + NO_2^- + NO_3^-.$$

Assumption of a steady-state concentration for $NO_2(aq)$ yields

$$[NO_2(aq)] = \frac{(1 + 8\tau_m k_{A1^*/4^*} H_{NO_2} p_{NO_2})^{1/2} - 1}{4\tau_m k_{A1^*/4^*}} \tag{99}$$

and, in turn,

$$R_{1^*/4^*} = \frac{1}{2\tau_m} \left\{ H_{NO_2} p_{NO_2} + \frac{1 - (1 + 8\tau_m k_{A1^*/4^*} H_{NO_2} p_{NO_2})^{1/2}}{4\tau_m k_{A1^*/4^*}} \right\}. \tag{100}$$

Here τ_m is the convective mixing time constant (k_{as}^{-1}). This model led to a treatment, in terms of the two parameters H_{NO_2} and $k_{A1^*/4^*}$, that accounted for the dependence of the rate of uptake on p_{NO_2} and τ_m to within 10% over the indicated range in p_{NO_2} and over a threefold variation in τ_m. The values of H_{NO_2} and $k_{A1^*/4^*}$ obtained from this treatment were $(7.0 \pm 0.5) \times 10^{-3}$ M atm^{-1} and $(1.0 \pm 0.1) \times 10^8$ m^{-1} s^{-1}, respectively, at 22°C, where the error bars were empirically estimated. At higher NO_2 partial pressures ($p_{NO_2} \gtrsim 3 \times 10^{-5}$ atm) the rate of reactive dissolution was systematically greater than that accounted for by the slow-reaction treatment. This was attributed to the presence of $N_2O_4(aq)$ at these high partial pressures.

It is of interest to examine the relative values of the characteristic mixing time in the study of Lee and Schwartz to address self-consistency of their treatment. In particular, that treatment requires that the characteristic time of reaction τ_r exceed $3\tau_m^2/\tau_d$, consistent with the assumed absence of reaction in the surface film. The comparison of these quantities is given in Table 22; $3\tau_m^2/\tau_d$ is evaluated as $3\tau_m^2 D_{NO_2} a^2$, where for the surface : volume ratio a, the value 8 cm^{-1} has been employed, representing an upper-limit estimate to this quantity for an aqueous bubble column (Calderbank, 1967). It is seen that the required condition is fulfilled (with the possible exception of a single point) and thus that there is no inconsistency in the authors' treatment.

A concern that must be raised regarding the interpretation of the kinetic data of Lee and Schwartz (1981b) is that of appropriateness of the slow-reaction model to a second-order reaction. Although the model posits that the bulk solution in which reaction takes place is characterized by a uniform concentration (as determined by the competition of convective mass transport and reaction), it is clear that this concentration must exhibit a distribution reflecting the stochastic nature of the convective mixing process; it

Table 22. Examination of Surface Reaction in the Study by Lee and Schwartz (1981b)

p_{NO_2} (atm)	τ_r (s)[a]
9.71(−6)	7.4(−2)
1.66(−6)	4.3(−1)
4.90(−7)	1.5
1.04(−7)	6.9

τ_m (s)	$3\tau_m^2/\tau_d$ (s)[b]
1.69	1.1(−2)
2.14	1.8(−2)
3.17	3.9(−2)
4.27	7.0(−2)
5.26	10.6(−2)

[a] Evaluated as $(2H_{NO_2}k_{A1^*/4^*}p_{NO_2})^{-1}$, for $H_{NO_2} = 7 \times 10^{-3}$ M atm^{-1} and $k_{A1^*/4^*} = 1.0 \times 10^{8}$ M^{-1} s^{-1} as given by Lee and Schwartz.

[b] Upper-limit estimate, evaluated as $3\tau_m^2 D_{NO_2} a^2$ for a taken as 8 cm^{-1} (Calderbank, 1967).

is recalled that k_{as} represents only an average rate coefficient for convective mixing. In the case of a first-order reaction, this treatment would appear to be appropriate even for a nonuniform bulk concentration, since the local rate of reaction R is proportional to the first power of the local reagent concentration [X], and, in turn, the average reaction rate $\overline{R}$ is proportional to the average concentration $[\overline{\mathrm{X}}]$ as inferred from k_{as}. However, in the case of a second-order reaction, this approach must be questioned since the average reaction rate $\overline{R}$ is proportional to $\overline{[\mathrm{X}]^2}$, which cannot be taken as $[\overline{\mathrm{X}}]^2$.

In the absence of a more detailed treatment, it does not appear possible to estimate the magnitude or even the direction of the errors in $k_{A1^*/4^*}$ and H_{NO_2} resulting from application of the uniform concentration model. One would note, however, that at the two extremes of the slow reaction regime, the second-order reaction approaches the phase-mixed and convectively controlled situations, just as is the case with first-order reactions. At both extremes the model would appear to apply exactly, irrespective of reaction order, leading to unequivocal determination of H_{NO_2} (convective-controlled limit, $\tau_m/\tau_r \gg 1$) and $H_{NO_2}^2 k_{A1^*/4^*}$ (phase-mixed, $\tau_m/\tau_r \ll 1$). One finds from Table 22 that τ_m/τ_r in the experiment of Lee and Schwartz ranged from 0.24 to 71, i.e., fairly closely approaching both extremes. The close adherence of the measurements to the predictions of the model [Eq. (100)] over the entire range of τ_m/τ_r (cf. Figure 6 of Lee and Schwartz, 1981*b*) lends empirical support to application of this model to the case of a second-order reaction.

The values of H_{NO_2} and $k_{A1*/4*}$ obtained by Lee and Schwartz are compared to other determinations in Section 7.1.

6.5. Uptake of NO and $NO_2(N_2O_3)$

The presence of NO in addition to NO_2 admits the possibility of reaction

$$NO(aq) + NO_2(aq)(N_2O_3(aq)) \overset{w}{\rightarrow} 2HNO_2(2H^+ + 2NO_2^-) \qquad [A2*/5*]$$

in addition to reaction [A1*/4*]. Studies of the uptake of NO + $NO_2(N_2O_3)$ interpreted according to penetration theory have been conducted by Hofmeister and Kohlhaas (1965), Corriveau and Pigford (1971), and Komiyama and Inoue (1980).

The study by Hofmeister and Kohlhaas employed a laminar water jet of variable path length (2–6 cm). The water jet was exposed to a NO–NO_2 gas mixture in which the composition was varied from 10 to 80% N(IV) (N(IV) $\equiv NO_2 + 2N_2O_4$); the total pressure was not specified, nor was it indicated whether an inert gas such as N_2 was present. The rates of reactions [A1*/4*] and [A2*/5*] were determined from measurements of the amounts of uptake of total acid (Q_{H^+}) and nitrite ($Q_{NO_2^-}$) as

$$\begin{aligned} Q_{N_2O_4} &= Q_{H^+} - Q_{NO_2^-} \\ Q_{N_2O_3} &= Q_{NO_2^-} - \tfrac{1}{2}Q_{H^+} \end{aligned} \qquad (101)$$

From the ratio of the slope to intercept of plots of the amount of uptake of N_2O_3 as a function of contact time [see Eq. (16)] the authors reported $k_{A5*/2*} = 68\ s^{-1}$ at 25°C; we have replotted the data for N(IV) = 40, 50, 60, 70, and 80% and obtained $k_{A5*/2*} = 117, 99, 53, 68$, and $111\ s^{-1}$, yielding an average $k_{A5*/2*} = (90 \pm 12)\ s^{-1}$. The authors present a single plot of $Q_{N_2O_3}$ versus $p_{N_2O_3}$ (for a specified contact time). From the slope of this plot (and from the slope-intercept ratio of the plots of $Q_{N_2O_3}$ vs. contact time) it is possible to infer the flux of N_2O_3 and, in turn, obtain the value $q_{N_2O_3} = 3.3 \times 10^{-3}$ kmol m^{-2} atm^{-1}, although this is done with considerable trepidation since the data employed in evaluating $p_{N_2O_3}$ were not specified.

A further concern that must be raised regarding this study is that of application of penetration theory to this system as if the two reactions [A1*/4*] and [A2*/5*] take place in parallel without interaction. We noted above that the quantitative application of penetration theory requires knowledge of the identity of the diffusing species. In an aqueous system containing both N_2O_3 and N_2O_4 it is not clear *a priori* that the two reactions will occur without interaction, e.g., by reaction such as $2N_2O_3(aq) = N_2O_4(aq) + 2NO(aq)$. A test for possible interaction can be made by examining $Q_{N_2O_4}$ as a function of contact time, as also determined by Hofmeister and Kohlhaas. Values of $k_{A4*/1*}$ obtained in this way for N(IV) = 50, 60, 70, and 80% were 64, 580, 53, and 58 s^{-1}, respectively—i.e., mutually inconsistent and substantially different from values determined from studies with N_2O_4 only, as listed in Table 16. Consequently, the determination of $k_{A5*/2*}$ must be viewed with caution.

In a similar study (Corriveau and Pigford, 1971) a wetted-sphere absorber was employed to determine the rate of uptake of N_2O_3 from the mixed N_2O_3–N_2O_4 system. Again the separate rates of uptake were determined from measured rates of uptake of acidity and nitrite. The apparatus did not afford time resolution; thus only $q_{N_2O_3} = H_{N_2O_3}(k_{5*/2*}D_{N_2O_3})^{1/2}$ was determined. The authors present a graph of their data plotted as $J_{N_2O_3}$ versus interfacial N_2O_3 partial pressure; from the slope of this graph $q_{N_2O_3}$ is found to be 1.59×10^{-3} kmol m^{-2} s^{-1} atm^{-1} at 25°C. Unfortunately, examination of a plot of $J_{N_2O_4}$ versus $p_{N_2O_4}$ which should be linear with slope of $q_{N_2O_4}$, exhibits no such regularity and very little resemblance to the authors' plot of such data for N_2O_4 only. Thus we are again left with a result that must be viewed with caution.

The results of these two studies are summarized in Table 23.

In the study by Komiyama and Inoue (1980) the simultaneous uptake of NO and NO_2 was studied at much lower pressures of the reagent gases ($p_{NO} \sim 10^{-3}$ atm; $p_{NO_2} \sim 10^{-4}$ atm). The rate law describing this uptake was reported as

$$J_{NO} = J_{NO_2} = q(p_{NO}p_{NO_2})^{3/4}. \tag{102}$$

Under the conditions of these studies the rate of nitrate production was reported to be "negligibly small," and, indeed, for a given p_{NO_2} the reported rate of uptake in the presence of NO was substantially greater than in the absence of NO. Thus for $p_{NO_2} = 4.1 \times 10^{-5}$ atm and $p_{NO} = 4.2 \times 10^{-4}$ atm the rate of uptake of NO_2 was eightfold greater than in the absence of NO. This finding implies a rapid aqueous-phase reaction of NO and NO_2.

To address the reaction rate quantitatively, Komiyama and Inoue carried out a series of runs at a fixed ratio of $p_{NO}/p_{NO_2} = 10.2$. This ratio of partial pressures was selected with the objective of maintaining equal interfacial

Table 23. Direct Contact Measurements of Rate of Uptake of N_2O_3 (25°C)

Study	q^a (10^{-3} kmol m^{-2} s^{-1} atm^{-1})	$H_{N_2O_3}k^{1/2}_{A5*/2*}$ [b] (M atm^{-1} $s^{-1/2}$)
Hofmeister and Kohlhaas (1965)	3.3	8.8
Corriveau and Pigford (1971)	1.6	4.3

[a] Defining equation: $J_{N_2O_3} = qp_{N_2O_3}$.

[b] Evaluated as $J_{N_2O_3}/D^{1/2}_{N_2O_3}$ for $D_{N_2O_3}$ taken as 1.4×10^{-9} m^2 s^{-1}.

concentrations of the dissolved gases, i.e.,

$$\mathrm{H_{NO}}p_{\mathrm{NO}} = \mathrm{H_{NO_2}}p_{\mathrm{NO_2}} \tag{103}$$

for the value of $\mathrm{H_{NO_2}}$ that had been inferred from the authors' study of the uptake of NO_2 outlined above. This condition was desired so that the diffusion and reaction of NO and NO_2 could be treated identically to a second-order reaction, i.e.,

$$J_{\mathrm{NO}} = J_{\mathrm{NO_2}} = \tfrac{1}{2}(\tfrac{4}{3}\overline{D}k_{\mathrm{A2^*/5^*}})^{1/2}(\mathrm{H_{NO}}p_{\mathrm{NO}}\mathrm{H_{NO_2}}p_{\mathrm{NO_2}})^{3/4} \tag{104}$$

[see Eq. (88)]. Such interpretation would apply provided the following conditions are satisfied:

1. $\mathrm{H_{NO}}p_{\mathrm{NO}} = \mathrm{H_{NO_2}}p_{\mathrm{NO_2}}$.
2. The rate of reaction [A2*/5*] exceeds the rate of [A1*/4*] to such an extent that depletion of N(IV) by the latter reaction is negligible; i.e., $k_{\mathrm{A2^*/5^*}}\mathrm{H_{NO}}\mathrm{H_{NO_2}}p_{\mathrm{NO}}p_{\mathrm{NO_2}} \gg k_{\mathrm{A1^*/4^*}}\mathrm{H^2_{NO_2}}p^2_{\mathrm{NO_2}}$.
3. The principal aqueous-phase diffusing species are NO(aq) and NO_2(aq) (and not N_2O_3(aq) or N_2O_4(aq)).
4. The diffusion coefficients D_{NO} and $D_{\mathrm{NO_2}}$ are approximately equal and may be represented by an average value $\overline{D}$.
5. The reaction is sufficiently rapid that it may be treated as diffusive mass-transport controlled.

Under the assumption that the several conditions are satisfied, $k_{\mathrm{A2^*/5^*}}$ may be evaluated from the measured value of q as

$$k_{\mathrm{A2^*/5^*}} = \frac{3q^2}{\overline{D}(\mathrm{H_{NO}}\mathrm{H_{NO_2}})^{3/2}}\,. \tag{105}$$

Because of the assumption inherent in the experimental design that [NO(s)] = [NO_2(s)], it is necessary in evaluation $k_{\mathrm{A2^*/5^*}}$ by (105) to employ Komiyama and Inoue's value of $\mathrm{H_{NO_2}}$, i.e., 2.35×10^{-2} M atm^{-1} at 15°C; $\mathrm{H_{NO}} = 2.30 \times 10^{-3}$ M atm^{-2} and $\overline{D}$ is evaluated as $\tfrac{1}{2}(D_{\mathrm{NO}} + D_{\mathrm{NO_2}}) = \tfrac{1}{2}(1.95 + 1.57) \times 10^{-9}$ m^2 s^{-1} = 1.74×10^{-9} m^2 s^{-1}. From the measured value of q (1.1×10^{-3} kmol m^{-2} s^{-1} atm$^{-3/2}$) one obtains $k_{\mathrm{A2^*/5^\cdot}} = 5.3 \times 10^9$ M^{-1} s^{-1}. This rate constant is essentially equal to the diffusion-controlled encounter rate constant of the two species (Benson, 1960), thus implying, if this interpretation is correct, an extremely rapid reaction between NO and NO_2.

In an additional series of experiments the ratio $p_{\mathrm{NO}}/p_{\mathrm{NO_2}}$ was varied over the range 3–20; expression (102 describing the rate of uptake continued to obtain, with the value of q unchanged from that in the series of runs in which [NO(s)] and [NO_2(s)] were maintained putatively equal. This behavior is inconsistent with the model leading to (105). However, departure from (105) might not be expected to be too great, as can be seen by the following argument, which rests on an alternative interpretation of these experiments.

Assume $H_{NO}p_{NO} \gg H_{NO_2}p_{NO_2}$. Then the aqueous-phase NO concentration may be approximated as uniform at the value $H_{NO}p_{NO}$ since depletion of NO(aq) by reaction would be much less than that of NO_2(aq). In this limit the rate of uptake may be approximated as a pseudo-first-order reaction of NO_2 and

$$J_{NO_2} = H_{NO_2}[k^{(1)}D_{NO_2}]^{1/2}; \tag{106}$$

here $k^{(1)} = k_{A2*/5*}[NO(aq)] = k_{A2*/5*}H_{NO}p_{NO}$. Hence

$$J_{NO_2} = (D_{NO_2}k_{A2*/5*})^{1/2}(H_{NO}p_{NO})^{1/2}(H_{NO_2}p_{NO_2}). \tag{107}$$

More generally, J_{NO_2} may be written as

$$J_{NO_2} = \left(\frac{\overline{D}}{3}\right)^{1/2} k_{A2*/5*}^{1/2}(H_{NO}H_{NO_2}p_{NO}p_{NO_2})^{3/4}f(\alpha) \tag{108}$$

where α is the dimensionless ratio

$$\alpha \equiv \frac{H_{NO}p_{NO}}{H_{NO_2}p_{NO_2}}$$

and $f(\alpha)$ is also dimensionless. For $\alpha = 1$, $f = 1$; i.e., the situation is that leading to (104). For $\alpha \gg 1$, comparison of (104) and (107) shows that

$$f \sim 3^{1/2}\left(\frac{D_{NO_2}}{\overline{D}}\right)^{1/2} \alpha^{-1/4} \tag{109}$$

A sketch of the function f is shown in Figure 3. (Here and subsequently we approximate $\overline{D} = D_{NO_2}$.) This function is approximately equal to 1 for α within an order of magnitude of unity and for values of α outside this range decreases only slowly. Because of this slow variation it is seen that irrespective of the value of α, departure from Eq. (104) would not be expected to be too great for a limited range of α. Thus for a spread in α of a factor of 6.7 (corresponding to the range of p_{NO}/p_{NO_2} employed by Komiyama and Inoue), one would expect a "scatter" of at most ±25%, depending on the value of α, from the dependence given by (104). This "scatter" is consistent with that observed by Komiyama and Inoue. Thus the variation of the rate of uptake as $(p_{NO}p_{NO_2})^{3/4}$ need not be taken as evidence for the validity of Komiyama and Inoue's value of H_{NO_2}.

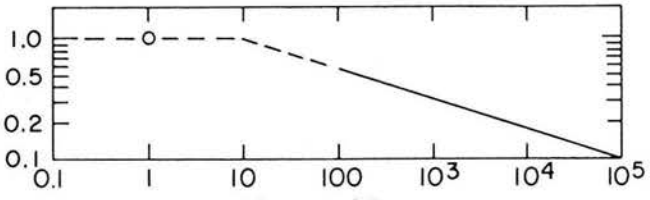

Figure 3. Ratio of rate of uptake of NO_2 under diffusive mass-transport-controlled conditions for $H_{NO}p_{NO}/H_{NO_2}p_{NO_2} = \alpha \neq 1$ to that for $\alpha = 1$.

The alternative interpretation developed here leads to

$$H_{NO_2}^{3/2} k_{A2^*/5^*} = \frac{3q^2}{H_{NO}^{3/2} D_{NO_2} \bar{f}^2} \tag{110}$$

[see Eq. (108)]; here $\bar{f}$ is the value of f at the midrange of p_{NO}/p_{NO_2}. For application of (110), it is necessary to know $\bar{f}$, which, however, depends on H_{NO_2}. Fortunately, this dependence is weak. In particular for $p_{NO}/p_{NO_2} = 10.2$, values of H_{NO_2} within an order of magnitude of Komiyama and Inoue's value of 2.35×10^{-2} M atm^{-1} would lead to $\bar{f} \approx 1$. Hence for H_{NO_2} in this range, (110) together with Komiyama and Inoue's measured value of q yields $H_{NO_2}^{3/2} k_{A2^*/5^*} = 2.1 \times 10^7$ m$^{1/2}$atm$^{-3/2}$ s^{-1} for values of H_{NO_2} within the range 2×10^{-3} M atm$^{-1} \le H_{NO_2} \le 2 \times 10^{-1}$ M atm^{-1}. It should be noted that although this discussion satisfactorily accounts for the lack of sensitivity of the rate law to the ratio p_{NO}/p_{NO_2}, it does little to allay the concern raised above regarding the large value of $k_{A2^*/5^*}$. Indeed, for H_{NO_2} less than Komiyama and Inoue's value of 2.35×10^{-2} M atm^{-1}, a value of $k_{A2^*/5^*}$ is required that is even greater than that given above. We return to further consideration of this value of $H_{NO_2}^{3/2} k_{A2^*/5^*}$ in Section 7.2.

The two interpretations of the simultaneous $\frac{3}{4}$-order uptake of NO and NO_2 are summarized in Table 24.

Before concluding this discussion, we briefly consider the several other assumptions that were made permitting the uptake of NO and NO_2 to be treated as a diffusion mass-transport-controlled reaction of these two oxides. Again we note that a significant fraction of dissolved N(IV) is present as N_2O_4; this fraction ranges from 6 to 39% for the NO_2 partial pressures employed, where for this evaluation we have employed $H_{NO_2} = 1.2 \times 10^{-2}$ M atm^{-1} and $K_{A7} = 6.5 \times 10^4$ M^{-1}. (If Komiyama and Inoue's values of these constants are employed, $F_{N_2O_4}$ ranges from 13 to 59%.) Thus concern must be raised again regarding the accuracy of the constants determined. Similar examination may be made of the concentration of N_2O_3 relative to that of NO or NO_2; in this case the equilibrium concentration of the compound oxide appears to be less than about 10%.

Table 24. Alternative Interpretations of Simultaneous $\frac{3}{4}$-Order Uptake of NO and NO_2[a]

Quantity	Value	Units
q[b]	1.1(−3)	kmol m^{-2} s^{-1} atm$^{-3/2}$
$k_{A2^*/5^*} = 3q^2/\bar{D}(H_{NO}H_{NO_2})^{3/2}$[c]	5.3(9)	M^{-1} s^{-1}
$H_{NO_2}^{3/2} k_{A2^*/5^*} = 3q^2/H_{NO}^{3/2} D_{NO_2} \bar{f}^2$[d]	2.1(7)	M$^{1/2}$ s^{-1} atm$^{-3/2}$

[a] Data of Komiyama and Inoue (1980), 15°C.

[b] Defining equation: $J_{NO} = J_{NO_2} = q(p_{NO}p_{NO_2})^{3/4}$.

[c] For assumed $H_{NO}p_{NO} = H_{NO_2}p_{NO_2}$; $\bar{D} = 1.74 \times 10^{-9}$ m^2 s^{-1}.

[d] For assumed $H_{NO}p_{NO} \gtrsim 2H_{NO_2}p_{NO_2}$; $D_{NO_2} = 1.57 \times 10^{-9}$ m^{-2} s^{-1}; $\bar{f} = 1$.

With respect to mass transport we would note that for the reaction to be in the diffusive regime, the criterion $\tau_r < 0.38\ \tau_m^2/\tau_d$ must be satisfied. For interpretation as diffusion-controlled reaction of NO and NO_2 [Eq. (104)], this criterion must be satisfied for both NO and NO_2, where

$$\tau_r(NO_2) = (H_{NO} p_{NO} k_{A2^*/5^*})^{-1}$$

and

$$\tau_r(NO) = (H_{NO_2} p_{NO_2} k_{A2^*/5^*})^{-1}.$$

Evaluation of these quantities for values of H_{NO_2} and $k_{A2^*/5^*}$ proposed by Komiyama and Inoue (1980) leads to no inconsistency. For interpretation as diffusion-controlled uptake of NO_2 (with excess [NO]), the requirement must be met only for NO_2; again, no inconsistency is indicated.

7. SYNTHESIS

The preceding sections have reviewed measurements, obtained by a variety of techniques, of the Henry's law solubility and/or kinetics of aqueous-phase reaction of the nitrogen oxides in liquid water. These experiments lead to results that may be expressed in terms of products of various powers of the Henry's law coefficients of the appropriate species and/or rate constants of the appropriate reactions. For the most part, however, we have refrained from combining the results of these studies to yield the values of the Henry's law coefficients and rate constants, reserving that component of this review until the various studies themselves have been reviewed, so that all relevant studies may be taken into account. Having completed the review of the various individual experiments, we proceed in this section to consider the results of these experiments in their entirety with the objective of obtaining recommended values of the Henry's law coefficients and aqueous-phase rate constants that exhibit the greatest consistency with this body of experimental data. As is seen later, it is not possible to ascribe unique values to these quantities because of unrecognized determinate errors in the various studies and/or inappropriate application of the model by which the experimental measurement is interpreted. Nevertheless, as is seen, it is possible to recommend values of these quantities that lie within rather narrow uncertainty bounds.

7.1. Reaction [1*/4*]

In the case of reaction [1*/4*] the quantities for which there are experimental measurements are listed in Table 25. Examination of this set of quantities shows that these experiments may be expressed in terms of the five elementary constants, H_{NO_2}, $H_{N_2O_4}$, K_{A7}, $k_{A1^*/4^*}$, and $k_{A4^*/1^*}$. However, we

Table 25. Experimentally Measured Quantities Pertinent to Mixed- and Aqueous-Phase Reactions [1] and [4]

Measured Quantity		Method	Data Source
1.	$H_{N_2O_4}k_{A4^*/1^*}(\equiv k_{M4^*/1^*})$	Indirect—nitrous acid decomposition, etc.	Table 5
2.	$k_{A4^*/1^*}$	Aqueous pulse radiolysis, etc.	Table 13
3.	$H_{N_2O_4}k^{1/2}_{A4^*/1^*}$	Direct contact, penetration theory	Table 15
4.	$H_{N_2O_4}k^{-1/2}_{A4^*/1^*}$	Direct contact, penetration theory	Table 16
5.	$H^2_{NO_2}k_{A1^*/4^*}(\equiv k_{M1^*/4^*})$	Indirect—nitrous acid decomposition, etc.	Table 5
6a.	H_{NO_2}	Thermochemical cycles (paths II and III)	Schwartz and White (1981)
6b.	H_{NO_2}	Convective mass-transport uptake of NO_2	Table 19
6c.	H_{NO_2}	Slow-reaction study of NO_2 uptake	Section 6.4
7.	$k_{A1^*/4^*}$	Slow-reaction study of NO_2 uptake	Section 6.4
8.	$H^{3/2}_{NO_2}k^{1/2}_{A1^*/4^*}$	Direct contact, penetration theory	Table 18
9.	K_{A7}	Pulse radiolysis	Schwartz and White (1981)

note that the relationships

$$H_{N_2O_4} = H^2_{NO_2}K_{A7}K^{-1}_{G7} \tag{111}$$

and

$$k_{A4^*/1^*} = k_{A1^*/4^*}K^{-1}_{A7} \tag{112}$$

introduce two constraints on this set of constants and thus that the number of independent elementary constants (degrees of freedom) necessary for description of this reaction system is reduced to three. (Here and subsequently we consider the gas-phase equilibrium constant K_{G7} well established and not subject to further refinement in consideration of these experiments.) For the moment, however, it is useful to retain a redundant set of constants, since, depending on the predominant aqueous-phase species (NO_2 or N_2O_4), various experimental results are expressible in terms of either H_{NO_2} and $k_{A1^*/4^*}$ or $H_{N_2O_4}$ and $k_{A4^*/1^*}$.

In the discussion that follows we employ a graphical method that appears to be quite useful for the interpretation of these experiments. As is seen later, this method allows the data from all pertinent experiments to be compared and used in selecting a set of recommended elementary constants and in estimating the uncertainty of these constants. This approach thus contrasts with algebraic approaches that have been employed previously [e.g., Sherwood et al. (1975) and Stedman (1979), as well as the primary literature already cited]. We first consider experiments the results of which are expressible in terms of only $H_{N_2O_4}$ and/or $k_{A4^*/1^*}$ (Table 25, items 1–4). For example, consider a given measurement of $k_{M4^*/1^*}$ (= $H_{N_2O_4}k_{A4^*/1^*}$), as listed in Table 5, e.g., the value 5.92×10^2 M atm^{-1} s^{-1} derived from Abel and H. Schmid (1928c). This result can be considered a single equation in the two unknowns $H_{N_2O_4}$ and $k_{A4^*/1^*}$, which can be satisfied by any pair of values of $H_{N_2O_4}$ and $k_{A4^*/1^*}$ such that their product is equal to the measured value. This set of solutions constitutes a curve in the plane whose axes are $k_{A4^*/1^*}$ and $H_{N_2O_4}$, representing the locus of points (in $k_{A4^*/1^*}$–$H_{N_2O_4}$ space) that satisfy this particular experimental result. For the coordinate axes taken as log $k_{A4^*/1^*}$ and log $H_{N_2O_4}$, this locus of points is represented by a straight line, as given in Figure 4, line *e*. The slope of this line is −1, corresponding to the equation

$$\log H_{N_2O_4} + \log k_{A4^*/1^*} = \log(592).$$

The other experimental determinations of $H_{N_2O_4}k_{A4^*/1^*}$ in Table 5 lead to the

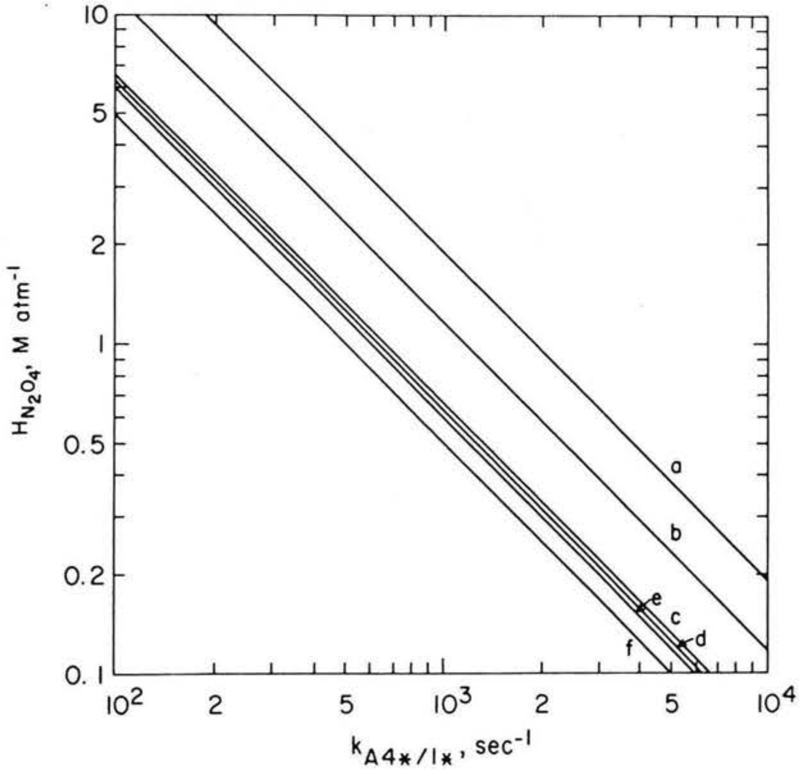

Figure 4. Measurements of $H_{N_2O_4}k_{A4^*/1^*}$ displayed in log $H_{N_2O_4}$–log $k_{A4^*/1^*}$ plane: (*a*) Heckner (1973); (*b*) Komiyama and Inoue (1978); (*c*) G. Schmid and Bähr (1964); (*d*) Abel and H. Schmid (1928d); (*e*) Abel and H. Schmid (1928c); (*f*) Jordan and Bonner (1973). All measurements at or corrected to 25°C.

remaining lines shown in Figure 4, i.e., to a family of parallel lines all with slope of -1. In principle, for all these measurements carried out at (or corrected to) the same temperature, all these lines should be coincident. The "spread" in these lines represents experimental error.

We now consider other experiments. In Figure 5 are shown the results of experiments measuring $H_{N_2O_4}k^{1/2}_{A4*/1*}$ and $H_{N_2O_4}k^{-1/2}_{A4*/1*}$ (Tables 15 and 16). These experiments lead to lines (in the log $k_{A4*/1*}$–log $H_{N_2O_4}$ plane) of slope $-1/2$ and $+1/2$, respectively. Again considerable spread in the data is evidenced, as seen in the breadth of the two sets of lines. Also shown in Figure 5, as indicated by the filled circles, are the points of intersection as inferred from each of the three experiments in which both $H_{N_2O_4}k^{1/2}_{A4*/1*}$ and $H_{N_2O_4}k^{-1/2}_{A4*/1*}$ were measured. These points represent presumptively unique solutions of these sets of data for $H_{N_2O_4}$ and $k_{A4*/1*}$ (two equations in two unknowns), and indeed, assuming highly accurate and precise measurements, such a procedure would lead to a correct evaluation of these quantities. However, as may be seen in Figure 5, the uncertainty in the measured data admits a considerable spread in the values of $H_{N_2O_4}$ and $k_{A4*/1*}$ that may be inferred from the region of intersection of these "bands."

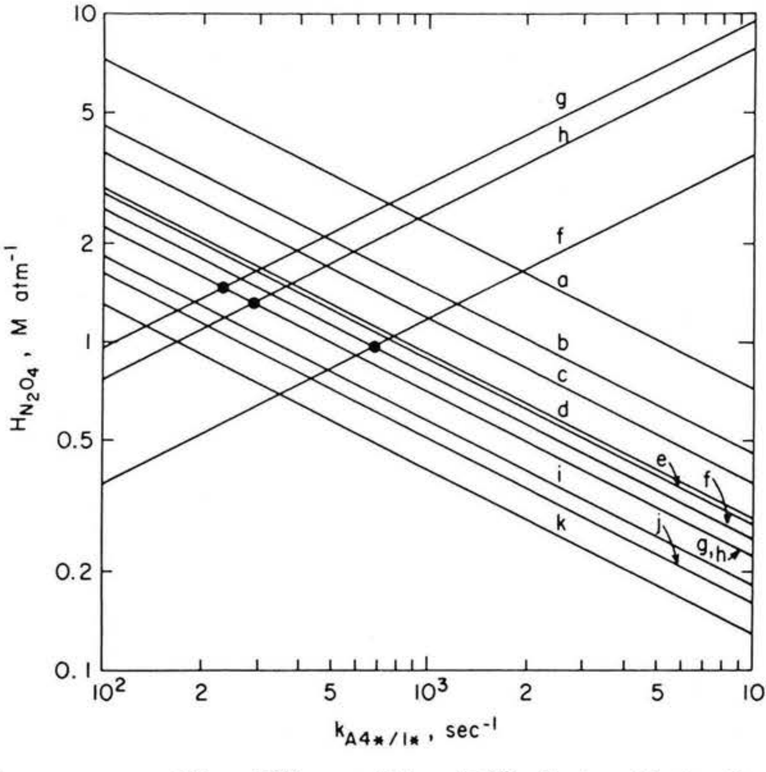

Figure 5. Measurements of $H_{N_2O_4}K^{1/2}_{A4*/1*}$ and $H_{N_2O_4}k^{-1/2}_{A4*/1*}$ displayed in log $H_{N_2O_4}$–log $k_{A4*/1*}$ plane (filled circles indicate intersections of individual experimental deteminations): (*a*) Komiyama and Inoue (1980), flat-surface contactor; (*b*) ibid., bubbler contactor; (*c*) Chilton and Knell (1972); (*d*) Dekker et al. (1959); (*e*) Gerstacker (1961); (*f*) Hoftyzer and Kwanten (1972); (*g*) Kramers et al. (1961); (*h*) Bartholomé and Gerstacker (1961); (*i*) Kameoka and Pigford (1977); (*j*) Wendel and Pigford (1958); (*k*) Corriveau and Pigford (1971). All measurements at or corrected to 25°C.

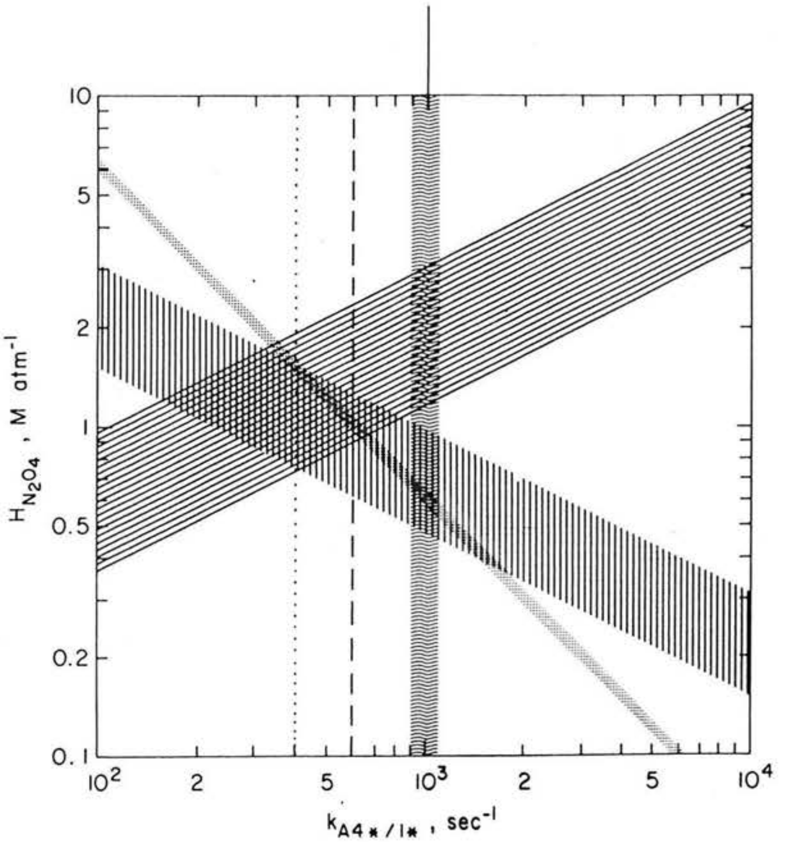

Figure 6. Summary plot of data on reactive dissolution of N_2O_4, displayed in log $H_{N_2O_4}$ –log $k_{A4*/1*}$ plane. ▒, $H_{N_2O_4}k_{A4*/1*}$; ▥, $H_{N_2O_4}k^{1/2}_{A4*/1*}$; ▨, $H_{N_2O_4}k^{-1/2}_{A4*/1*}$; ≋, -·-·-·, . . ., measurements of $k_{A4*/1*}$ by Grätzel et al. (1969), Treinin and Hayon (1970), and Moll (1966), respectively. All measurements at or corrected to 25°C except Grätzel et al., 20°C.

Comparison of Figures 4 and 5 suggests the utility of plotting these data on the same graph. This is done in Figure 6, where the spread of the data of the various types of experiment is now indicated by bands rather than lines representing the individual studies. In selecting the width of these bands we have somewhat arbitrarily excluded outlying results. In particular, in the case of $H_{N_2O_4}k_{A4*/1*}$ we rely heavily on the data of Abel and H. Schmid (1928c and d) and G. Schmid and Bähr (1964), for the reasons given in Section 4.1. Similarly in the case of determinations of $H_{N_2O_4}k^{1/2}_{A4*/1*}$ the band shown in Figure 6 reflects the recommended uncertainty in this quantity given in Section 6.1.

Also shown in Figure 6 are the results of the three studies leading to determination of $k_{A4*/1*}$, shown as vertical lines (Moll, 1966; Treinin and Hayon, 1970) or as a vertical band, representing the uncertainty estimate of the original authors (Grätzel et al., 1969). As previously noted, of the several studies we place highest confidence in the work of Grätzel et al. (1969), in view of the direct nature of the measurement, high reproducibility, and large number experimental runs.

Examination of Figure 6 shows rather satisfying agreement among the several types of experiment. In the absence of additional information the region of intersection of the bands resulting from the several types of experiment might serve as the basis for recommending values of $H_{N_2O_4}$ and $k_{A4^*/1^*}$. However, we defer such discussion to follow consideration of experiments yielding information on H_{NO_2} and $k_{A4^*/1^*}$.

Experimental results expressible in terms of H_{NO_2} and/or $k_{A1^*/4^*}$ only (Table 25, items 5–8) are displayed in Figure 7, as lines or bands in the log $k_{A1^*/4^*}$–log H_{NO_2} plane. (It should be pointed out that, to facilitate subsequent comparison with the N_2O_4 data, the scale of the log H_{NO_2} axis in this plot is twice that of the log $k_{A1^*/4^*}$ axis.) Values of H_{NO_2} obtained thermochemically are represented by the two overlapping horizontal bands, where the width of the band represents the propagated uncertainty estimate in the original equilibrium measurement(s). The value of H_{NO_2} obtained by Komiyama and Inoue (1980) as corrected here for temperature dependence (estimated) and N_2O_4 solubility is shown as a horizontal line, H_{NO_2} = 1.8

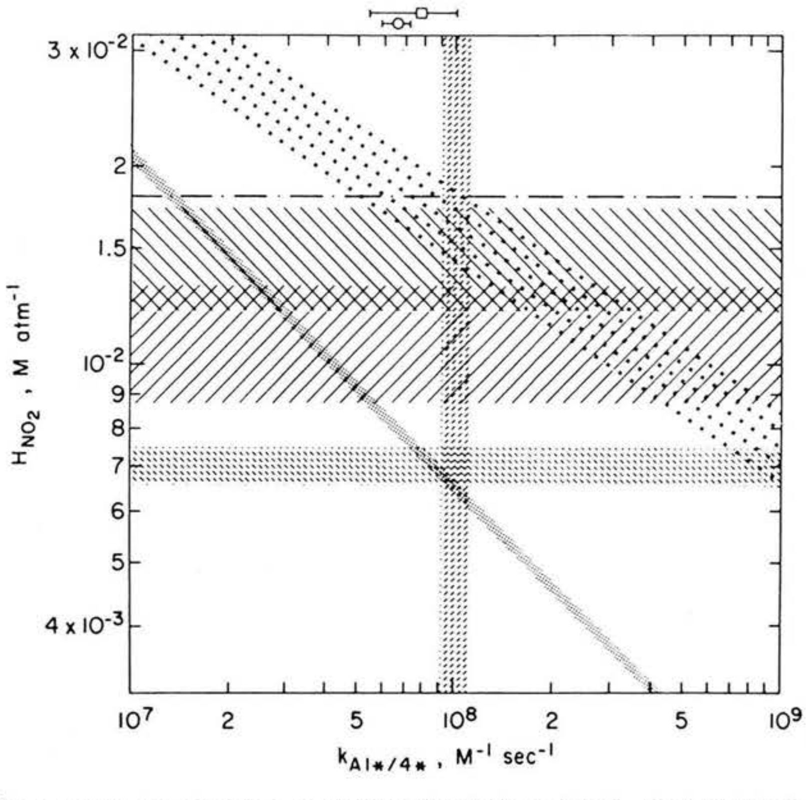

Figure 7. Summary plot of data on reactive dissolution of NO_2 displayed in log H_{NO_2}–log $k_{A1^*/4^*}$ plane. ▒, $H^2_{NO_2}k_{A1^*/4^*}$; ⁘, $H^{3/2}_{NO_2}k^{1/2}_{A1^*/4^*}$, Komiyama and Inoue (1980), 15°C; ⋱ and ⋰, H_{NO_2} and $k_{A1^*/4^*}$, Lee and Schwartz (1981a), 22°C; //// and \\\\, H_{NO_2} evaluated thermochemically, Schwartz and White (1981); -·-·-·-, H_{NO_2}, Komiyama and Inoue (1980), corrected, as indicated in text, to 25°C and for N_2O_4 solubility. Points and error bars at top of figure indicate measurements of K_{A7} when this figure is used in conjunction with Figure 6; see text. ○, Grätzel et al. (1969), 20°C; □, Treinin and Hayon (1970). All data for 25°C except as indicated.

$\times\ 10^{-2}$ M atm^{-1}. [The uncorrected value, not shown, is 2.35×10^{-2} M atm^{-1}. Also not shown is the value given by Andrew and Hanson (1961), 4×10^{-2} M atm^{-1}.] The value of H_{NO_2} (and estimated uncertainty) obtained by Lee and Schwartz (1981b) in their study of reaction [A1*/4*] in the slow-reaction regime is represented by a horizontal band; those authors' value and uncertainty of $k_{A1^*/4^*}$ are represented by a vertical band. Also represented in Figure 7 are the values of $k_{M1^*/4^*}$ $(= H^2_{NO_2}k_{A1^*/4^*})$ shown as a band of slope $-1/2$ (one decade per two decades); these data, of course, represent the same experimental measurements that led to $H_{N_2O_4}k_{A4^*/1^*}$ shown in Figure 6. Finally, we show as a band of slope $-1/3$ measurements of $H^{3/2}_{NO_2}k^{1/2}_{A1^*/4^*}$ as derived from the study by Komiyama and Inoue (1980); the limits of this band represent determinations with the two different contactors employed.

Examination of the NO_2 data as displayed in Figure 7 also reveals a reasonably well defined region of intersection, although there is some evident discrepancy. Such discrepancy would be lessened if the values of H_{NO_2} and $H^{1/2}_{NO_2}k^{3/2}_{A1^*/4^*}$ indicated in Figure 7 were shown to be too great; we proceed to present arguments that suggest that this may be the case.

With respect to the values of H_{NO_2} as determined by Komiyama and Inoue (1980), we have already addressed (Section 6.3 and Table 22) the question of whether the conditions for uptake solely by convective mass transport, as assumed by the authors, were in fact fulfilled. In that discussion it was shown that this condition was not fulfilled for the values of $k_{A1^*/4^*}$ that they obtained. This discussion can be extended to arbitrary, unknown values of $k_{A1^*/4^*}$ as follows. For a second-order reaction in which the characteristic reaction time τ_r is given by

$$\tau_r = (2H_{NO_2}k_{A1^*/4^*}p_{NO_2})^{-1}, \tag{113}$$

the condition for convective mass-transport-controlled uptake

$$\tau_r \gtrsim \frac{3\tau_m^2}{\tau_d} \tag{98}$$

is equivalent to

$$H_{NO_2}k_{A1^*/4^*} \leq \left(2p_{NO_2}\frac{3\tau_m^2}{\tau_d}\right)^{-1}. \tag{114}$$

This condition is readily displayed as a graph in the H_{NO_2}–$k_{A1^*/4^*}$ plane. In Figure 8 condition (114) is indicated for the extremes of p_{NO_2} that were employed by Komiyama and Inoue (1980) leading to their determination of H_{NO_2} (Table 19); here the mass-transport parameters given in Table 21 have been employed. Condition (114) is satisfied only for values of H_{NO_2} and $k_{A1^*/4^*}$ such that the point $(H_{NO_2},\ k_{A1^*/4^*})$ lies below and to the left of the line indicated for the partial pressure of the measurement. The line $H_{NO_2}k_{A1^*/4^*} = (2p_{NO_2} \cdot 3\tau_m^2/\tau_d)^{-1}$ evaluated at the lowest partial pressure employed (1.2×10^{-5} atm) for the stated mixing conditions intersects the line $H_{NO_2} = 2.35 \times 10^{-2}$ M atm^{-1} (as obtained from the measured rate of uptake under the assumption that the solubility is dominated by the Henry's law solubility) at the value of $k_{A1*/4*} = 1.2 \times 10^7$ M^{-1} s^{-1}. Thus the assumption that the reactive contribution to the uptake of NO_2 under these conditions is small ($\lesssim$10%) compared to that due to the physical solubility is valid only for $k_{A1*/4*} \lesssim 1.2 \times 10^7$ M^{-1} s^{-1}. If this condition is not satisfied, the value of H_{NO_2} inferred from the measurement will be too high because of the increased solubility due to reaction. This would certainly be the case, both for the value of $k_{A1*/4*}$ indicated by Komiyama and Inoue's own data (2.1×10^7 M^{-1} s^{-1}) and *a fortiori* for a value of $k_{A1*/4*}$ as great as that indicated by Lee and Schwartz (1981b) (1×10^8 M^{-1} s^{-1}). This discussion thus reinforces the previous inference that the value of H_{NO_2} given by Komiyama and Inoue (1980) is somewhat too great.

We now address measurements of $H^{3/2}_{NO_2}k^{1/2}_{A1*/4*}$. We first consider the appropriateness of treating these measurements according to diffusive mass-transport-controlled reaction. As noted in Section 6.3, the condition to be

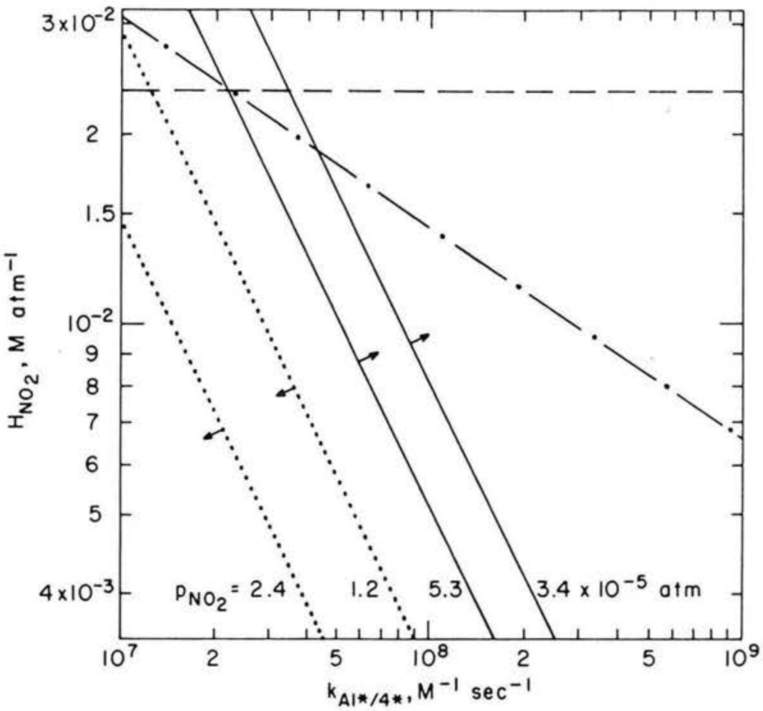

Figure 8. Examination of mass-transport regimes in study by Komiyama and Inoue (1980). ----- and -·-·-·-·- represent reported values of H_{NO_2} and $H^{3/2}_{NO_2}k^{1/2}_{A4*/1*}$, respectively (bubbler contactor, 15°C). Dotted lines represent bound to convective mass-transport regime for specified mass-transport conditions and for indicated p_{NO_2}; determination of H_{NO_2} at a given p_{NO_2} is valid only if point $k_{A1*/4*}$,H_{NO_2} lies below and to the left of this bound. Solid lines represent bound to diffusive mass-transport regime; determination of $H^{1/2}_{NO_2}k^{1/2}_{A1*/4*}$ is valid only if point $k_{A1*/4*}$,H_{NO_2} lies above and to the right of the bound.

satisfied is that

$$\tau_r \lesssim \frac{0.38\tau_m^2}{\tau_d}, \tag{96}$$

which is equivalent to

$$H_{NO_2}k_{A1^*/4^*} \geq \left(2p_{NO_2}\frac{0.38\tau_m^2}{\tau_d}\right)^{-1}. \tag{115}$$

Condition (115) is shown in Figure 8 for $p_{NO_2} = 5.3$ and 3.4×10^{-5} atm; the condition is satisfied for values of H_{NO_2} and $k_{A1^*/4^*}$ lying above and to the right of the indicated bounds at the respective partial pressures. It is seen that condition (115) would be satisfied for the range of partial pressures employed by Komiyama and Inoue $[(0.34\text{–}1.8) \times 10^{-4}$ atm$]$ for, say, $H_{NO_2} = 1 \times 10^{-2}$ atm and $k_{A1^*/4^*} = 1 \times 10^8\ M^{-1}$. As indicated in the discussion in Section 6.2, only for the very low end of the range of partial pressures employed $[(3.4\text{–}5.3) \times 10^{-5}$ atm$]$ would there appear to be a concern that condition (115) is not satisfied for the values of H_{NO_2} and $k_{A1^*/4^*}$ that come under consideration from examination of Figures 7 and 8. Thus we cannot account for a positive error in $H_{NO_2}^{3/2}k_{A1^*/4^*}^{1/2}$ on this basis.

We now address other potential sources of inaccuracy in measurements of $H_{NO_2}^{3/2}k_{A1^*/4^*}^{1/2}$. Measurements of this quantity from all available sources, as listed in Table 18, are shown in Figure 9. It may be seen that considerable spread is exhibited by these data. This spread would appear to be due both to the fact that the several studies were not conducted at the same temperature and to an increased fraction of dissolved N_2O_4 contributing to the measured rate of uptake at the higher NO_2 partial pressures. Thus the two determinations given by Takeuchi et al. (1977) at 15 and 25°C suggest a factor of ~ 1.65 decrease in $H_{NO_2}^{3/2}k_{A1^*/4^*}^{1/2}$ between these temperatures, although this inference must be regarded as somewhat tentative since an increase in temperature would most likely lead also to an increase in K_{A7} and hence in $F_{N_2O_4}$, the fraction of N(IV) present as N_2O_4. We have also noted that in the study by Komiyama and Inoue (1980) $F_{N_2O_4}$ would appear to be on the order of 20%. These considerations would appear to suggest that the band of slope $-1/3$ in Figure 7 may be too high by a factor of roughly $(1.2 \times 1.65)^{2/3} = 1.6$. Lowering of this band by such a factor would bring it substantially closer to the region of intersection defined by the remaining methods indicated in Figure 7.

We now turn to the simultaneous consideration of both sets of measurements, i.e., the "N_2O_4 data" shown in Figure 6 and the "NO_2 data" shown in Figure 7. This simultaneous consideration can be effected by superimposing the two graphs. (This can be facilitated by making a transparent overlay of Figure 7 to the scale of Figure 6.) In superimposing Figures 6 and 7 it is required that the bands representing the $H_{NO_2}^2k_{A1^*/4^*}$ and $H_{N_2O_4}k_{A4^*/1^*}$ data be superimposed. This constraint allows relative trans-

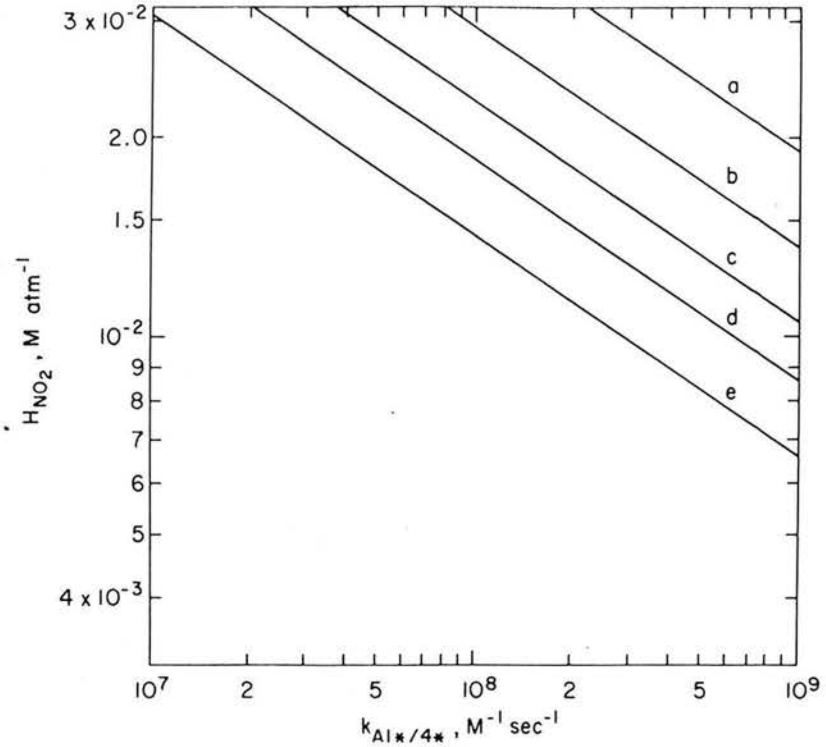

Figure 9. Measurements of $H_{NO_2}^{3/2}k_{A1^*/4^*}^{1/2}$ displayed in the log H_{NO_2}–log $k_{A1^*/4^*}$ plane: (*a*) Takeuchi et al. (1977), 15°C; (*b*) ibid., 25°C; (*c*) Sada et al. (1979), 25°C; (*d*) Komiyama and Inoue (1980), flat contactor, 15°C; (*e*) ibid., bubbler contactor, 15°C.

lation of the two figures in only one dimension, i.e., parallel to a line of slope − 1 in the log $H_{N_2O_4}$–log $k_{A4^*/1^*}$ plane. This single degree of freedom represents the variable K_{A7}. The constraint that the two bands representing $H_{NO_2}^2 k_{A1^*/4^*}$ and $H_{N_2O_4}k_{A4^*/1^*}$ be superimposed is mathematically equivalent to the constraint

$$H_{N_2O_4}k_{A4^*/1^*} = H_{NO_2}^2 k_{A1^*/4^*}K_{G7}^{-1} \tag{116}$$

obtained from (111) and (112), for specified values of the gas-phase equilibrium constant K_{G7}, which we have taken as well established. For any given relative position of Figures 6 and 7 [subject to (116)] the value of K_{A7} may be read off [by Eq. (112)] as the ratio of the abscissa scales of the two graphs. Once the relative position of the two graphs is fixed (i.e., K_{A7} is specified), it is seen that specification of the vertical coordinate specifies both H_{NO_2} and $H_{N_2O_4}$ and similarly that specification of a horizontal coordinate axis specifies both $k_{A1^*/4^*}$ and $k_{A4^*/1^*}$. Thus the three degrees of freedom in this system may be specified by relative translation of the two graphs (parallel to the "northwest–southeast" axis) and by specification of the two coordinates of a point in the plane.

At this juncture we should again point out [as discussed by Schwartz and

White (1981)] that the equilibrium constant K_{A7} has also been investigated experimentally. In two studies this quantity has been reported as $(6.54 \pm 10\%) \times 10^4$ M^{-1} [Grätzel et al. (1969); 20°C] and $(7.7 \pm 30\%) \times 10^4$ M^{-1} [Treinin and Hayon (1970); 25°C]; the error bars represent estimates given by Schwartz and White. These values of the equilibrium constant K_{A7} may be displayed on the superposition of Figures 6 and 7 by the device at the top of the figures. Shown at the top of Figure 7 are points at $k_{A1*/4*} = 6.54 \times 10^7$ and 7.7×10^7 M^{-1} s^{-1} and the corresponding error bars. For the two figures superimposed such that the value $k_{A4*/1*} = 10^3$ s^{-1} indicated by the vertical line at the top of Figure 6 overlays, say, the point $k_{A1*/4*} = 6.54 \times 10^7$ M^{-1} s^{-1} on Figure 7, then $K_{A7} = k_{A1*/4*}/k_{A4*/1*} = 6.54 \times 10^4$ M^{-1}.

Armed with Figures 6 and 7, we are now prepared to select a recommended set of elementary constants (and associated uncertainties) that describe the physical solubility and reaction kinetics in this system. The criterion that we have used in this selection is that the recommended range for the several constants should be such that it encompass at least partially the bands representing the several experimental methods, unless (as is the case with the measurement of $H_{NO_2}^{3/2} k_{A1*/4*}^{1/2}$) there is reason to suspect systematic error in the measurement. With respect to direct measurements of $k_{A4*/1*}$, we have included the determinations by Grätzel et al. (1969) and Treinin and Hayon (1970) but do not extend the range to encompass the measurement of Moll (1966) in view of the indirect nature of those measurements. By this admittedly arbitrary procedure we have selected the recommended range for the several constants given in Table 26. Within that range we have selected, again arbitrarily, a self-consistent [by Eqs. (111) and (112)] set of recommended values for the several quantities. These recommended values and uncertainty ranges should be useful for many purposes (e.g., estimation of rates in the ambient atmosphere) and should, additionally, serve as a point of departure for subsequent experiments that would more precisely define these quantities.

Table 26. Recommended Values and Uncertainties for Equilibrium and Rate Constants Describing Reactive Dissolution of NO$_2$ and N$_2$O$_4$ in Dilute Aqueous Solution, 20–25°C

Quantity	Minimum	Recommended	Maximum	Units
H_{NO_2}	0.7	1.0	1.3	10^{-2} M atm^{-1}
$H_{N_2O_4}$	0.45	1.0	2	M atm^{-1}
K_{A7}	6	7	9	10^4 M^{-1}
$k_{A1*/4*}$	0.35	0.7	1.0	10^8 M^{-1} s^{-1}
$k_{A4*/1*}$	0.6	1.0	1.6	10^3 s^{-1}

7.2. Reaction [2*/5*]

The quantities pertinent to the kinetics of reaction [2*/5*] for which there are experimental measurements are listed in Table 27. The Henry's law coefficient of NO is well established. The remaining elementary constants in which the measurements may be expressed are H_{NO_2}, $H_{N_2O_3}$, K_{A8}, $k_{A2^*/5^*}$, and $k_{A5^*/2^*}$. As was the case in the discussion of reaction [1*/4*], these quantities are not independent but are related in this case by

$$H_{N_2O_3} = H_{NO_2} K_{A8} (H_{NO} K_{G8}^{-1}) \tag{117}$$

and

$$k_{A5^*/2^*} = k_{A2^*/5^*} K_{A8}^{-1}, \tag{118}$$

where the gas-phase equilibrium constant K_{G8} is also taken as well established. Again for the moment we consider the N_2O_3 and NO + NO_2 experiments separately, returning subsequently to consideration of the entire set of measurements.

Measurements that can be expressed in terms of $H_{N_2O_3}$ and/or $k_{A5^*/2^*}$, displayed in the log $H_{N_2O_3}$–log $k_{A2^*/5^*}$ plane, are shown in Figure 10. Again, assuming accurate data, the lines representing the various measurements should intersect at a point. The departure from that situation indicated in Figure 10 represents inaccuracy in the measurements and/or interpretation. Inspection of Figure 10 suggests that the value of ($H_{N_2O_3}$, $k_{A5^*/2^*}$) obtained from the measurements by Hofmeister and Kohlhaas (1965) is considerably at variance with the remaining data. Earlier we noted potential concern with both this study, as well as that of Corriveau and Pigford (1971) in view of possible interaction with transport and reaction of NO_2 or N_2O_4; the prox-

Table 27. Experimentally Measured Quantities Pertinent to Mixed- and Aqueous-Phase Reactions [2] and [5]

Measured Quantity	Method	Data Source
1. $H_{N_2O_3}$	Thermochemical cycle ($K_{A5'}$)	Schwartz and White (1981)
2. $H_{N_2O_3} k_{A5^*/2^*} (\equiv k_{M5^*/2^*})$	Isotope exchange, diazotization	Table 9
3. $H_{N_2O_3} k_{A5^*/2^*}^{1/2}$	Direct contact, penetration theory	Table 23
4. $k_{A5^*/2^*}$	Aqueous pulse radiolysis	Table 13
5. H_{NO_2}	Review	Table 26
6. $H_{NO_2} k_{A2^*/5^*} (\equiv k_{M2^*/5^*}/H_{NO})$	Isotope exchange, diazotization	Table 9
7. $H_{NO_2}^{3/2} k_{A2^*/5^*}$	Direct contact, penetration theory	Table 24

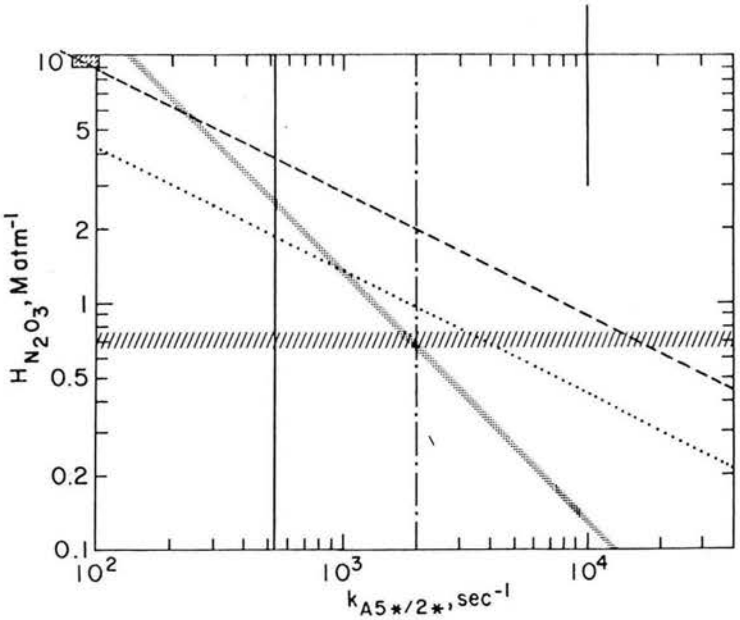

Figure 10. Summary plot of data on reactive dissolution of N_2O_3, displayed in log $H_{N_2O_3}$ –log $k_{A5*/2*}$ plane. ▨, $H_{N_2O_3}$ evaluated from data of Markovits et al. (1981); ▒, $H_{N_2O_3}k_{A5*/2*}$ inferred from diazotization and isotope exchange kinetics; ———— , and -·-·-, $k_{A5*/2*}$ measured in pulse radiolysis (Grätzel et al., 1970) and flash photolysis (Treinin and Hayon, 1970), respectively; ……. and ----, $H_{N_2O_3}k^{1/2}_{A5*/2*}$, measured by direct contact (Corriveau and Pigford, 1971; Hofmeister and Kohlhaas, 1965, respectively); ▨, region of ($H_{N_2O_3}$, $k_{A5*/2*}$) inferred from Hofmeister and Kohlhaas (1965). All measurements at or corrected to 25°C except for Grätzel el al. (1970), 20°C.

imity of the line representing the data of Corriveau and Pigford to the region of intersection of the remaining data may well be fortuitous. We note as well the factor of 4 discrepancy between the values of $k_{A5*/2*}$ reported by Grätzel et al. (1970) and Treinin and Hayon (1970); as noted in Section 5.4, neither measurement was taken over a sufficiently wide range of conditions as to command great confidence. Thus the region of intersection indicated in Figure 10 cannot be considered as setting very tight bounds on $k_{A5*/2*}$ or $H_{N_2O_3}$. A range of (0.4–3) × 10^3 s^{-1} for $k_{A5*/2*}$ and 0.6–3 M atm^{-1} for $H_{N_2O_3}$ would appear to be suggested.

We now consider measurements expressible in terms of $k_{A2*/5*}$ and/or H_{NO_2} (Figure 11). Here the band for H_{NO_2} represents the recommended range for that quantity presented in Table 26. The paucity of data precludes any extended discussion. However, it may be noted that the measurements of $H^{3/2}_{NO_2}k_{A2*/5*}$ [derived from the reinterpretation of the data of Komiyama and Inoue (1980)] suggest a value of $k_{A2*/5*}$ in excess of 10^{10} M^{-1} s^{-1}, i.e., unrealistically high.

We now consider both the N_2O_3 and the NO + NO_2 data simultaneously, as may be effected by superimposing Figures 10 and 11. Here the constraint

$$H_{N_2O_3}k_{A5*/2*} = H_{NO_2}k_{A2*/5*}(H_{NO}K^{-1}_{G8}) \qquad (119)$$

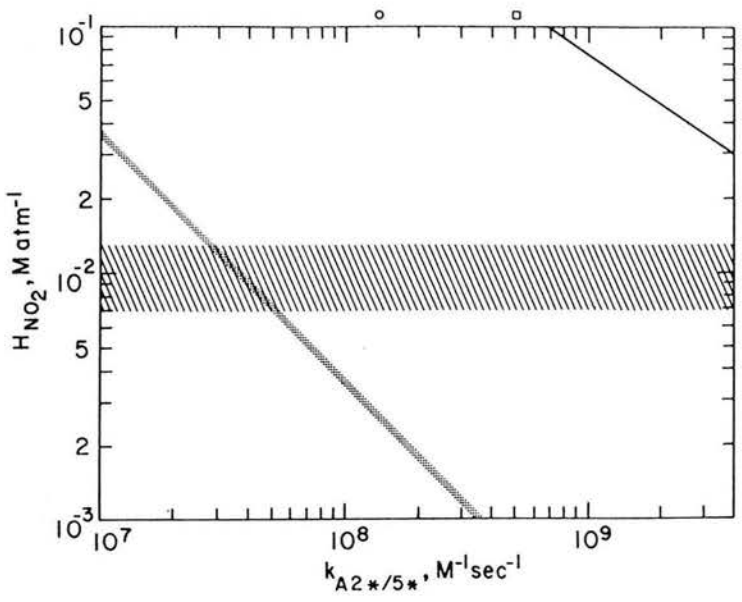

Figure 11. Summary plot of data on simultaneous reactive dissolution of NO and NO_2, displayed in log H_{NO_2}–log $k_{A2*/5*}$ plane. ▨, H_{NO_2}, recommended value and uncertainty (Table 26); ▒, $H_{NO_2}k_{A2*/5*}$ inferred from diazotization and isotope exchange kinetics; ————, $H^{3/2}_{NO_2}k_{A2*/5*}$ as inferred from measurements by Komiyama and Inoue (1980), 15°C. Points at top of diagram indicate measurements of K_{A8} when this diagram is used in conjunction with Figure 10; see text. ○, Grätzel et al. (1970), 20°C; □, Treinin and Hayon (1970). All data for 25°C except as indicated.

obtained from (117) and (118) requires superposition of the bands representing $H_{NO_2}k_{A2*/5*}$ and $H_{N_2O_3}k_{A5*/2*}$, with relative translation permitted only parallel to a line of slope -1. For any given relative position of Figures 10 and 11, the value of K_{A8} may be read as the ratio of the two abscissa scales. Also indicated by the device at the top of Figures 10 and 11 are the values of K_{A8} determined by Grätzel et al. (1970) and by Treinin and Hayon (1970).

From the range of values of the several elementary constants obtained in the superposition of Figures 10 and 11 we have selected a recommended set of these quantities and estimated uncertainties, where the uncertainties encompass the measurements shown in Figures 10 and 11 (with the exception of the value for $H^{3/2}_{NO_2}k_{A2*/5*}$). In this process we have employed the value and uncertainties for H_{NO_2} from Table 26 without additional refinement. The recommended values and uncertainties are given in Table 28.

7.3. Temperature Dependence

As noted above, the temperature dependence of the several experimentally measured quantities of describing the rate of uptake or reaction of the nitrogen oxides in water may be expressed as an activation energy associated

Table 28. Recommended Values and Uncertainties for Equilibrium and Rate Constants Describing Reactive Dissolution of NO + $NO_2(N_2O_3)$ in Dilute Aqueous Solution (20–25°C)

Quantity	Minimum	Recommended	Maximum	Units
H_{NO_2}	0.7	1.0	1.3	10^{-2} M atm^{-1}
$H_{N_2O_3}$	0.6	1.0	2.3	M atm^{-1}
K_{A8}	1.4	3	5	10^4 M^{-1}
$k_{A2*/5*}$	0.1	0.3	1	10^8 M^{-1} s^{-1}
$k_{A5*/2*}$	0.4	1.0	2	10^3 s^{-1}

with the process, evaluated as

$$E_a(q) = -R\frac{d\ln q}{dT^{-1}}.$$

In principle, the activation energies associated with the several experiments can be resolved into the activation energies and enthalpies of reactions of the several elementary processes, entirely analogously to the resolution of the rate quantities themselves into the rate coefficients and equilibrium constants of the elementary reactions. In practice, however, the available data for the temperature dependence of both reaction systems [1*/4*] and [2*/5*] are quite limited, and consequently we are able to carry out this resolution only to a very limited extent.

The available data describing the temperature dependence of reactions [1*/4*] and [2*/5*] are summarized in Table 29. From this table it is seen that only in the case of data pertaining to the temperature dependence of $H_{N_2O_4}$ and $k_{A4*/1*}$ is there sufficient information to allow resolution into the separate terms. This resolution is shown graphically in Figure 12, which may be interpreted entirely analogously to Figure 6, except that the axes are now $E_a[A4^*/1^*]$ and $\Delta H^\circ(H_{N_2O_4})$. The region of intersection of the data represented in this figure is encompassed by the recommended values

Table 29. Temperature Dependence of Experimentally Determined Rate Quantities in Reactions [1*/4*] and [2*/5*]

Quantity	E_a (kcal mol^{-1})	Reference to Text
$k_{M4*/1*} \equiv H_{N_2O_4}k_{A4*/1*}$	+5.9	Section 4.1
$H_{N_2O_4}k^{1/2}_{A4*/1*}$	+0.5 ± 0.7	Section 6.1
$H_{N_2O_4}k^{-1/2}_{A4*/1*}$	−4.3 ± 0.3	Section 6.1
$k_{M1*/4*} \equiv H^2_{NO_2}k_{A1*/4*}$	−7.8	Section 4.1
$k_{M5*/2*} \equiv H_{N_2O_3}k_{A5*/2*}$	+5.4 ± 1.7	Section 4.2
$k_{M2*/5*} \equiv H_{NO}H_{NO_2}k_{A2*/5*}$	−4.1 ± 1.7	Section 4.2

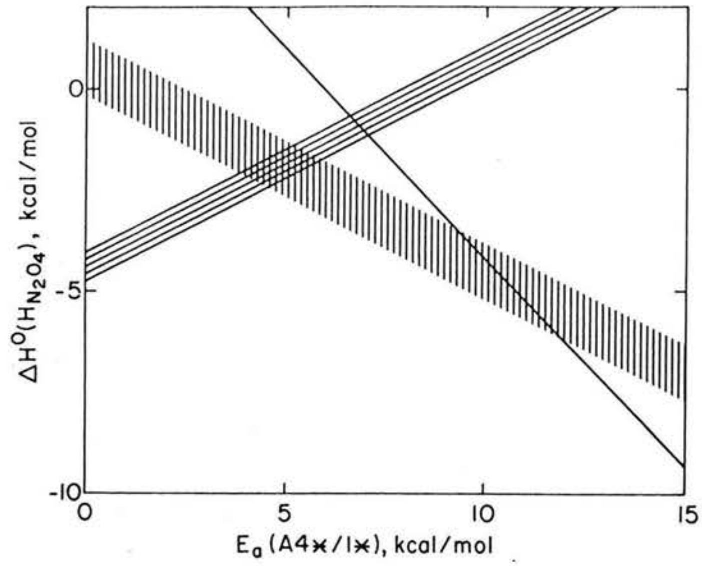

Figure 12. Summary plot of data on temperature dependence of reactive dissolution of N_2O_4 displayed in the $\Delta H°[H_{N_2O_4}]$, $E_a[A1^*/4^*]$ plane. ———, $E_a(H_{N_2O_4}k_{A4^*/1^*})$; ||||||||||||||||||||, $E_a(H_{N_2O_4}k^{1/2}_{A1^*/4^*})$; ////////////////, $E_a(H_{N_2O_4}k^{-1/2}_{A4^*/1^*})$.

$E_a[A^*/1^*] = 7.5 \pm 2.5$ kcal mol^{-1} and $\Delta H°(H_{N_2O_4}) = -(2.5 \pm 1.5)$ kcal mol^{-1}. Insufficient information is available to permit resolution of the remaining temperature dependence data summarized in Table 29 into the corresponding enthalpies of solution and activation energies for the indicated elementary reactions.

7.4. Sources of Error

It is of interest to speculate on the causes for the lack of closer agreement between the several experiments that have been reviewed. Much of the above discussion has focused on appropriateness of the mixed-phase reaction model employed to describe the system under examination and on correct identification of the transported species, NO_2 or N_2O_4, and to the extent possible corrections have been made or the studies excluded from the final comparisons. Less easily addressed are possible systematic errors, such as in calibration of mass-transport properties and extinction coefficients. Even more difficult to address are considerations of reagent purity, but it must be emphasized that both neat NO_2 (N_2O_4) and dilute NO_2 in N_2 or air as supplied by manufacturers are frequently contaminated with lower oxides and/or with oxyacids and further that NO_2 may be inadvertently contaminated by conventional gas-handling apparatus. The effects of contaminants, including contaminants in water, would be most pronounced in studies at low NO_2 partial pressures, and as noted in Section 8, there have been a number of studies in which these effects are indicated. We would thus urge extreme attention to purity of reagents in any future studies.

8. OTHER STUDIES AND SOLUTE EFFECTS

In this section we consider other studies examining the rate of uptake of nitrogen oxides by aqueous solution, including studies of the effects of dissolved solutes. In some of these studies, as reviewed in Section 8.1, the phase-mixing conditions were not sufficiently well characterized to allow quantitative interpretation in terms of Henry's law coefficients and kinetic rate constants. Nonetheless, it remains possible to gain insight into the processes taking place in these experiments, and, as we shall see, it would appear that reaction of NO_2 with dissolved impurities may influence the observed rate of uptake.

The interaction of NO and NO_2 with dissolved solutes in aqueous solution has received comparatively little study, much of that qualitative, although in some cases it is possible to derive quantitative kinetic information making use of solubility coefficients obtained above. Such interactions are of potential importance not only in interpreting laboratory studies, but also in describing reactions of NO and NO_2 with dissolved materials present in atmospheric and surface liquid water. A further application has included development of efficient means of sampling nitrogen oxides for chemical analysis, although interest in such methods has somewhat waned with the advent of chemiluminescent methods for the determination of these gases. An additional application is the search for possible wet scrubbers for removal of nitrogen oxides from flue gases (Counce, 1980; Faucett et al., 1978).

8.1. NO_2 + Liquid Water

Measurements of the fraction of NO_2 taken up by bubbling NO_2 in air through water (NO_2 partial pressures 3×10^{-7} to 0.12 atm) were reported by Borok (1960). At higher NO_2 partial pressures the fractional absorption of NO_2 decreased with decreasing partial pressures, as expected for uptake by the second-order reaction [A1*/4*]. However, for partial pressures below 2.5×10^{-6} atm, the fraction absorbed was found to increase with decreasing partial pressure. These results, if correct, would imply a mechanism for removal of $NO_2(g)$ other than reaction [A1*/4*], although insufficient information is available for identification of this mechanism. Subsequent work, such as that by Lee and Schwartz (1981b), has given no indication of any departure from a second-order rate law for the uptake of NO_2 by water, thus suggesting the possibility that the increased efficiency for removal of NO_2 at low partial pressures found by Borok may have been due to contamination by reactive impurities.

The experimental data of Borok (1960) were subsequently interpreted to yield a "Henry's law" coefficient for NO_2 (Hermann and Matteson, 1980; Matteson, 1979) evaluated as the ratio of the dissolved nitrite concentration in the bubbler solution to the partial pressure of NO_2 in the gas that was passed through the bubbler. The value obtained, $H_{NO_2} = 0.55$ M atm^{-1} (Matteson, 1981), is some fiftyfold greater than that which has been inferred in the present analysis. This high value for H_{NO_2} undoubtedly reflects the reactive solubility of NO_2 (by reaction [A1*/4*] and/or with impurities) rather than the purely physical solubility that is represented by Henry's law.

The experimental studies by Herrmann and Matteson (1980), in which suspended water droplets (3-mm diameter) were exposed to a flowing mixture of NO_2 in nitrogen [$p_{NO_2} = (1–3) \times 10^{-4}$ atm] might also be mentioned here. The water drops were removed from the flowing gas stream after exposures of 5–30 s and subsequently analyzed for NO_2^-. Experimental results were presented as the average aqueous-phase nitrite concentration (in the collected drops) as a function of the duration of exposure of the drop to the flowing gas mixture for various values of the water vapor supersaturation ratio (ratio of the water vapor pressure to the equilibrium water vapor pressure of the suspended drop at the temperature of the liquid). At longer exposure times ($\gtrsim 30$ s) the aqueous-phase nitrite concentration approached a constant "saturation" value. The authors attribute this "saturation" to a solubility equilibrium between $NO_2(g)$ and nitrite ion NO_2^-, which they proceed to address in terms of their value (0.55 M atm^{-1}) for the "Henry's law" coefficient for NO_2. It must be emphasized that the equilibrium in these studies, if any, between $NO_2(g)$ and NO_2^- is *not* the Henry's law equilibrium, which strictly denotes the equilibrium between gaseous NO_2 and the physically dissolved material, since NO_2^- can be formed from NO_2 only by chemical reaction. It is further readily established that the material analyzed as nitrite cannot have been present as physically dissolved NO_2; for $p_{NO_2} = 10^{-4}$ atm, the characteristic time describing the removal of $NO_2(aq)$ by reaction [A1*/4*], evaluated as $(2H_{NO_2}p_{NO_2}k_{A1^*/4^*})^{-1}$, would be approximately 5×10^{-3} s, i.e., orders of magnitude less than the duration of exposure of the drops to $NO_2(g)$. Hence the time dependence of the approach to "saturation" cannot have been due simply to the kinetics of mass transport and physical dissolution (as assumed by Herrmann and Matteson) but must reflect the reactive dissolution as well. It is possible also to address whether the "saturation" reported by Herrmann and Matteson represents achievement of chemical equilibrium in this system. An approach to this is to consider the characteristic time of reaching equilibrium for reaction [M1′]:

$$2NO_2(g) \overset{w}{=} HNO_2(aq) + H^+ + NO_3^- \qquad [M1']$$

evaluated as

$$\tau^{(1')} = \frac{[NO_3^-]_{eq}}{H^2_{NO_2}k_{A1^*/4^*}p^2_{NO_2}}. \qquad (120)$$

Here it is assumed that the only reaction taking place is [M1′] and further that the reaction takes place under phase-mixed conditions, i.e., aqueous phase saturated in NO_2. In fact, neither assumption would be expected to hold for the NO_2 partial pressures and drop sizes employed, and consequently (120) would underestimate the actual characteristic time of achieving equilibrium. Even so, the values of $\tau^{(1')}$ obtained by (120), (3.9–17) × 10^2 s, substantially exceed the contact times characteristic of the approach to "saturation." Consequently, it would appear that the "saturation" reported by Herrmann and Matteson (1980) is also not due to chemical equilibrium. In principle, it would appear possible to interpret these measurements in terms of the pertinent mass-transport rates, reaction kinetics, and chemical equilibria. Unfortunately, however, since the concentration measurements are presented only as the ratio to an unspecified "saturation" concentration, such interpretation cannot be given.

An interesting experimental study that deserves mention is that by Beilke (1970), who addressed the "washout" of NO_2 (as well as SO_2 and CO_2) by recirculating artificial "rain" falling through a chamber containing the gas (initial concentration 3×10^{-8} atm). Exposure times extended up to 30 min for rainfall rates ranging from 1 to 50 mm h^{-1}. Experimental results were expressed in terms of a washout coefficient λ (units: s^{-1}) describing the exponential decrease (with time) of the concentration of the gas remaining in the chamber. Values of λ varied with rainfall rate and mean drop diameter; the latter dependence is indicative of mass-transport restriction to the rate of uptake of the gas by the falling droplets. In the case of NO_2 there was some indication of a nonexponential decay, i.e., values of λ decreased during the experiment. A typical value of λ was $1.6 \times 10^{-4}\ s^{-1}$, for rainfall rate $I = 2.8 \times 10^{-7}\ m\ s^{-1}$ (1 mm h^{-1}), mean drop diameter of 0.85 mm, and temperature 20°C.

It is instructive to compare the observed value of the washout coefficient to values that might be expected from equilibrium or kinetic considerations. If it is assumed that the decrease in gas-phase concentration is due entirely to loss as dissolved material in the artificial rain, it is readily established that the washout coefficient may be evaluated in terms of the concentration of the dissolved material as

$$\lambda = \frac{\overline{C}I\mathbf{R}T}{pZ}$$

where λ = washout coefficient (s^{-1})
$\overline{C}$ = average aqueous-phase concentration (M)
I = rainfall rate ($m\ s^{-1}$)
$\mathbf{R}$ = universal gas constant (liter atm $mol^{-1}\ K^{-1}$)
T = absolute temperature (K)
p = gas-phase partial pressure (atm)
Z = chamber height (m)

For dissolution of NO_2 by Henry's law only, $\overline{C} = H_{NO_2}p_{NO_2}$, and $\lambda = H_{NO_2}I\mathbf{R}T/Z$. For the conditions given above λ is evaluated to be $7 \times 10^{-8}\ s^{-1}$, where we have taken the chamber height as 1 m (cf. chamber volume

1 m^3). Since this value is orders of magnitude lower than the observed washout coefficient at this partial pressure (1.6×10^{-4} s^{-1}), substantial reactive dissolution of NO_2 is indicated. It is possible also to evaluate λ under the assumption that reaction [A1] proceeds to equilibrium rapidly on the time scale of the exposure of the drops to the gas. In this case $\bar{C}$ = $[NO_3^-] + [NO_2^-] + [HNO_2] \approx 1 \times 10^{-3}$ M and $\lambda \approx 0.2$ s^{-1}, orders of magnitude greater than the observed rate. This comparison both indicates the high potential washout rate if this equilibrium were to be reached under the conditions of the experiment and at the same time establishes that the system is far from equilibrium.

Finally, it is possible to evaluate the washout rate that might be expected if the uptake rate were controlled by reaction kinetics. Here we need to estimate the time t that the drops are exposed to the gas in the chamber. This quantity may be evaluated assuming (as suggested by Beilke) ballistic trajectories for the drops; again for assumed $Z = 1$ m, $t \approx 1$ s. The washout rate λ is then evaluated as $\lambda = 2R_{1*/4*}\ \mathbb{R}T\ t/pZ$; for $R_{1*/4*}$ evaluated as $2H^2_{NO_2}k_{A1*/4*}p^2_{NO_2}$ (i.e., no mass-transport limitation) $\lambda \approx 4 \times 10^{-9}$ s^{-1}, orders of magnitude less than the observed value. The fact that the observed value so greatly exceeds the value calculated for uptake only by reaction [A1*/4*] establishes that there is a mechanism of uptake other than this reaction. Such a mechanism might be the reaction of NO_2 with dissolved impurities, which would be consistent with the observation, noted above, that λ decreased with time during an experimental run, perhaps reflecting depletion of the impurity reagent species.

Recently Ohta et al. (1981) reported results of measurements of NO_2 partial pressures in effluent gas (initially containing NO_2 in the range 6×10^{-7} to 10^{-4} atm; carrier gas unspecified) bubbled through distilled, deionized water. Within 20 min the partial pressure of NO_2 in the effluent gas was found to reach a constant value; the relationship between the effluent partial pressure and the final composition of the solution was reported as

$$[H^+][NO_3^-][HNO_2] = K'_{obs}p^4_{NO_2}, \qquad (121)$$

where K'_{obs} has the value 2.4×10^3 M^3 atm^{-4} and the expression is valid for $6 \times 10^{-7}\ \text{atm} \leq p_{NO_2} \leq 4 \times 10^{-5}$ atm for 16–17°C. Final concentrations of aqueous species were unspecified but evidently were in the range 1–40 $\times\ 10^{-6}$ M over the indicated partial pressure range. We note that by the acid dissociation equilibrium for nitrous acid, Eq. (121) may be written in terms of the dissociated species as

$$[H^+]^2[NO_3^-][NO_2^-] = K_{obs}p^4_{NO_2} \qquad (122)$$

where $K_{obs} = K'_{obs}K_{12} = 1.2$ and where we have made use of the value $K_{12} = 5.1 \times 10^{-4}$ M employed by Ohta et al. The observed relationship (121) between solution composition and NO_2 partial pressure was attributed by the authors to establishment of equilibrium [M1′] in their system. However, the apparent value for $K_{M1'}$ was much less than that given by other investigators (Pick, 1920; Schwartz and White, 1981) and depended as well on the second power of NO_2 partial pressure.

We have severe misgivings about this interpretation of measurements of Ohta et al. First, we note that there is no theoretical justification for a dependence of an equilibrium constant on the second (or any) power of one of the reagent partial pressures; alternatively, an observed relationship such as (121) should be reflective of the reaction stoichiometry. Moreover, the authors fail to demonstrate that chemical equilibrium is in fact achieved; certainly the evidence adduced, namely, that the effluent NO_2 partial pressure has become invariant, can in no way be taken as indicative of achievement of chemical equilibrium. Rather, this condition would be expected generally with such an experimental arrangement for kinetic and/or mass-transport-controlled reactive uptake, with the effluent partial pressure governed by the amount of reagent gas taken up by the solution during the contact time.

It is of interest to speculate on possible reasons that might account for Ohta et al.'s observations. Denoting the concentration $[H^+] = C$, we find that from the stoichiometry of reaction [M1], Eq. (122) gives for the amount of material taken up by solution

$$C = (4K_{obs})^{1/4} p_{NO_2}, \tag{123}$$

i.e., proportional to the first power of the partial pressure of NO_2. We note that for convective-controlled uptake

$$\frac{dC}{dt} = k_L a H_{NO_2} p_{NO_2},$$

or for a contact time t,

$$C = k_L a H_{NO_2} p_{NO_2} t. \tag{124}$$

Assuming that in all cases a similar contact time was employed (the authors indicate that "equilibrium" was attained within 20 min), we may identify (123) and (124), obtaining

$$k_L a = \frac{(4K_{obs})^{1/4}}{H_{NO_2} t}.$$

For $t = 20$ min and $H_{NO_2} = 1 \times 10^{-2}$ M atm^{-1}, we obtain an estimate $k_L a \approx 0.1\ s^{-1}$; such a value is not unreasonable for a laboratory bubbler and supports the suggestion that uptake in this system was convectively controlled. Further examination of this suggestion is obtained by comparison of τ_r evaluated for the partial pressures indicated, with estimates of τ_d and of τ_m^2/τ_d (see Table 21). These comparisons indicate that both criteria for convective-controlled uptake [Eqs. (97) and (98)] are fulfilled, thus lending further support to this interpretation of these results. Unfortunately, further analysis cannot be undertaken because of the lack of data in the original paper. However, it seems indisputable that the data do not support the authors' claim of chemical equilibrium.

8.2. NO_2 + Aqueous Solution

Oxidation of dissolved NO_2 by O_2 is a potentially important atmospheric reaction in view of the high partial pressure of O_2 and the large negative free-energy change for this reaction. Although reaction of gaseous NO_2 and O_2 is not reported, aqueous-phase reaction must be considered because of possible solvent stabilization of intermediate species. Lee and Schwartz (1981a) have examined, by means of a bubbler reactor (cf. Lee and Schwartz, 1981b), the rate of formation of ionic products when NO_2 is reacted with water alternately by use of N_2 and air as carrier gas. Within the sensitivity of the measurements (~8%), no change in reaction rate was observed for NO_2 partial pressures of as low as 5×10^{-8} atm. At that value of p_{NO_2} for the phase-mixing conditions employed, the measured value of $R_{A1^*/4^*}$ was 1.1×10^{-11} M s^{-1} (22°C). Hence an upper limit to the rate of aqueous-phase reaction of NO_2 with dissolved O_2 (in equilibrium with air) expressed as a first-order mixed-phase rate constant may be given as $0.08 \times R_{A1^*/4^*}/p_{NO_2} \approx 2 \times 10^{-5}$ M atm^{-1} s^{-1}.

Several studies have addressed the influence of acid, base, or other dissolved species on the rate of uptake of N_2O_4 by water as measured in the fast-reaction regime. Generally these studies have indicated that such interaction is slight. Thus Kameoka and Pigford (1977) reported that the rate of uptake of N_2O_4, $q \equiv (J_{N_2O_4}/p_{N_2O_4})$ is unchanged for absorption into water or 0.05 M H_2SO_4; for absorption into 0.2 M NaOH, an increase in q of 7% was reported. Hoftyzer and Kwanten (1972) reported a slight decrease of q with increasing ionic strength for absorption into solutions (concentration range unspecified) of NaOH, Na_2SO_4, NaCl, HNO_3, K_2SO_4, and $Al_2(SO_4)_3$ but again no specific interaction with any of these substances. It may be noted that at higher concentrations of NaOH (1–5 M) the rate of uptake has been found to decrease (Chilton and Knell, 1972), apparently because of the increased viscosity and consequent diminished rate of diffusion in the absorbing solution (Kameoka and Pigford, 1977).

An enhancement of the rate of N_2O_4 uptake was reported (Chilton and Knell, 1972) for a solution of potassium iodide (1 M). This enhanced rate of uptake presumably reflects the role of $NO_2(N_2O_4)$ in oxidizing the iodide ion (Szabó et al., 1956).

$$NO_2 + I^- \rightarrow NO_2^- + \tfrac{1}{2}I_2$$

The influence of dissolved ionic species has also been examined at lower NO_2 partial pressures, at which NO_2 rather than N_2O_4 would be the predominant transported species. The rate of uptake of NO_2 by NaOH solution (0.063 M) was reported to be the same as that into water (Sada et al., 1979) for $p_{NO_2} = (3\text{–}8) \times 10^{-4}$ atm. We note also that the study by Komiyama and Inoue (1980) (p_{NO_2} as low as 1×10^{-5} atm) employed 0.01 M NaOH. Similarly, Takeuchi et al. (1977) found the rate of uptake into urea solutions (0.1 and 1 M) unchanged from that into water. However, substantial enhancement of the rate of uptake was reported (Takeuchi et al., 1977) for solutions of oxidizing (MnO_4^-) or reducing species (I^-, SO_3^{2-}, HSO_3^-).

Although reaction of $NO_2(N_2O_4)$ with dissolved S(IV) has been examined in several studies (Nash, 1979; Sato et al., 1979; Takeuchi, 1977) these reactions are not yet well understood. Evidently NO_2 may either act as an oxidizing agent (Nash, 1979) or interact more specifically with the dissolved S(IV) (Sato et al., 1979). The latter authors report, in addition to formation of sulfate and dithionate $S_2O_6^{2-}$, the formation of hydroxylamine disulfonate $HON(SO_3)_2^{2-}$. The sequence of reactions leading to these products is not understood. In particular, possible reactions of nitrite (or nitrous acid) may be implicated; in this connection we note that hydroxylamine disulfonate is the principal product of the reaction of nitrite with sulfite (Oblath et al., 1981; Seel and Knorre, 1961).

Quantitative information on the rate of reaction of NO_2 with dissolved S(IV) is available from the study by Takeuchi et al. (1977). In that study the rate of NO_2 uptake was measured with a bubbler reactor as a function of p_{NO_2} (2×10^{-5} to 2×10^{-4} atm) and S(IV) concentration. The apparent reaction order with respect to p_{NO_2} was found to decrease with increasing concentration of SO_3^{2-} or HSO_3^-, approaching unity at concentrations of 0.01 and 0.2 M, respectively, The rates of these reactions were interpreted according to the reaction

$$NO_2(aq) + S(IV)(aq) \rightarrow \text{products} \qquad [A21]$$

taking place in the diffusion-controlled regime. (The products of reaction were not determined.) For the rate of [A21] much greater than that of [A1*/4*] the uptake of NO_2 is pseudo-first-order. For NO_2, the predominant aqueous-phase N(IV) species, the rate of uptake of NO_2 per unit interfacial area is given by (15) by setting $m = 1$ and $k_A = k_{A21}[S(IV)]$, i.e.,

$$J_{NO_2} = H_{NO_2}(k_{A21}D_{NO_2})^{1/2}[S(IV)]^{1/2}p_{NO_2}.$$

The results of these studies are summarized in Table 30. These studies would appear to establish a fairly fast reaction of dissolved NO_2 with sulfite and bisulfite ions: for $H_{NO_2} \approx 1 \times 10^{-2}$ M atm^{-1} (Table 26), $k_{A21} \approx 1 \times 10^7$ and 3×10^5 M^{-1} s^{-1}, respectively. Again it should be noted that there may be some inaccuracy in the rate constant values given because of the fraction of dissolved N(IV) present as N_2O_4 in equilibrium with NO_2 in the partial pressure range investigated (4×10^{-5} to 2×10^{-4} atm), viz., 5–30%.

Quantitative information on the kinetics of the reaction of NO_2 with ferrous ion (Fe^{2+}) may be obtained, albeit indirectly, from the kinetics of the oxidation of Fe^{2+} by nitrous acid (Abel et al., 1936). In that study the

Table 30. Measurements of Rate of Reaction of NO_2 with SO_3^{2-} and HSO_3^-[a]

Reaction	$H_{NO_2}(k_{A21}D_{NO_2})^{1/2}$ (kmol m^{-2} s^{-1} atm^{-1} $M^{-1/2}$)	$H_{NO_2}k_{A21}^{1/2}$[b] ($M^{1/2}$ atm^{-1} $s^{-1/2}$)	k_{A21}[c] M^{-1} s^{-1}
$NO_2(aq) + SO_3^{2-} \rightarrow$ products	1.55(−3)	34.6	1(7)
$NO_2(aq) + HSO_3^- \rightarrow$ products	2.33(−4)	5.22	3(5)

[a] Data of Takeuchi et al. (1977) for 25°C.

[b] Evaluated for $D_{NO_2} = 2.00 \times 10^{-9}$ m^2 s^{-1}.

[c] Evaluated for $H_{NO_2} = 1 \times 10^{-2}$ M atm^{-1}.

observed rate law was

$$\frac{d[\mathrm{Fe}^{3+}]}{dt} = k_{\mathrm{obs}} \frac{[\mathrm{Fe}^{2+}][\mathrm{HNO}_2]^2}{p_{\mathrm{NO}}} . \tag{125}$$

This rate law was interpreted according to the following mechanism, which is similar to that inferred for nitrous acid decomposition (Abel and Schmid, 1928c):

$$\begin{array}{lll}
2\mathrm{HNO}_2 \overset{w}{=} \mathrm{NO(aq)} + \mathrm{NO}_2\mathrm{(aq)} & \text{(rapid equilibrium)} & [-\mathrm{A}2'] \\
\mathrm{NO}_2\mathrm{(aq)} + \mathrm{Fe}^{2+} \rightarrow \mathrm{NO}_2^- + \mathrm{Fe}^{3+} & \text{(slow, rate determining)} & [\mathrm{A}22] \\
\mathrm{NO}_2^- + \mathrm{H}^+ = \mathrm{HNO}_2 & \text{(rapid equilibrium)} & [-\mathrm{I}2] \\
\mathrm{NO(aq)} = \mathrm{NO(g)} & \text{(rapid equilibrium)} & [-\mathrm{H}_{\mathrm{NO}}] \\
\hline
\mathrm{Fe}^{2+} + \mathrm{HNO}_2 + \mathrm{H}^+ = \mathrm{Fe}^{3+} + \mathrm{NO(g)} + \mathrm{H}_2\mathrm{O} & & [\mathrm{A}23]
\end{array}$$

Equilibria [A2′] and $[\mathrm{H}_{\mathrm{NO}}]$ maintain an aqueous-phase NO_2 concentration

$$[\mathrm{NO}_2\mathrm{(aq)}] = \frac{1}{K_{\mathrm{A}2'}\mathrm{H}_{\mathrm{NO}}} \frac{[\mathrm{HNO}_2]^2}{p_{\mathrm{NO}}} . \tag{126}$$

Hence

$$\begin{aligned} R_{\mathrm{A}23} = \frac{d[\mathrm{Fe}^{3+}]}{dt} &= k_{\mathrm{A}22}[\mathrm{Fe}^{2+}][\mathrm{NO}_2\mathrm{(aq)}] \\ &= \frac{k_{\mathrm{A}22}}{K_{\mathrm{A}2'}\mathrm{H}_{\mathrm{NO}}} \frac{[\mathrm{Fe}^{2+}][\mathrm{HNO}_2]^2}{p_{\mathrm{NO}}} . \end{aligned} \tag{127}$$

Comparison of (127) with (125) gives

$$\begin{aligned} k_{\mathrm{A}22} &= k_{\mathrm{obs}} K_{\mathrm{A}2'} \mathrm{H}_{\mathrm{NO}} , \\ &= k_{\mathrm{obs}} \frac{K_{\mathrm{M}2'}}{\mathrm{H}_{\mathrm{NO}_2}} , \end{aligned} \tag{128}$$

where we have used Eq. (48). From the value $k_{\mathrm{obs}} = 4.0\ \mathrm{M}^{-2}\ \mathrm{atm}^{-1}\ \mathrm{s}^{-1}$ at 25°C obtained by Abel et al. (1936) we obtain $k_{\mathrm{A}22} = 5.0 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, where we have employed the values $K_{\mathrm{M}2'} = 1.26 \times 10^2\ \mathrm{M}^2\ \mathrm{atm}^{-2}$ (Table 2) and $\mathrm{H}_{\mathrm{NO}_2} = 1 \times 10^{-2}\ \mathrm{M}\ \mathrm{atm}^{-1}$ (Table 26).

In addition to the studies noted above, a number of studies have qualitatively addressed the interaction of NO_2 with dissolved aqueous species by examining the fraction of NO_2 absorbed by passing a dilute gaseous mixture of NO_2 through a bubbler containing the solution of interest. The uptake of NO_2 is particularly enhanced by reducing species I^-, HSO_3^-, SO_3^{2-}, S^{2-}, $S_2O_3{}^{2-}$, $S_2O_4{}^{2-}$, Sn^{2+}, Cu^+, Fe^{2+}, $Fe(CN)_6^{4-}$ and other ferrous complexes, and AsO_2^- (Christie et al., 1970; Kobayashi et al., 1977, 1980; Nash, 1970a). Addition of arsenite ion (AsO_2^-) to 0.1 *M* NaOH has been shown to substantially enhance NO_2 absorption efficiency (Christie et al., 1970; Margeson et al., 1977; Merryman et al., 1973; Nash, 1970a), with the absorbed NO_2 reduced with high yield to nitrite ion (Christie et al., 1970). In the case of the other species listed above, analysis of nitrogen products does not appear to have been conducted, although evolution of NO was noted for a number of these species (Kobayashi et al., 1977). Kobayashi et al. have pointed out a rough correlation between the efficiency of NO_2 removal by a solution of a given species and the redox potential of that species: the better the reducing agent, the more efficient the removal.

Of the several studies cited, that of Nash (1970a) merits further discussion. First, NO_2 (ca. 3 ppm) was bubbled through the solution under examination. In the absence of a reactive solute the fraction of NO_2 absorbed under the conditions employed was low (water and 0.05 M sulfuric acid, 7%; 0.1 M alkali, 14%). The concentration of the reactive solute was then adjusted until the fraction of NO_2 removed was 50 or 90%, and the corresponding solute concentration was reported. Although the details of mass transport and reaction are not known, this procedure would appear to permit evaluation of relative rate constants (rate constant ratios) since for a fixed fraction of NO_2 absorbed, similar spatial profiles of NO_2 concentration would be expected for different solutes. Nash's results are shown in Table 31. Also shown are the rate constants for reaction of $NO_2(aq)$ with the various solutes X, evaluated relative to the rate constant for reaction of NO_2 with sulfite ion (1×10^7 M^{-1} s^{-1}) inferred above from the work by Takeuchi et al. (1977), as

$$k_{NO_2-X} = k_{A21} \frac{C_{SO_3^{2-}}}{C_X} \tag{129}$$

Several of the rate constants evaluated in this way are seen to be quite large, approaching the diffusion controlled encounter rate constant (ca. 5×10^9 M^{-1} s^{-1}) (Benson, 1960). Reaction products were not identified, although Nash noted the development of a yellow color on reaction of NO_2 with phenoxide ion and aromatic bases, indicating formation of a nitro compound. Reaction of NO_2 with dissolved organics and organic amines in aqueous solution has been reported also by Kobayashi et al. (1977), Levaggi et al. (1972), and Challis and Kyrtopoulos (1976, 1977).

Interaction of NO_2 with dissolved oxidants has received relatively little study. Reaction is reported with MnO_4^- (Takeuchi et al., 1977), XeO_3, and OsO_4 (Rigdon and Crawford, 1971). No analysis of products has been reported. Aqueous-phase oxidation of NO_2 to NO_3^- by hydrogen peroxide has been employed as the basis of a method for determination of gas-phase NO_2. Martens et al. (1973) report a high conversion of NO_2 (ca. 2×10^{-4} atm) to NO_3^- in 2 h by a solution of 1 M H_2O_2. The mechanism and kinetics apparently have not been studied. The overall reaction may well proceed by [A1*/4*] followed by oxidation of nitrite ion (Anbar and Taube, 1954). In view of the potential atmospheric importance of direct reaction of NO_2

Table 31. Relative Reactivities of Various Solutes with $NO_2(aq)$, Based on Data of Nash (1970a)

Solute, X	C_{50}[a] (mM)	C_{90}[a] (mM)	k_{NO_2-X} ($M^{-1}\,s^{-1}$)
Neutral solutions			
Azide, N_3^-	1800	—[c]	7.2(4)
Thiosulfate, $S_2O_3^{2-}$	1250	—	1.0(5)
Sulfanilate	1000	—	1.3(5)
Iodide, I^-	125	1200	1.1(6)
Aniline	45	—	2.9(6)
Sulfite, SO_3^{2-}	13	150	1(7)
Ferrocyanide, $Fe(CN)_6^{4-}$	13	150	1.0(7)
p-Anisidine	3	—	4.3(7)
Alkaline solution, pH 13			
Barbituric acid	30	—	4.3(6)
Phenol	5	100	[1.5–2.6](7)
Arsenite	3	100	[1.5–4.3](7)
Acetylacetone	4	40	3.5(7)
p-Cresol	0.7	8	1.9(8)
Thymol	0.1	1	1.4(9)
o-Methoxyphenol	0.07	0.7	2.0(9)

[a] Concentrations at which fractional removal of NO_2 was 50% or 90%, respectively.

[b] Evaluated relative to value for sulfite, $k_{NO_2-SO_3^{2-}} = 1 \times 10^7\ M^{-1}\,s^{-1}$, derived from data of Takeuchi (1977).

[c] Blanks indicate that 90% removal of NO_2 was not attained for saturated solution.

with H_2O_2 and also of the large negative free-energy change of reaction, the kinetics of this process merit further investigation.

8.3. Aqueous Methods for Chemical Analysis of NO_2

A large number of studies have addressed the removal of NO_2 from a gas mixture by bubbling through aqueous solution as a means of sampling NO_2 from ambient air or from flue gases (Driscoll, 1974) for the purpose of chemical analysis. By and large, these methods have been plagued with low and variable efficiency of sampling and variable and nonstoichiometric product yield. The present discussion briefly examines these methods, with particular attention to aqueous-phase reactions of NO_2.

A variety of aqueous solutions have been employed as absorber solutions. Methods initially proposed included absorption directly into an acetic acid solution containing diazotization and coupling reagents (Saltzman, 1954) or into sodium hydroxide solution (Jacobs and Hochheiser, 1958). It was subsequently shown that the sodium hydroxide abosrber suffered from low and variable collection efficiency (Christie, 1970; Huygen and Steerman, 1971; Meadows and Stalker, 1966; Merryman et al., 1973; Mulik et al., 1974; Nash, 1970b), and consequently a variety of additives have been employed to enhance this efficiency: arsenite (Christie, 1970; Merryman et al., 1973); guaiacol (*o*-methoxy phenol) (Nash, 1970b); and various amines and/or sulfonates (Huygen and Steerman, 1971; Mulik et al., 1974). With respect to absorption directly into solution of the diazotization and coupling reagents, there is also evidence that the presence of these reagents may affect absorption efficiency. Saltzman (1954) proposed the possibility of direct reaction of NO_2 with sulfanilic acid in addition to reaction [1*/4*]; we note in this context that reaction of NO_2 with sulfanilate anion was shown by Nash (1970a). On the other hand, Huygen (1970) indicates that the reaction occurs with the amine coupling reagent. In this context we also note that evolution of NO has been observed when NO_2 is bubbled through the Saltzman absorber solution (Ellis, 1964; Levaggi et al., 1972).

In addition to considerations of absorber efficiency, there has been extended discussion in the literature addressing the stoichiometry of the reactive dissolution process. If dissolution of NO_2 into aqueous solution were to proceed entirely by reaction [1*/4*],

$$2NO_2(g) + H_2O(l) \rightarrow 2H^+ + NO_2^- + NO_3^-, \qquad [1^*/4^*]$$

then the stoichiometric coefficient (defined here as apparent moles nitrite produced in solution per mole of $NO_2(g)$ absorbed) would be 0.5. In some studies a calibration factor has been reported as moles nitrite formed per mole of $NO_2(g)$ introduced into the bubbler; in this case, if absorption of NO_2 were not complete, the calibration factor so defined would be correspondingly diminished. The choice of nitrite as the referenced anion is a consequence of the analytical method generally employed, which is nominally specific to nitrite ion, viz., acid diazotization of sulfanilic acid followed by coupling reaction to form a diazo dye species having a high extinction coefficient.

The literature regarding the stoichiometric coefficient appropriate for the various analytical methods (and modifications) is also quite extensive and cannot be reviewed here. Suffice it to say that the stoichiometric coefficient is generally higher than the value 0.5 that would be expected for uptake of NO_2 by reaction [1*/4*] only; values reported have ranged from 0.7 to 1 (Buck and Stratmann, 1967; Crecelius and Forwerg, 1970; Huygen and Steerman, 1971; Saltzman, 1954; Scaringelli et al., 1970). Evidently as well, the stoichiometric coefficient may depend on the NO_2 partial pressure, increasing with decreasing NO_2 partial pressure (Buck and Stratmann, 1967; Crecelius and Forwerg, 1970), although the lack of such a dependence has been emphasized by others (e.g., Scaringelli et al., 1970).

It is beyond the scope of the present review to account for all the above observations; nonetheless, it is possible to apply the results of the review of NO_2 aqueous kinetics to gain insight into the processes taking place when NO_2 is sampled by means of an aqueous bubbler. Specifically, we address conditions that must be satisfied for NO_2 to be effectively removed from a gas mixture by aqueous-phase reaction on bubbling the gas through aqueous solution. An upper limit to the amount of NO_2 removed may be evaluated by assuming the liquid volume to be saturated in NO_2 at the incident partial pressure; whether this condition is satisfied depends on the rate of convective mixing compared to that of depletion of aqueous NO_2 by reaction. Under the assumption that the liquid is saturated in NO_2, the rate of reaction of NO_2 is

$$M_{\text{react}} = V_l \mathrm{H}_{\mathrm{NO_2}} p_{\mathrm{NO_2}} k^{(1)} \tag{130}$$

where M_{react} is the amount of NO_2 reacted per unit time (mol s^{-1}), V_l is the liquid volume (liters), and $k^{(1)}$ is the pseudo-first-order rate constant for reaction of dissolved NO_2; for a second-order reaction with rate constant $k^{(2)}$, $k^{(1)}$ would be evaluated as $k^{(2)}$ times the concentration of the second reagent.

The rate of depletion of NO_2 evaluated by (130) is to be compared to the rate at which NO_2 enters the bubbler in the incoming gas mixture, evaluated as

$$M_{\text{enter}} = \frac{p_{\mathrm{NO_2}} F_g}{\mathbf{R}T} \tag{131}$$

where M_{enter} also has units of moles per second, and F_g is the gas flow rate in liters per second.

A necessary condition, which must be satisfied for the scrubber to remove the incident NO_2 with high efficiency, is that M_{react} evaluated by (130) greatly exceed M_{enter}, i.e., that

$$k^{(1)} \gg \frac{F_g}{V_l \mathrm{H}_{\mathrm{NO_2}} \mathbf{R}T}\,. \tag{132}$$

The right-hand side of (132) may be evaluated for conditions typically employed (Saltzman, 1954), i.e., $F_g = 6.7 \times 10^{-3}$ liter s^{-1} (0.4 liter/min) and $V_l = 1.5 \times 10^{-2}$ liter; the resulting value (ca. 2 s^{-1}) may be compared with $k^{(1)}$ evaluated for various mechanisms. For reaction of NO_2 by reaction [1*/4*], $k^{(1)} = k_{\mathrm{A}1^*/4^*} \mathrm{H}_{\mathrm{NO_2}} p_{\mathrm{NO_2}} = 1.0 \times 10^{-2}\ s^{-1}$ for $p_{\mathrm{NO_2}} = 10^{-8}$ atm. Clearly, reaction [1*/4*] cannot be an effective means for removal of NO_2 in the bubbler. This calculation thus supports the empirical finding, noted above, of a low efficiency for absorption of NO_2 by water or by 0.1 M OH^- solution as employed in the Jacobs–Hochheiser method. We conclude further that for NO_2 to be efficiently removed from the incident gas mixture, as is shown to be the case with the Saltzman reagent (e.g., Levaggi et al., 1972) or with 0.1 M OH^- solution containing guaiacol (Nash, 1970b) or arsenite (Christie et al., 1970), there must be direct reaction of dissolved NO_2 with the dissolved reagent(s) present; i.e., subsequent reaction of nitrite would not account for the enhanced absorption. This conclusion may be substantiated further by evaluating $k^{(1)}$ for NO_2 reaction with these reagents. For example, for NO_2 reacting with sulfanilic acid, as specified in the Saltzman (1954) method (3×10^{-2} M), we employ the rate constant $1.3 \times 10^5\ M^{-1}\ s^{-1}$ evaluated (Table 31) from the data of Nash (1970a), under the assumption that the rate constant for sulfanilate anion as studied by Nash is not too dissimilar from that for sulfanilic acid. The resulting value, $k^{(1)} \approx 4 \times 10^3\ s^{-1}$, easily satisfies condition (132), strongly supporting the suggestion (Saltzman, 1954) of a direct reaction of NO_2 with sulfanilic acid. Such a direct reaction occurring in parallel with reaction [1*/4*] could account for the observed stoichiometric factor greater than 0.5 expected for uptake by reaction [1*/4*] only. Furthermore, the proportion of NO_2 uptake by direct reaction with dissolved reagent rather than by reaction [1*/4*] would be expected to increase with decreased NO_2 partial pressure as the concentration of physically dissolved NO_2 decreased, consistent with the observations by Buck and Stratmann (1967) and Crecelius and Forwerg (1970). Similar evaluations may be made, again using the rate constants evaluated in Table 31, for NO_2 reacting with guaiacol or arsenite, again establishing that the direct reaction of dissolved NO_2 with these reagents is responsible for the high absorption efficiencies obtained.

8.4. NO + Aqueous Solution

As noted above, NO is reversibly soluble and nonreactive in liquid water in the absence of other reagents. The aqueous-phase reactions of NO in the presence of NO_2 have also been discussed. We thus restrict this discussion to other aqueous-phase reactions of NO that may be pertinent to the incorporation of this gas into ambient liquid water.

The aqueous-phase reaction of NO with O_2,

$$2NO(aq) + O_2(aq) \rightarrow 2NO_2(aq),$$

or perhaps the overall reaction

$$2NO(aq) + O_2(aq) \xrightarrow{w} 2H^+ + NO_2^- + NO_3^-$$

may be significant in view of the known gas-phase reaction

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g).$$

The rate of the aqueous-phase reaction does not appear to have been determined. Although Seddon and Sutton (1963) report that for $[NO] = 1 \times 10^{-4}$ M and $[O_2] = 1 \times 10^{-3}$ M, NO is "rapidly and quantitatively" oxidized to HNO_2, presumably the reaction is second order in NO and first order in O_2, as is the gas-phase reaction (Baulch et al., 1980). Hence, in view of the low solubilities of both NO and O_2 ($H \approx 2 \times 10^{-3}$ M atm^{-1}, corresponding to $C(\text{aq})/C(\text{g}) = H\mathbf{R}T \approx 0.05$), one would anticipate that the rate of aqueous-phase reaction might be less than that of the gas-phase reaction at the equilibrium partial pressures of the gases and thus negligibly slow at characteristic ambient partial pressures.

Nitric oxide is nonreactive with acid, base, and a variety of anions and cations: Cl^-; ClO_4^-; PO_4^{-3}; SO_4^{2-}; BO_3^{3-}; acetate; Na^+; and Li^+ (Armor, 1974). It reacts as a complexing agent with transition metal ions such as Fe^{2+} and Cr^{2+} (Armor and Buchbinder, 1973; Kustin et al., 1966) and is capable of oxidizing mild reducing agents such as Sn(II) (Nunes and Powell, 1970a). Nitric oxide is oxidized by strong oxidants: MnO_4^-; ClO_2^- [for both of which evolution of NO_2 was noted (Kobayashi et al., 1977)]; and H_2O_2. The species MnO_4^- (e.g., Groth and Calabro, 1969) and H_2O_2 (e.g., Martens et al., 1973) are commonly employed as oxidants in solutions for absorbing nitrogen oxides for analytical determination. The mechanism and kinetics of oxidation of NO by H_2O_2 are not well understood. Bajeva et al. (1979) report a study of the rate uptake of NO (0.07–0.24 atm) by aqueous H_2O_2 (0.13–0.5 M). The rate of uptake $J_{NO} = qp_{NO}[H_2O_2]^{1/2}$ was interpreted according to mixed-phase reaction in the fast reaction (diffusion-controlled) regime. For $[H_2O_2] \gg H_{NO}p_{NO}$, this expression for the rate of uptake indicates a rate law for aqueous-phase reaction

$$R = k^{(2)}[H_2O_2][NO]. \tag{133}$$

At 25°C the value $k^{(2)} = 5.7 \times 10^2$ M^{-1} s^{-1} was obtained. Seddon and Sutton (1963), however, report a much slower reaction rate. For $[H_2O_2] = 10^{-4}$ M and $[NO] = 2 \times 10^{-3}$ M (i.e., $p_{NO} = 1$ atm), the reaction rate is reported as less than 2×10^{-10} M s^{-1}; i.e., assuming rate law (133) $k^{(2)} \leq 1 \times 10^{-3}$ M^{-1} s^{-1}. The reason for the discrepancy is not known.

Aqueous-phase reaction of NO with dissolved S(IV) has been studied by Nunes and Powell (1970b), Takeuchi et al. (1977), and Martin et al. (1981). The latter authors, working in acid solution (pH = 2), report no reaction and are able to place an upper limit to the reaction rate. For a rate law taken as first order in S(IV) and NO, Martin et al. report

$$R < 1 \times 10^{-2}[S(IV)][NO]. \tag{134}$$

In contrast, in basic solution NO evidently undergoes rapid reaction with S(IV). Nunes and Powell (1970b), working with solutions 0.1–1 M in $[OH^-]$, report a reaction rate of the form

$$R = k_1[NO][S(IV)] + k_2[NO]; \tag{135}$$

at 25°C $k_1 = 0.45$ M^{-1} s^{-1} and $k_2 = 0.13$ s^{-1}. The product *N*-nitrosohydroxylamine-*N*-sulfonate, $O_3S(NO)NO^{2-}$, is stable in alkaline solution but liberates N_2O as the solution is made acidic. Rapid reaction of NO with sulfite ion is reported also by Takeuchi et al. (1977). In that study a stirred bubbler was employed for introduction of NO ($1.5–10 \times 10^{-4}$ atm in N_2)

into sodium sulfite solution (0.02–0.8 M). Uptake of NO was in the fast reaction (diffusion controlled regime), i.e., independent of the convective mass-transport coefficient k_L. The rate of uptake was reported as

$$J_{NO} = qp_{NO}^{3/2}, \tag{136}$$

where $q = 1.2 \times 10^{-4}$ kmol m^{-2} s^{-1} atm$^{-3/2}$ was independent of $[SO_3^{2-}]$ over the concentration range studied. This finding suggests a rate law

$$\frac{d[NO]}{dt} = -2k^{(2)}[NO]^2, \tag{137}$$

where $k^{(2)}$ is a pseudo-second-order rate constant. The value obtained for $k^{(2)}$, 6.0×10^8 M^{-1} s^{-1} at 25°C, is quite high; compare this with the diffusion-controlled encounter rate coefficient (ca. 5×10^9 M^{-1} s^{-1}) (Benson, 1960). The range of applicability of (134)–(137) in terms of both $[SO_3^{2-}]$ and pH is not known. Further investigation of this reaction system appears warranted.

9. SUMMARY

The reactive dissolution of nitrogen oxides NO_2 and NO into aqueous solution is a potentially important process relative to the fate of these substances in the atmosphere. The quantitative description of this process requires knowledge of the pertinent equilibrium constants (including Henry's law coefficients) and kinetic rate constants (Anderson, 1982; Durham et al., 1981; Lee and Schwartz, 1981a; Peters and Carmichael, 1982). These quantities are directly relevant as well to development of analytical methods for these compounds, development of flue-gas scrubbers, and interpretation of the mechanism of toxicity of these compounds to plant and animal systems.

There is a wide and diverse literature pertaining to the mechanism and kinetics of the reactive dissolution of nitrogen oxides into aqueous solution, including indirect measurements of phase-mixed kinetics and measurements of aqueous-phase kinetics, as well as measurements of the kinetics of reactive uptake by means of gas–aqueous reactors. This literature is critically reviewed, and recommended values of the several equilibrium and kinetic constants are given, along with uncertainty estimates based somewhat subjectively on the spread in the data. Reactions of NO_2 and NO with dissolved solutes are also reviewed, and, where possible, estimates of kinetic rate constants are presented. However, there remain large uncertainties in the stoichiometry, mechanism, and kinetics of some of these reactions.

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NOMENCLATURE

p_X	Partial pressure of species X (atm)
[X]	Aqueous-phase concentration of species X (M)
a_X	Activity of species X (m)
y_X	Activity of coefficient of species X
H_X	Henry's law coefficient of species X ($M\ atm^{-1}$)
K	Equilibrium constant. May refer to gas-, aqueous-, or mixed-phase equilibrium as indicated by subscript G, A, or M
R	Aqueous-phase rate ($M\ s^{-1}$)
k	Rate coefficient. May refer to aqueous- or mixed-phase reaction as indicated by subscript A or M
k_{as}	Stochastic rate coefficient for convective mass transport between surface and bulk aqueous solution (s^{-1})
k_L	Liquid-side mass-transfer coefficient ($m\ s^{-1}$)
m	Order of aqueous-phase reaction
a	Specific interfacial area or surface area per unit volume of solution (m^{-1})
J_X	Flux of species X into solution ($kmol\ m^{-2}\ s^{-1}$)
$Q_X(t)$	Amount of species X taken up by solution in time t ($kmol\ m^{-2}$)
D_X	Aqueous-phase diffusion coefficient of species X ($m^2\ s^{-1}$)
q	Empirical coefficient relating flux and partial pressure
τ	Characteristic time of indicated process (s)
τ_r	Characteristic time of reaction
τ_m	Characteristic time of convective mixing
τ_d	Characteristic time of diffusion
F_{NO_2}, $F_{N_2O_4}$	Fraction of N(IV) present as NO_2 or N_2O_4, respectively
E_a	Empirical energy of activation of indicated process ($kcal\ mol^{-1}$)

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