A new method for estimating rate constants for trace gas reactions within stratospheric sulphuric acid aerosol droplets

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Abstract. Uptake of trace gases by|stratospheric aerosol can be significant particularly after large injections of volcanic sulphur. A theoretical scheme is presented to quantify the rate at which trace gases diffuse into these aerosol droplets. Rate constants for 19 trace gases are calculated and it is found that the rates vary from a value of $2 \cdot 85 \times 10^{-7} s^{-1}$ for CCl_4 to $8 \cdot 08 \times 10^{-7} s^{-1}$ for NO. The calculations are characterised by their ease of application and can be incorporated into stratospheric chemical models.

Keywords. Sulphate aerosol; rate constants; trace gases.

1. Introduction

Recent studies on Antarctic O_3 loss (Pyle *et al* 1992) highlight the importance of heterogeneous reactions of trace gases on various surfaces believed to be present at significant levels in the stratosphere. These are:

Type I polar stratospheric clouds (PSCs) nominally composed of nitric acid trihydrate $HNO_3 \cdot 3H_2O$

Type II polar stratospheric clouds which are crystals of relatively pure water ice. These form at lower temperatures than type I clouds and are believed to be nucleated by type I clouds

Sulphuric acid aerosol which is nominally a liquid phase surface generally composed of 60–80 weight% H_2SO_4.

While PSCs, as their name suggests, are formed primarily in the cold winter stratosphere at high latitudes, sulphuric acid aerosol is present year-round at all latitudes and may influence stratospheric chemistry on a global basis, particularly after large injections of volcanic sulphur (as in the recent Pinatubo eruption) periodically increase their abundances and surface area. During such periods uptake of various trace gases on these aerosols may be significant. This paper aims to quantify the rate at which trace gases diffuse into the aerosol droplets.

2. Rate limiting mechanisms

In order for an aqueous-phase reaction to occur in a droplet the most important mass transfer steps are:

(i) Diffusion of gaseous species from the bulk gas to the surface of the droplet.
(ii) Transfer across the gas–liquid interface.
(iii) Ionisation of the species, if it occurs.

(iv) Diffusion of the dissolved species in the aqueous phase.

(v) Aqueous phase chemical reaction.

These processes occur in series and the overall rate of reaction of a dissolving and reacting species is controlled by the slowest of these steps.

The treatment of the first three of the above mentioned processes has been adequately described by (Schwartz 1986) for trace gas transfer to cloud droplets. A transfer coefficient k_t, was used to describe the transport of gases from the gas phase across the air–water interface to the surface of the droplet, and vice-versa. The rate of change of concentration calculated by the above method are adequate when *aqueous phase diffusion* is *not* a limiting factor. However, aqueous phase reactions of many species may be rate limited by diffusion of the species *throughout* the droplet. In such a situation, a model describing the aqueous phase chemistry within droplets, is severely constrained by rate kinetics data. Theoretical predictions of trace gas constituents in the stratosphere with the help of one, two, and three dimensional models, without incorporating these heterogeneous reactions cannot account for the chemical losses accurately. Also, measurements are often only available under laboratory conditions while heterogeneous chemistry in the stratosphere occur at much lower pressures and temperatures.

The above discussion points to the necessity for developing a scheme which enables one to estimate rate constants for trace gases diffusing into sulphuric acid aerosol droplets theoretically. This paper provides the basis for such a scheme.

2. Assumptions

The stratospheric aerosol layer is primarily composed of liquid droplets of sulphuric acid and water (these are actually supercooled liquid droplets).

The droplets are spherical.

Humidities are in the range 1–10 ppmv at 100 hPa ($10^{-4} - 10^{-3}$ hPa) under normal stratospheric temperatures (220–250 K) corresponding to a weight percent within a narrow range of 68–86% (Steele and Hamill 1981).

The chemistry occurs at around 16 km (107 hPa) $\sim 5 \times 10^{-4}$ hPa. This gives the weight percent of H_2SO_4 at 220 K as 71·63%.

Mass transport of trace gases into these droplets is governed by a *first order irreversible* process – a reasonable assumption considering the fact that the solute concentrations are much less than the solvent concentrations.

3. Theory

A convenient means of examining the mass-transport aspects in a given situation of interest is evaluation and comparison of the characteristic times of the appropriate chemical reactions. This allows one to find out readily whether a particular reaction is sufficiently slow or fast–a fact crucial to the understanding of atmospheric chemistry.

The characteristic time describing diffusive mass transport for reactions occurring in spherical droplets is given by (Schwartz 1984):

$$\tau = \frac{D^2}{4\pi^2 D_{aq}} \tag{1}$$

where D_{aq} is the aqueous phase diffusion coefficient and D the drop diameter. This characteristic time describes the rate of depletion of the dissolved substances by the liquid phase reaction. For a species undergoing irreversible first order reaction the reaction rate $k_L = \tau^{-1}$.

We have computed D_{aq} from the relation

$$D_{aq} = \frac{7 \cdot 4 \times 10^{-8} (\chi M)^{1/2} \, T}{\mu V_1^{0 \cdot 6}} \, cm^2 \, s^{-1} \qquad (2)$$

where

D_{aq} = mutual diffusion coefficient of solute at very low concentrations in solvent ($cm^2 \, s^{-1}$),

M = Molecular weight of solvent (g/mol)

T = temperature (K)

μ = viscosity of solvent (cp)

V_1 = Molar volume of solute at its normal boiling temperature (cm^3/mol)

χ = association factor of solvent (dimensionless).

Equation (2) is the Wilke–Chang estimation method (Reid *et al* 1986) which is in essence an empirical modification of the Stokes–Einstein relation:

$$D_{aq} = \frac{RT}{6\pi\mu r} \qquad (3)$$

(where the terms have their usual meanings).

4. Parameter evaluation

Table 1 shows some physical properties of sulphuric acid, that are useful in our analysis, particularly with regard to parameter evaluation.

4.1 *Estimation of molecular weight of solvent*

From table 1 we find that at about $73 \cdot 1\%$ H_2SO_4 (the desirable weight percent for our calculation), the M.P. is $-38 \cdot 9°C$. This implies that ($H_2SO_4 \cdot 2H_2O$) should not exist as a *liquid* at temperatures below $-38 \cdot 9°C$. Yet, observations show that the sulphate aerosol droplets are in the *liquid state* even at $-55°C$. This is because the sulphate aerosol exists as a supercooled liquid even at 220 K ($-55°C$).

Thus, we conclude that the composition of the sulphate aerosols is ($H_2SO_4 \cdot 2H_2O$) which also corresponds to approximately the right weight percent range (Steele and Hamill 1981).

Table 1.

Composition	Mol. wt.	M.P. (°C)	Weight percent (%)
H_2SO_4	98·02	10·36(100%) 3·0(98%)	100
H_2SO_4, H_2O	116·09	8·62	84·4
$H_2SO_4, 2H_2O$	134·10	−38·9	73·1
$H_2SO_4, 6H_2O$	206·17	−54·0	47·5

4.2 *Estimation of molar volume of solute*

A number of additive methods are discussed by Partington (1949). Each element and certain bond linkages are assigned numerical values, so that the molar volume at the normal boiling point can be calculated by the addition of those values for estimating the critical volume. However the Tyn and Calus method is recommended for estimating the molar volumes at the b.p. (Reid *et al* 1986), where the average error for 32 compounds is only 2%. A reliable value of the critical volume must be available, however.

Experimental data for the molar volume V_b, at normal boiling temperature were available only for HCl, Cl_2, H_2O, CH_4.

According to this method V_b is estimated empirically from the critical volume:

$$V_b = 0.285 \, V_c^{1.048} \tag{4}$$

Table 2 lists out the molar volume of some important trace gases calculated by this method.

From table 2 by comparing the calculated molar volumes with observations (when available), we find that the predictions are fairly accurate (the maximum difference being less than 7% of the observed values). We calculated V_c values for the trace gases from the American Institute of Physics Handbook (Gray 1963).

4.3 *Association factor of solvent* (χ)

Wilke and Chang (Reid *et al* 1986) recommended that χ be chosen as 2·6 if the solvent is water, 1·9 if it is methanol, 1·5 if it is ethanol, and 1·0 if it is unassociated.

In the present calculation we adopted a value of 2·6 for χ.

Table 2.

Specie	$V_c, cm^3 \, mol^{-1}$	$V_b, cm^3 \, mol^{-1}$	Expt. Obs
NO	57·7	19·8	
NO_2	167·8	61·15	
N_2O	97·4	34·58	
O_3	88·8	31·43	
HCl	80·9	28·5	30·6
HF	69·2	24·17	
Br_2	127·2	45·7	
Cl_2	123·8	44·46	45·5
F_2	66·3	23·11	
H_2O	57·1	19·76	18·7
CO	93·2	33·02	
CO_2	93·9	33·28	
$CClF_3$	180·4	65·98	
CCl_4	275·9	102·98	
CCl_2F_2	216·7	79·95	
CCl_3F	247·8	92·02	
HCN	138·8	50·13	
CH_4	99·2	35·25	35·7
C_2H_4	130·4	46·95	

4.4 *Viscosity of sulphuric acid aerosol*

We adopted a value of 60 cp for the viscosity of sulphuric acid aerosol. This is the value of the viscosity of sulphuric acid solution at $-50°C$ for a 40% solution (No value was reported at 74%). This value was quoted in The Physico-Chemical Constants of Binary Systems in Concentrated Solutions by Timmermans (1960).

5. Estimation of reaction rates of trace gases

We first estimated the binary diffusion coefficient D_{aq} for trace gases using equation (2) and the procedures outlined in section (3). These are shown in table 3.

We then determined the characteristic times using equation (1). Since the aerosol size distribution varies with altitude, we adopted a value of 0.05μ as a typical value of these particles at 107 hPa (Hofmann 1990). Equation (1) gives the characteristic time for diffusive transport into a single droplet. However, we are interested in the macroscopic reaction rate per unit physical volume which corresponds to the term k_L in most governing differential equations describing mass transport of chemical species. As a first approximation (and an upper limit) the reaction rate per unit physical volume is evaluated as the droplet phase rate times the liquid volume fraction.

In our calculation we have adopted a value of 6.0×10^{-13} as the volume fraction of stratospheric sulphuric acid aerosols at 107 hPa (Hofmann 1990).

For the sake of completeness we list out the theoretically calculated reaction rates $k_L(s^{-1})$ along with the corresponding D_{aq}, $(cm^2 s^{-2})$ values.

Table 3.

Specie	$D_{aq}, cm^2 s^{-1} \times 10^{-5}$	$k_L, s^{-1} \times 10^{-7}$
NO	0.085	8.08
NO_2	0.04	3.8
N_2O	0.061	5.8
O_3	0.064	6.08
HCl	0.069	6.46
HF	0.075	7.13
Br_2	0.05	4.75
Cl_2	0.052	4.94
F_2	0.077	7.32
H_2O	0.085	8.08
CO	0.06	5.7
CO_2	0.062	5.89
$CClF_3$	0.04	3.8
CCl_4	0.03	2.85
CCl_2F_2	0.04	3.8
CCl_3F	0.034	3.23
HCN	0.049	4.63
CH_4	0.06	5.7
C_2H_4	0.051	4.85

6. Conclusions

A straightforward scheme has been outlined to estimate rate constants for trace gas reactions with H_2SO_4 aerosols. We find that these vary from a value of $2\cdot85 \times 10^{-7}\,s^{-1}$ for CCl_4 to $8\cdot08 \times 10^{-7}\,s^{-1}$ for NO (table 3). These can be incorporated into stratospheric chemical models describing distribution of trace gases within droplets.

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