

Compilation and evaluation of gas-phase diffusion coefficients of reactive trace gases in the atmosphere: Volume 1. Inorganic compounds

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Abstract:

10 Diffusion of gas molecules to the surface is the first step for all gas-surface reactions. Gas phase diffusion can influence and sometimes even limit the overall rates of these reactions; however, there is no database of the gas phase diffusion coefficients of atmospheric reactive trace gases. Here we compile and evaluate, for the first time, the diffusivities (pressure-independent diffusion coefficients) of atmospheric inorganic reactive trace gases reported in the literature. The measured diffusivities are then compared with estimated values using a semi-empirical method developed by Fuller et al. 15 (1966). The diffusivities estimated using Fuller's method are typically found to be in good agreement with the measured values within $\pm 30\%$, and therefore Fuller's method can be used to estimate the diffusivities of trace gases for which experimental data are not available. The two experimental methods used in the atmospheric chemistry community to measure the gas phase diffusion coefficients are also discussed. A different version of this compilation/evaluation, which will be updated when new data become available, is uploaded online (<https://sites.google.com/site/mingjintang/home/diffusion>).

1 Introduction

25 Airborne particles, including aerosol particles, cloud, fog, rain droplets, and ice crystals, are ubiquitous in the atmosphere. The interactions of atmospheric trace gases with these particles, i.e. heterogeneous reactions, play important roles in many aspects of atmospheric chemistry (Abbatt et al., 2012; Kolb et al., 2010; Ravishankara, 1997). For example, the heterogeneous reaction of ClONO₂ with polar stratospheric clouds (PSCs) is 30 a key step to re-activate chlorine in the stratosphere and thus plays a critical role in

stratospheric ozone depletion (Molina, 1996; Solomon, 1999). In the troposphere, the reactions of trace gases with mineral dust (Dentener et al., 1996; Usher et al., 2003), sea salt (Finlayson-Pitts, 2003; Rossi, 2003), soot (Monge et al., 2010), organic aerosols (Stemmler et al., 2006), ice particles (Abbatt, 2003; Huthwelker et al., 2006), and liquid 5 cloud droplets (Lelieveld and Crutzen, 1990) can significantly impact the budgets of NO_x, O₃, and OH radicals. These reactions can also change the compositions of aerosol particles, e.g. mineral dust (Laskin et al., 2005; Sullivan et al., 2007), sea salt (Gard et al., 1998; Rossi, 2003), and organic aerosols (George and Abbatt, 2010), thus modifying their cloud formation ability (Cziczo et al., 2009; Reitz et al., 2011; Sullivan et al., 2009b).
10 The removal, production, and/or transformation of gaseous pollutants due to the interactions with indoor surfaces may play an important role in indoor air quality and human health (Nazeroff and Cass, 1989).

Heterogeneous interactions of trace gases with particles in the atmosphere (and with all 15 surfaces) are very complex and usually consist of several steps (Davidovits et al., 2011; Pöschl et al., 2007): 1) gas molecules diffuse towards the surface; 2) gas molecules collide with the surface, and some are then accommodated on the surface; 3) molecules adsorbed on the surface can desorb from the surface, undergo reactions on the surface, or diffuse into the bulk, and get dissolved and/or react with other species in the bulk; 4) gaseous products formed in the heterogeneous reactions can diffuse towards the surface, 20 desorb from the surface, and finally diffuse into the gas phase. The overall kinetics of a heterogeneous reaction can be described by the uptake coefficient, γ , which is the net probability that a molecule X undergoing collision with a surface is actually taken up by the surface. The uptake coefficient links the processes at the interface and beyond with an apparent first order loss of X in the gas phase (Ammann et al., 2013; Crowley et al., 25 2010):

$$\frac{d[X]_g}{dt} = -k_I[X]_g = -0.25 \cdot \gamma \cdot c(X) \cdot [SS] \cdot [X]_g \quad (E1)$$

where $[X]_g$ is the concentration of X in the gas phase (molecule cm⁻³), k_I is the apparent first order loss rate of X, $c(X)$ is the average molecular speed (cm s⁻¹) of X, and $[SS]$ is the concentration of the surface area available for the heterogeneous uptake (cm² cm⁻³).

The uptake of a trace gas onto the surface can cause depletion of the trace gas close to the surface, leading to an effective uptake coefficient, γ_{eff} , which is smaller than the true uptake coefficient, γ . The relation between γ_{eff} and γ , under appropriate steady state assumptions, can be described by the following equation (Davidovits et al., 1995; 5 Davidovits et al., 2011):

$$\frac{1}{r_{eff}} = \frac{1}{\gamma} + \frac{1}{\Gamma_{diff}} \quad (E2)$$

where Γ_{diff} describes the gas phase diffusion limitation. Formulas to calculate Γ_{diff} have been derived in previous studies (Davidovits et al., 1995; Fuchs and Sutugin, 1970; Pöschl, 2011). Γ_{diff} depends on the geometry of the surface (e.g., surface of a spherical 10 particle, or inner wall of a cylindrical flow tube), the size of the surface (e.g., diameter of the particle or the flow tube) and the diffusion coefficient of the trace gas in the bath gas (Crowley et al., 2010).

For the uptake onto mono-disperse spherical particles, several methods can be used to calculate Γ_{diff} (Pöschl et al., 2007), for example, the Fuchs-Sutugin equation:

$$15 \quad \frac{1}{\Gamma_{diff}} = \frac{0.75 + 0.286Kn}{Kn \cdot (Kn + 1)} \quad (E3)$$

where Kn is the Knudsen number, given by

$$Kn = \frac{6D(X)}{c(X) \cdot d_p} \quad (E4)$$

where $D(X)$ is the diffusion coefficient of X ($\text{cm}^2 \text{ s}^{-1}$), d_p is the diameter of the particle (cm), and $c(X)$ is average molecular speed of X (cm s^{-1}). For fast uptake processes (i.e. 20 large uptake coefficients) and big particles, gas-phase diffusion of X can limit the overall rate of the uptake of X onto the surface. A method used to calculate Γ_{diff} for poly-dispersed aerosol particles have also been developed (Tang et al., 2012; Tang et al., 2014). As shown in Eqs. (E3) and (E4), the diffusion coefficient determines to which extent the effective uptake coefficient is impacted by gas phase diffusion. An accurate 25 knowledge of the diffusion coefficient is thus important to apply the uptake coefficient to atmospheric particles and to derive the true uptake coefficient from the experimentally measured uptake coefficient in laboratory studies. Aerosol flow tubes (Hallquist et al., 2000; Tang et al., 2012; Thornton et al., 2003; Vlasenko et al., 2009), droplet train flow

reactors (Deiber et al., 2004; Worsnop et al., 1989), and aerosol chambers (Mogili et al., 2006; Wahner et al., 1998) are widely used to investigate the heterogeneous interaction of airborne particles or droplets with trace gases. The effect of diffusion in the gas phase on the uptake of a trace gas onto spherical particles at 760 Torr (N_2) and at 296 K is 5 illustrated in Figure 1a. N_2O_5 , with a diffusion coefficient of $0.085 \text{ cm}^2 \text{ s}^{-1}$ at 760 Torr and at 296 K (Wagner et al., 2008) and an average molecular speed of $24\,096 \text{ cm s}^{-1}$, is used as the representative trace gas for the calculations. For spherical particles with diameters of $<200 \text{ nm}$, when the true uptake coefficient is <0.1 , the influence of gas phase diffusion, defined as $(\gamma - \gamma_{\text{eff}})/\gamma$, is smaller than 5%. When the true uptake coefficient 10 is <0.001 , the influence of gas phase diffusion is $<7\%$ for particles with diameters of $<20 \mu\text{m}$. Increasing the particle diameter and the uptake coefficient will increase the effect of gas phase diffusion, and gas phase diffusion becomes important with $(\gamma - \gamma_{\text{eff}})/\gamma$ larger than 20% for fast uptake ($\gamma > 0.04$) onto larger particles ($d_p > 2 \mu\text{m}$), as shown in Figure 1a.

15 In addition, especially when the heterogeneous reactions of interest are slow, coated or wetted wall flow tubes are used in laboratory studies, in which the solid or liquid substraces form a film on the inner wall of the flow tube to interact with the trace gas under investigation (Abbatt and Molina, 1992; Adams et al., 2005; Hanson et al., 1992; Pouvesle et al., 2010). For the uptake onto the inner wall of a cylindrical tube, Γ_{diff} is 20 given by (Hanson et al., 1992; Wagner et al., 2008):

$$\frac{1}{\Gamma_{\text{diff}}} = \frac{c(X) \cdot d_t}{4 \times 3.66 \cdot D(X)} \quad (\text{E5})$$

where d_t is the inner diameter of the flow tube (cm). The quantitative effect of gas phase diffusion on the uptake of a trace gas onto the inner wall of a cylindrical flow tube (inner diameter: 2.0 cm) at 296 K is shown in Figure 1b as a function of pressure (N_2). N_2O_5 is 25 again used as the representative trace gas. When the true uptake coefficient is $< 1 \times 10^{-5}$, the effect of gas phase diffusion is relatively small ($< 25\%$) even at high pressure (close to 1 atm). Increase in the true uptake coefficient enhances the effect of gas phase diffusion. Therefore, in a lot of studies coated-wall flow tubes are operated at low pressures of He, to increase the gas phase diffusion rate and thus suppress the effect of 30 gas phase diffusion on the overall effective uptake rate. When the true uptake coefficient

is close to 0.1, as shown in Figure 1b, the uptake onto the wall is entirely controlled by gas phase diffusion ($\gamma_{\text{eff}}/\gamma$ is ~0.1) and therefore the upper limit for accurate uptake measurement using this method is around 0.1. Another type of coated wall flow tubes in which the solid substance under investigation is coated on the outer wall of the injector 5 instead of the inner wall of the flow reactor has also be used (Bedjanian et al., 2005; Gershenzon et al., 1995), and details on how to derive γ from γ_{eff} are provided by Gershenzon et al. (1995).

The interaction of trace gases with surfaces, and therefore gas phase diffusion coefficients, are not only important in the investigation of atmospheric heterogeneous reactions, but 10 are also important to describe the efficiency of diffusion denuders which are widely used to collect trace gases or to separate trace gases from aerosol particles. For example, denuder tubes in which inner walls are coated with adsorbents are widely used to capture trace gases such as HNO_3 (Braman et al., 1982; Durham et al., 1987; Eatough et al., 1985), HONO (Ferm and Sjodin, 1985), and NH_3 (Braman et al., 1982) for online/offline 15 analysis, and to separate aerosol particles from gases (e.g., to separate NH_3 from particulate NH_4^+). Aerosol particles which remain in the flow exiting the denuders can then be collected for further online/offline analysis, and artifacts due to interferences of trace gases (for example, particulate nitrate versus gaseous HNO_3 , and ammonium versus NH_3) can be minimized (Ferm, 1986). Denuders are also widely used in laboratory 20 studies to remove reactive trace gases to terminate heterogeneous reactions (Sullivan et al., 2009a), or selectively remove reactive trace gases whose detection can interfere with others (Ammann et al., 1998). In addition, catalytic tubes are used to convert trace gases to products which can then be more easily detected. For example, the widely used chemiluminescence method to measure NO_2 is based on conversion of NO_2 to NO in a 25 catalytic conversion tube coated with metal films such as nickel or gold (Fahey et al., 1985). The removal and/or conversion of trace gases in a denuder or catalytic tubes requires the diffusion of trace gases towards and collision with the inner wall, and therefore the knowledge of diffusion coefficients is helpful for the optimization of the design of denuder and catalytic conversion tubes (Murphy and Fahey, 1987).

30 The importance of further research on atmospheric heterogeneous reactions has been underscored (Abbatt et al., 2014; Kolb et al., 2010), the necessity of adopting consistent

terminology, formalism, parameters in the heterogeneous reaction studies has been highlighted (Kolb et al., 2010; Pöschl et al., 2007), and comprehensive models have been developed to take into account all the steps involved in heterogeneous reactions (Pöschl et al., 2007; Shiraiwa et al., 2010). Two independent international panels, the IUPAC 5 Subcommittee for Gas Kinetic Data Evaluation (Ammann et al., 2013; Crowley et al., 2010) and the NASA/JPL Panel for Data Evaluation (Sander et al., 2011) have been evaluating and recommending the experimental kinetic data for atmospheric heterogeneous reactions. However, gas phase diffusion coefficients of atmospheric reactive trace gases have only been occasionally measured during the investigation of 10 heterogeneous reactions and development of denuder methods. To the best of our knowledge, these data have not been compiled previously. When unavailable, these values have to be estimated, and even sometimes were arbitrarily chosen, leading to additional errors. Therefore, a compilation and/or evaluation of measured diffusion coefficients is clearly required. We note that there are several databases on the binary gas 15 phase diffusion coefficients (Berezhnoi and Semenov, 1997; Gordon, 1977; Marrero and Mason, 1972); however, the existing databases focus on stable gases which are of limited relevance for atmospheric chemistry.

Here we compile and evaluate the diffusion coefficients of atmospheric inorganic reactive 20 trace gases reported in the literature, with the hope that this work will enhance the dissemination of the reported diffusion coefficients and stimulate further experimental measurements. We also compare the measured values to those estimated using Fuller's method, in order to evaluate the performance of this method. Fuller's method is a semi-empirical method to directly estimate the gas phase diffusivities (Fuller et al., 1966; Fuller et al., 1969).

25 The diffusivities of organic species are beyond the scope of this paper (the only included organic molecule is $\text{CH}_3\text{SO}_3\text{H}$). The uptake of organics, particularly oxygenated organics, onto aerosol particles and cloud droplets can also be important in the atmosphere. **We have started to compile and evaluate the diffusion coefficients of organic species of atmospheric interest, and plan to publish another review in the near future.** Marrero and 30 Mason (1972) compiled the diffusivities of some alcohols, ketones, aldehyde, and carbonic acids, though many of them may not be of direct atmospheric interests.

2 Methodology

2.1 Gas phase diffusivity

The theory describing diffusion in binary gas mixtures at low to moderate pressure can be derived by solving the Boltzman equation, and the diffusion coefficient can be expressed as (Reid et al., 1987):

$$D(A, B, P) = \frac{0.00266 T^{1.5}}{P \sqrt{M(A, B)} \sigma^2 \Omega_D} \quad (\text{E6})$$

where $D(A, B, P)$ is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) of gas A in gas B at a pressure of P (bar), T is the temperature (K), $M(A, B)$ is equal to twice of the reduced mass of molecule A and molecule B, σ is the characteristic length (10^{-1} nm), and Ω_D is the dimensionless diffusion collision intergral. To derive Eq. (E6), it is also assumed that the gases investigated obey the ideal-gas law and gas A is only present in trace amount compared to B.

To estimate diffusion coefficients using Eq. (E6), the values of σ and Ω_D need to be calculated/estimated. Ghosal et al. (1993) used the Lernnard-Jones method to estimate the

diffusion coefficients of a variety of atmospheric trace gases, and Ivanov et al. (2007) found that the diffusion coefficients of OH, HO₂, and O₃ estimated by the Lernnard-Jones method agree well with their experimentally measured values. However, to calculate σ and Ω_D , the Lennard-Jones method require molecular paramaters which are not readily available.

Several empirical/semi-empirical methods are available to directly estimate diffusion coefficient, e.g., the method proposed by Fuller et al. (1966, 1969). Reid et al. (1987) compared the estimated diffusion coefficients of a large range of molecules using different methods, including the Lernnard-Jones method and Fuller's method, with measured values, and found that Fuller's method in general yields the smallest errors.

Therefore, in this work Fuller's method is used.

2.1.1 Fuller's method

Measured gas-phase diffusion coefficients, $D(A, B, P)$, usually reported in $\text{cm}^2 \text{ s}^{-1}$, depend on the pressure under which the diffusion coefficients were measured. Pressure

independent diffusion coefficients (torr $\text{cm}^2 \text{ s}^{-1}$), $D(A,B)$, sometimes called diffusivities, are reported by dividing $D(A,B,P)$ by the pressure. In this work for clearance and consistence, the pressure independent diffusion coefficient, $D(A,B)$, is referred as diffusivity, and all the reported diffusion coefficients are converted to diffusivities.

5 The diffusivity of gas A in gas B, estimated using Fuller's method, can be described by (Fuller et al., 1966; Fuller et al., 1969):

$$D(A,B) = \frac{1.0868 \cdot T^{1.75}}{\sqrt{m(A,B)}(\sqrt[3]{V_A} + \sqrt[3]{V_B})^2} \quad (\text{E7})$$

where $D(A,B)$ is the diffusivity of A in B (Torr $\text{cm}^2 \text{ s}^{-1}$) at the temperature of T (K), and $m(A, B)$ (g mol^{-1}) is given by

$$10 \quad m(A,B) = \frac{2}{(1/m_A + 1/m_B)} \quad (\text{E8})$$

where m_A and m_B are the molecular weights (g mol^{-1}) of A and B, and V_A and V_B are the dimensionless diffusion volumes of A and B, respectively. Pressure is given in Torr instead of SI units (e.g., Pa) in this work, because Torr is widely used as the pressure unit in flow tube studies and many diffusivities are reported in torr $\text{cm}^2 \text{ s}^{-1}$. The dimensionless

15 diffusion volumes of a few simple molecules, including N_2 , O_2 , He , H_2O , NH_3 , SO_2 , Cl_2 , and Br_2 , are listed in Table 1, and the diffusion volume of air is 19.7. The diffusion volume of a molecule, if not listed in Table 1, can be calculated by summing the diffusion volumes of all the atoms it contains:

$$V = \sum n_i V_i \quad (\text{E9})$$

20 where n_i is the number of the atom with a diffusion volume of V_i contained by the molecule. The diffusion volumes of a few atoms of atmospheric interest are listed in Table 1. Readers are referred to Table 11-1 in page 588 of Reid et al. (1987) for the diffusion volumes of other molecules and atoms not included in Table 1 of this paper.

25 The atomic diffusion volumes are determined by regression analysis of experimental data on gas phase diffusion coefficients of a large range of molecules. Calculation of molecular diffusion volumes from atomic diffusion volumes may lead to different errors for different molecules. The diffusion volume of SO_2 would be 35.12 if derived from

atomic diffusion volumes according to Eq. (E9), and it is 41.8 (as listed in Table 1) which is directly calculated from extensive experimental dataset of gas phase diffusivities of SO₂. As shown in Tables 2-5, we find that compared to the experimental values, the diffusivities estimated using Fuller's method are typically 20-50 % larger for atmospheric 5 trace gases **that** we include in this work. We suggest that this mainly results from underestimation of molecular diffusion volumes derived from atomic diffusion volumes.

The diffusion of a trace gas, A, in the binary mixture of B1 (e.g., N₂) and B2 (e.g., H₂O), can be calculated as (Reid et al., 1987; Fickert et al., 1999):

$$\frac{1}{D(A,B1,B2)} = \frac{x(B1)}{D(A,B1)} + \frac{x(B2)}{D(A,B2)} \quad (E10)$$

10 where $x(B1)$ and $x(B2)$ are the molar fractions of B1 and B2 in the mixture, $D(A,B1,B2)$, $D(A,B1)$, and $D(A,B2)$ **are** the diffusivities of A in the binary mixture (of B1 and B2), B1, and B2, respectively.

2.2 Measurements of diffusion coefficients

Gas phase diffusion coefficients have been measured since late 19th century, and many 15 experimental methods have been developed (Marrero and Mason, 1972); however, most (if not all) of these methods can only be applied to relatively stable gases and thus are not suitable for determining the diffusivities of atmospheric reactive trace gases. To our knowledge only two methods, i.e. flow tubes and denuders, have been used to measure the diffusivities of trace gases by the atmospheric chemistry community. Both methods 20 use the same principle: a flow containing the trace gas is delivered through a tube (usually cylindrical) which is coated on its inner wall with very reactive substance and thus serves as a perfect sink for trace gas molecules colliding with the wall. Therefore, the overall loss rate of the trace gas is entirely controlled by its diffusion in the gas phase towards the wall and not influenced by the reactivity of the surface. The two methods are 25 briefly discussed below.

2.2.1 Flow tubes

If the inner wall of a cylindrical flow tube is very reactive towards the trace gas, the loss rate of the trace gas onto the wall can then be used to determine the gas phase diffusion

coefficient. Under laminar flow conditions, $D(A,B,P)$ can be related to the measured wall loss rate, k_w , by

$$D(A, B, P) = \frac{k_w r_t^2}{3.66} \quad (E11)$$

where r_t is the radius of the flow tube (Zasyplkin et al., 1997). This equation is only valid

5 for conditions under which the Peclet number, Pe , is larger than 20 (Zasyplkin et al., 1997). Pe is given by

$$Pe = \frac{2r_t v}{D(A,B,P)} \quad (E12)$$

where v is the linear flow velocity in the flow tube. It is necessary to measure $D(A,B,P)$ at different pressure to derive the diffusivity, $D(A,B)$. If the wall serves as a perfect sink for

10 the trace gas, $D(A,B)$ measured at different pressure should show good agreement (Fickert et al., 1999; Liu et al., 2009).

2.2.2 Denuders

A laminar flow containing stable mixing ratios of the trace gas passes through the denuder which consists of several sections with the same length. The trace gas is 15 collected on the inner wall of each sections and converted to a stable absorbate, which is then quantified offine to determine the collection efficiency, E (Ferm and Sjodin, 1985):

$$E = \frac{c_i - c_{i+1}}{c_i} \quad (E13)$$

where c_i and c_{i+1} are the amount of absorbate being collected on the i th and $(i+1)$ th

sections, respectively. For a cylindrical tube whose inner wall acts as a perfect sink for

20 the trace gas, E can be related to the diffusion coefficient, $D(A,B,P)$ by:

$$1 - E = 0.819e^{-11.489\Delta} + 0.0975e^{-70.1\Delta} - 0.0325e^{-179\Delta} \quad (E14)$$

$$\Delta = \frac{D(A,B,P) \cdot L}{F} \quad (E15)$$

where L is the length of each section of the denuder (cm), and F is the volume flow rate of the flow passing through the denuder ($\text{cm}^3 \text{ s}^{-1}$) (Ferm and Sjodin, 1985).

It is important for both methods to ensure that the wall remains as a perfect sink for the trace gas during the experiment so that the overall loss of the trace gas is controlled by gas phase diffusion. In a flow tube experiment, this can be checked by measuring the diffusion coefficients at different pressures over a broad range (Fickert et al., 1999; 5 Ivanov et al., 2007). A denuder is normally operated at constant pressure (close to atmospheric pressure) and therefore it is often not verified whether the inner wall of the denuder is a perfect sink. Fast-response online detectors are often available to measure the decay of trace gases in a flow tube, enabling relatively quick determination of the diffusivities. The denuder method usually requires a substantial period to collect enough 10 samples which will then be post-processed and analyzed, making it quite labourious. Therefore, the flow tube method appears to be a better method for the determination of diffusivities in the gas phase. We recommend that such measurements should be performed over a broad range of pressure, in order to ensure that the inner wall serves as a perfect sink.

15 **3 Results**

The recommended diffusivities in air are summarized in Table 2. Since the diffusivity of a trace gas in air is approximately the same to its diffusivity in N₂/O₂, no adjustment was made if measurements were performed in N₂/O₂ instead of air. The diffusivities of some important reactive trace gases in air (or in N₂/O₂), e.g., HO₂, O₃, HOCl, and ClONO₂, 20 have not been experimentally determined, and therefore no recommendation can be made. However, these species are listed in Table 2 to highlight the urgency to measure their diffusivities. A different version of this compilation/evaluation, which largely follows the format of online reports prepared by the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (<http://iupac.pole-ether.fr/>), is uploaded online 25 (<https://sites.google.com/site/mingjintang/home/diffusion>) and will be updated when new data are available.

For trace gases whose diffusivities were measured under the same (or similar) conditions by more than one study, the preferred diffusivity is the average of the measured values and the given uncertainty is the corresponding standard deviation, after excluding studies 30 whose results appear significantly different. However, except for a few trace gases (e.g.,

HNO₃ and NH₃), the diffusivities of most trace gases have only been reported by one study. If there is only one experimental value available, the experimental value is temporarily preferred, and the given uncertainty reflects the difference between the measured and estimated diffusivities, e.g., if the estimated diffusivity is 30% larger than 5 the measured value, an uncertainty of $\pm 30\%$ is given to the preferred value.

Preferred diffusivities in air (or N₂/O₂) at 296 K are recommended. If the measurement was not carried out at 296 K, the original diffusivity was adjusted to 296 K, assuming that the temperature dependence can be described by Fuller's method:

$$D(296) = D(T) \cdot \left(\frac{296}{T}\right)^{1.75} \quad (\text{E16})$$

10 where T is the temperature (K) at which the measurement was performed, and $D(296)$ and $D(T)$ are the diffusivities at the temperature of 296 K and T , respectively. If the difference between T and 296 K is ≤ 10 K, the difference in the diffusivities is not larger than 6% which is negligible compared to the uncertainties of reported diffusivities, and thus no adjustment due to temperature difference was performed.

15 In the following subsections, we compile and discuss experimental gas phase diffusivities reported in the literature, and compare them to estimated values using Fuller's method. Diffusivities for individual molecules are then recommended if possible.

3.1 HNO₃ and NH₃

20 The diffusivities of HNO₃ were all measured by using denuders at 296-298 K. As shown in Table 3, all the reported values agree well with each other except a much smaller value reported by De Andrade et al. (1992). The preferred diffusivity of HNO₃ in air at 296 K, (87 \pm 7) Torr cm² s⁻¹, is the average value of all the measurements except De Andrade et al. (1992). On average the estimated diffusivity using Fuller's method is $\sim 30\%$ larger than the measured values.

25 As shown in Table 3, the diffusivity of NH₃ in N₂ (or air/O₂) was measured over a wide temperature range (293-523 K) prior to 1960, and the reported values at 296-298 K agree very well with more recent measurements in N₂ using flow tubes (Hanson and Kosciuch, 2003) and denuders (Braman et al., 1982; Spiller et al., 2003). The preferred diffusivity of

NH_3 in N_2 (or air/ O_2) at 296 K, (176 ± 10) Torr $\text{cm}^2 \text{ s}^{-1}$, is the average of those reported by all the studies at this temperature. The estimated diffusivities using Fuller's method agree very well with the measured ones.

3.2 NO, NO_2 , NO_3 , N_2O_5 , and HONO

5 The diffusivities of NO and N_2O_5 in N_2 were only determined once, to the best of our knowledge. The results are listed in Table 4. The estimated diffusivities using Fuller's method are 2% higher than the measured values for NO, and 45% for N_2O_5 . Since their diffusivities were only reported once and the measured values agree reasonably well with estimates using Fuller's method, the reported values are preferred. Uncertainties of $\pm 10\%$,
10 and $\pm 50\%$ are given to the preferred diffusivities of NO and N_2O_5 , reflecting the difference between the measurement and the estimation. More measurements are needed to reduce the relatively large uncertainty of the diffusivity of N_2O_5 , considering the importance of its uptake onto airborne particles in both the troposphere and the stratosphere.

15 The diffusivity of NO_2 in N_2 was measured once by Chambers and Sherwood (1937). A high partial pressure of NO_2 was used in the experiment and therefore the presence of N_2O_4 in the system was significant. The diffusivity of NO_2 was experimentally determined by assuming that the diffusivity of NO_2 is a factor of 1.43 of that of N_2O_4 . The measurements were carried out at two different temperatures, and the estimated
20 diffusivities using Fuller's method are 35% larger than the measured values, as shown in Table 4. The preferred diffusivity of NO_2 in N_2 at 296 K, (106 ± 37) Torr $\text{cm}^2 \text{ s}^{-1}$, is based on the value reported at 283 K by Chambers and Sherwood (1937), extrapolated to 296 K. The given uncertainty ($\pm 35\%$) reflects the difference between the measurement and the estimation at 283 K.

25 The diffusivities of NO_3 radicals in N_2 , O_2 , He, and H_2O were determined using a flow tube (Rudich et al., 1996). The measured diffusivity in N_2 , as expected, agrees very well with that in O_2 . The estimated diffusivities using Fuller's method are 50% larger than the measured values for NO_3 radicals. The preferred diffusivity of NO_3 radicals in N_2 at 296 K, (92 ± 46) Torr $\text{cm}^2 \text{ s}^{-1}$, is based on the measurement of Rudich et al. (1996) at 273 K
30 and extrapolated to 296 K using Eq. (E16). The large uncertainty we give to the preferred

value reflects the relatively significant difference between the measurement and the estimation using Fuller's method, and highlights that further measurements are desired.

The diffusivity of HONO in He was measured to be (433 ± 38) Torr $\text{cm}^2 \text{ s}^{-1}$ at 294 K (Hirokawa et al., 2008) and (490 ± 50) Torr $\text{cm}^2 \text{ s}^{-1}$ at 300 K (El Zein and Bedjanian, 2012)

5 using flow tubes, as listed in Table 4. The two studies are in good agreement, and differences between the measured and estimated diffusivities are $<20\%$. The diffusivity of HONO in air at 298 K reported by Benner et al. (1988) is significantly smaller than that reported at 296 K by Ferm and Sjodin (Ferm and Sjodin, 1985), though denuders were used in both studies. The preferred diffusivity of HONO in air at 296 K, 10 (96 ± 26) Torr $\text{cm}^2 \text{ s}^{-1}$, is the average of those reported by the two studies (Benner et al., 1988; Ferm and Sjodin, 1985). Since the difference between the two studies is statistically significant, further studies, preferably using a flow tube, are needed to reduce the uncertainty of the diffusivity of HONO in air (or N_2 , O_2).

3.3 SO_2 , SO_3 , H_2SO_4 , and $\text{CH}_3\text{SO}_3\text{H}$

15 The diffusivity of SO_2 in air was measured at 263 K (Mason and Monchick, 1962), 293 K (Andrew, 1995), and 298 K (Fish and Durham, 1971). The reported values in these three studies agree well with the estimates using Fuller's method, as shown in Table 5. The preferred diffusivity of SO_2 in air at 296 K, (94 ± 13) Torr $\text{cm}^2 \text{ s}^{-1}$, is the average of the values measured by Andrew (1955) and Fish and Durham (1971) at room temperature.

20 The diffusivity of SO_3 in N_2 was measured at 295 K by Lovejoy and Hanson (1996) and at 300 K by Jayne et al. (1998), both using flow tubes. The measured diffusivities agree well with each other, and are also in good agreement with the estimated values. The preferred diffusivity of SO_3 in air at 296 K, (91 ± 6) Torr $\text{cm}^2 \text{ s}^{-1}$, is the average of those reported by Lovejoy and Hanson (1996) and Jayne et al. (1998).

25 The diffusivities of H_2SO_4 in N_2 were reported to be (85 ± 15) Torr $\text{cm}^2 \text{ s}^{-1}$ at 295 K (Lovejoy and Hanson, 1996), (71 ± 5) Torr $\text{cm}^2 \text{ s}^{-1}$ at 298 K (Hanson and Eisele, 2000), and (67 ± 1) Torr $\text{cm}^2 \text{ s}^{-1}$ at 303 K (Pöschl et al., 1998). All three studies used flow tubes. As shown in Table 5, the diffusivity reported by Lovejoy and Hanson (1996) is in excellent agreement with the estimated value, while the values reported by Pöschl et al. 30 (1998) and Hanson and Eisele (2000) agree with the estimated ones reasonably well

(within ~30%). The preferred diffusivity of H_2SO_4 in N_2 at 296 K, (74 ± 10) Torr $\text{cm}^2 \text{s}^{-1}$, is the average of the three studies. No adjustment due to the temperature difference is done because difference in the diffusivities between 296 K and the temperatures at which the measurements were carried out is very small.

5 The diffusivity of $\text{CH}_3\text{SO}_3\text{H}$ in N_2 at 296 K was determined to be 60 Torr $\text{cm}^2 \text{s}^{-1}$ (Hanson, 2005). The uncertainty was not clearly stated in the original study, and the measured value is 30% lower than that estimated using Fuller's method. The preferred diffusivity of $\text{CH}_3\text{SO}_3\text{H}$ in N_2 , is recommended to be (60 ± 18) Torr $\text{cm}^2 \text{s}^{-1}$, and the uncertainty associated with the preferred value reflects the difference between the measured diffusivity and the estimated one.

10 3.4 O_3 , OH , HO_2 , and H_2O_2

15 The diffusivity of O_3 was only measured by one flow tube study, to be (410 ± 25) Torr $\text{cm}^2 \text{s}^{-1}$ at 295 K in He (Ivanov et al., 2007), and the estimated value by Fuller's method is 27% higher, as shown in Table 5. Unfortunately no measurement of the diffusivity of O_3 in air (or N_2/O_2) has been performed and therefore no reccommodation can be made, despite the central importance of O_3 in the troposphere and stratosphere.

20 The diffusivities of OH radicals were measured at 218-298 K in He and at 243-318 K in air (Liu et al., 2009). The results are in good agreement with the diffusivities in He (Bertram et al., 2001; Ivanov et al., 2007) and air (Ivanov et al., 2009) at room temperature reported by the same group, as shown in Table 5. The preferred diffusivity of OH radicals in air at 296 K, (179 ± 20) Torr $\text{cm}^2 \text{s}^{-1}$, is the average of values reported by Ivanov et al. (2007) and Liu et al. (2009).

25 The diffusivity of HO_2 radicals in He was measured using flow tubes at 296 K (Ivanov et al., 2007; Lovejoy and Hanson, 1996), and the results reported by these two studies are in good agreement, as shown in Table 5. The diffusivity of HO_2 radicals in He, estimated using Fuller's method, is 40% larger than the measured values. The diffusivity of HO_2 radicals in air (or N_2/O_2) has not been measured and thus no reccommodation can be made. The uptake of HO_2 radicals onto aerosol particles in the troposphere is suggested to be very fast and may have a significant impact on the oxidation capacity of the

troposphere (Mao et al., 2013). Therefore an accurate determination of the diffusivity of HO₂ in air (or N₂/O₂) is clearly of importance.

Only one study measured the diffusivity of H₂O₂ (in air), and a value of (143±3) Torr cm² s⁻¹ at 333 K was reported (McMurtrie and Keyes, 1948). The estimated diffusivity using Fuller's method, is 27% larger than the measured value. The preferred diffusivity of H₂O₂ in air is (143±43) Torr cm² s⁻¹ at 333 K and (116±35) Torr cm² s⁻¹ at 296 K. An uncertainty of ±30% is given for the preferred values, taking into account the difference between the measured and estimated values.

3.5 Halogen species

3.5.1 HOX and HX

The diffusivity of HOBr was measured to be (237±1) Torr cm² s⁻¹ at 255 K (Adams et al., 2002) and (319±48) Torr cm² s⁻¹ at 274 K (Fickert et al., 1999) in He, and (84±7) Torr cm² s⁻¹ in N₂ at 274 K (Fickert et al., 1999), using flow tubes. As shown in Table 6, the estimated diffusivity using Fuller's method is ~10% larger than the measured value for HOBr in N₂. The preferred diffusivity of HOBr in N₂ at 274 K, (84±9) Torr cm² s⁻¹, is based on the measurement of Fickert et al. (1999), and the uncertainty of the preferred value reflects the difference (~10%) between the measurement and the estimation. To the best of our knowledge, the diffusivity of HOCl has not been reported.

The diffusivity of HOI in He was measured to be (191±38) Torr cm² s⁻¹ at 243 K and (225±12) Torr cm² s⁻¹ at 253 K (Holmes et al., 2001), and the estimated values using Fuller's method are ~30% larger. No measurement of the diffusivity in air/N₂/O₂ has been reported. The diffusivities of HOBr and HOI in gaseous H₂O were also measured (Adams et al., 2002; Holmes et al., 2001), and the estimated values using Fuller's method are 110% and 194% larger than the measured diffusivities in H₂O, as shown in Table 6. In contrast, the estimated diffusivities of HOBr in He and N₂ and of HOI in He are in reasonably good agreement with the measured values. This may indicate that intermolecular interaction may occur between HOBr/HOI and H₂O molecules, thus slowing down the diffusion.

The diffusivities of HCl in N₂ was measured in the temperature range of 324-523 K (Mian et al., 1969), and the difference between the measured and estimated values are <20%, as shown in Table 6. If the diffusivity measured at 324 K is adjusted to that at 296 K using Eq. (E16), it gives a value of 113 Torr cm² s⁻¹. This agrees well with the 5 diffusivity (122 Torr cm² s⁻¹) of HCl measured in air at 296 K using denuders (Matusca et al., 1984). The preferred diffusivity of HCl in N₂ at 296 K, (118±7) Torr cm² s⁻¹, is the average of the values reported by Matusca et al. (1984) at 296 K and Mian et al. (1969) after being extrapolated to 296 K.

Only one study reported the diffusivity of HBr, which was measured in N₂ from 10 336-525 K (Mian et al., 1969). As shown in Table 6, the differences between the measured and estimated diffusivities are usually <20%. The preferred diffusivity of HBr in N₂, (95±29) Torr cm² s⁻¹, is an extrapolation of the measured value at 336 K by Mian et al. (1969) to 296 K using Eq. (16), and the uncertainty reflects the difference between the measured and estimated diffusivities of HBr in N₂ at 336 K.

15 3.5.2 Nitrogen-containing halogen species

The diffusivities of ClNO₂ in N₂ and He were measured at 275 K in a flow tube study (Fickert et al., 1998), and the agreement with estimated values is within 20%. The preferred diffusivities of ClNO₂ in N₂ are recommended to be (75±15) Torr cm² s⁻¹ at 20 275 K and (85±17) Torr cm² s⁻¹ at 296 K, based on the measurement of Fickert et al. (1998). The assigned uncertainty reflects the difference between the measured and estimated diffusivity at 275 K. The diffusivities of ClONO₂ or BrONO₂ have not been reported, despite their importance in the stratosphere and possibly also in the troposphere.

3.5.3 X₂ and XY

The diffusivity of Cl₂ in air was reported to be (94±2) Torr cm² s⁻¹ at 293 K (Andrew, 25 1955). Though the measurement is in excellent agreement with the estimation, an uncertainty of ±10% is given to the preferred value at 296 K, i.e. (94±10) Torr cm² s⁻¹. The diffusivities of Br₂ in air was measured to be (69±3) Torr cm² s⁻¹ at 293 K (Andrew, 1955), (80±3) Torr cm² s⁻¹ at 301 K (Brockett, 1966), and (81±1) Torr cm² s⁻¹ at 298 K (Lugg, 1968). As shown in Table 6, all three measurements are in good agreement with

the estimation. The preferred diffusivity of Br_2 in air at 296 K, (75 ± 6) Torr $\text{cm}^2 \text{ s}^{-1}$, is the average of the values reported by Andrew (1955), Brockett (1966), and Lugg (1968). The reported diffusivities of I_2 in air at 298 K and in N_2 at 273 K (Trautz and Muller, 1935) agree reasonably well with the estimated values (with $\pm 20\%$). The preferred diffusivity of 5 I_2 in air at 298 K, (64 ± 13) Torr $\text{cm}^2 \text{ s}^{-1}$, is based on the value reported by Trautz and Muller (1935).

The diffusivities of ICl in He measured using a flow tube at 278 and 293 K (Braban et al., 2007), show good agreement with the estimated values. The discrepancy between measured and estimated diffusivities for ICl in H_2O is significantly larger than that in He. 10 Similar discrepancies were also observed for HOBr and HIO in H_2O , as discussed in section 3.5.1, and this may suggest that in general Fuller's method works better for diffusivities in N_2 , O_2 , air, and He than that in gaseous H_2O . The diffusivity of BrCl or ICl in air/ N_2/O_2 has not been reported.

3.6 Temperature dependence of diffusivities

15 Only a few studies measured the diffusivities of atmospheric reactive trace gases at several temperatures. The diffusivities of NH_3 , HCl , and HBr in N_2 were measured from ~ 300 K to >500 K. As shown in Tables 3 and 6, over the broad temperature ranges investigated, the measured diffusivities agree well with the estimated values using Fuller's method. However, the temperature ranges (300-500 K) in which the diffusivities 20 of NH_3 , HCl , and HBr were determined are of little atmospheric relevance.

Using a flow tube, Liu et al. (2009) measured the diffusivities of OH radicals in air over the range of 243-318 K. The diffusivities reported by Liu et al. (2009) and those estimated using Fuller's method are plotted in Figure 2 as a function of temperature. The ratios of the estimated diffusivity to the measured one (red curve, right y-axis) are also 25 shown in Figure 2, suggesting that Fuller's method can predict the diffusivities of OH radicals over a broad temperature range within $\pm 30\%$. The diffusivities of most of atmospheric reactive trace gases have not been measured at different temperatures, although the temperature dependence may be reasonably well estimated using Fuller's method.

4 Conclusions

The critical role of heterogeneous reactions in atmospheric chemistry has been widely accepted, and the necessity of adopting consistent terminology and having high quality of kinetic data have also been well recognized (Ammann et al., 2013; Crowley et al.,

5 Kolb et al., 2010; Pöschl et al., 2007; Sander et al., 2011). The diffusion of gas molecules towards the surface is the first step in a heterogeneous reaction, and it can influence and sometimes even control the overall rate of the uptake of a trace gas onto the surface. However, to the best of our knowledge, there is no database about the gas phase diffusion coefficients of atmospheric reactive trace gases.

10 In this work we have compiled and evaluated the available experimental data for the diffusivities of atmospheric inorganic reactive trace gases. The measured diffusivities are also compared with those estimated using Fuller's semi-empirical method. It is found that Fuller's method can typically estimate the diffusivities within $\pm 30\%$. Therefore, in cases where the diffusivity of a trace gase has not been measured, Fuller's method can be used
15 to estimate the diffusion coefficient.

The preferred diffusivities together with estimated uncertainties are tabulated to provide a quick and simple overview of the data currently available. This compilation/evaluation is also uploaded online (<https://sites.google.com/site/mingjintang/home/diffusion>), enabling further updates when new data become available.

20 It should be noted that further measurements may change the uncertainties and/or the currently preferred values. Another aim of this work is to help indentify and highlight areas of uncertainty or lack of data, therefore stimulating further measurements. We have started to compile and evaluate the diffusion coefficients of organic species, which will be published in another review in the near future.

25

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Tables& Figures

Table 1. Dimensionless diffusion volumes of molecules and atoms of atmospheric interests. Data are taken from Table 11-1 in page 588 of Reid et al. (1987).

5

molecules				
species	N₂	O₂	He	H₂O
diffusion volume	18.5	16.3	2.67	13.1
species	NH₃	SO₂	Cl₂	Br₂
diffusion volume	20.7	41.8	38.4	69
atoms				
species	C	H	O	N
diffusion volume	15.9	2.31	6.11	4.54
species	Cl	Br	I	S
diffusion volume	21	21.9	29.8	22.9

Table 2. Summary of preferred diffusivities of atmospheric reactive trace gases in air at 296 K. Several trace gases without recommended diffusivities are also listed in this table to highlight the necessity of further measurements.

Species	Diffusivity (Torr cm ² s ⁻¹)	Species	Diffusivity (Torr cm ² s ⁻¹)
HNO ₃	87±7	NH ₃	176±10
NO	176±18	NO ₂	106±37
NO ₃	92±46	N ₂ O ₅	65±33
HONO	96±26		
SO ₂	94±13	SO ₃	91±6
H ₂ SO ₄	74±10	CH ₃ SO ₃ H	60±18
OH	178±20	HO ₂	n.m.
H ₂ O ₂	116±35	O ₃	n.m.
HOCl	n.m.	HOBr	84±9
HOI	n.m.	HCl	118±7
HBr	95±29	HI	n.m.
ClONO ₂	n.m.	ClNO ₂	85±17
BrONO ₂	n.m.		
Cl ₂	94±10	Br ₂	75±6
I ₂	53±13	BrCl	n.m.
ICl	n.m.		

5 n.m.: no measurements available.

Table 3. Summary of measured diffusivities of HNO_3 and NH_3 , and comparison with the estimated values.

Trace gas	Bath gas	Reference	T (K)	D_m	D_e	$(D_e - D_m)/D_m (\%)$
HNO_3	air	[a]	296	92±12	116	26
		[b]	296	79±8	116	47
		[c]	296	91±11	116	27
		[d]	298	90±2	116	29
		[f]	296	81±12	116	43
		[g]	298	31±1	116	274
NH_3	N_2	[h]	293	183	169	-8
		[i]	298	175	174	-1
		[i]	328	217	206	-5
		[i]	358	249	240	-4
		[j]	293	167±1	169	1
		[j]	373	258±1	257	0
		[j]	473	394±1	390	-1
		[j]	523	468±1	465	-1
		[k]	296	167±12	172	3
O_2		[h]	293	192	172	-10
		[j]	293	173±1	172	-1
		[j]	373	266±1	262	-2
		[j]	473	404±1	397	-2
air		[l]	293	173±6	172	-1
		[a]	296	180±12	167	-7
		[m]	298	173±9	169	-2

5

D_m : measured diffusivity ($\text{Tor}\text{r cm}^2 \text{s}^{-1}$); D_e : estimated diffusivity ($\text{Tor}\text{r cm}^2 \text{s}^{-1}$).

[a] (Braman et al., 1982); [b] (Eatough et al., 1985); [c] (Ferm, 1986); [d] (Durham and Stockburger, 1986); [f] (Benner et al., 1988); [g] (De Andrade et al., 1992); [h] (Trautz and Muller, 1935); [i] (Mason and Monchick, 1962); [j] (Weissman, 1964); [k] (Hanson and Kosciuch, 10 2003); [l] (Andrew, 1955); [m] (Spiller, 1989).

Table 4. Summary of measured diffusivities of NO, NO₂, NO₃, N₂O₅ and HONO, and comparison with the estimated values.

Trace gas	Bath gas	Reference	T (K)	D_m	D_e	$(D_e - D_m)/D_m (\%)$
NO	N ₂	[a]	293	176	179	2
NO ₂	N ₂	[b]	273	92	124	35
		[b]	283	98	132	35
NO ₃	N ₂	[c]	273	80±15	127	59
	O ₂	[c]	273	80±15	127	59
	He	[c]	273	345±25	510	48
	H ₂ O	[c]	273	120±15	181	50
N ₂ O ₅	N ₂	[d]	296	65	94	45
HONO	air	[e]	296	114±5	133	17
		[f]	298	78±23	135	73
	He	[g]	294	433±38	507	17
		[h]	300	490±50	525	7

5 D_m : measured diffusivity (Torr cm² s⁻¹); D_e : estimated diffusivity (Torr cm² s⁻¹).

[a] (Trautz and Muller, 1935); [b] (Chambers and Sherwood, 1937); [c] (Rudich et al., 1996); [d] (Wagner et al., 2008); [e] (Ferm and Sjodin, 1985); [f] (Benner et al., 1988); [g] (Hirokawa et al., 2008); [h] (El Zein and Bedjanian, 2012).

Table 5. Summary of measured diffusivities of SO_2 , SO_3 , H_2SO_4 , O_3 , OH , HO_2 , and H_2O_2 , and comparison with the estimated values.

Trace gas	Bath gas	Reference	T(K)	D_m	D_e	$(D_e - D_m)/D_m (\%)$
SO_2	air	[a]	263	79	78	-1
		[b]	293	85	93	9
		[c]	298	103	96	-7
SO_3	N_2	[d]	295	87 ± 8	95	9
		[e]	300	95 ± 3	98	3
H_2SO_4	N_2	[d]	295	85 ± 15	86	1
		[f]	303	67 ± 1	89	33
		[g]	298	71 ± 5	87	23
$\text{CH}_3\text{SO}_3\text{H}$	N_2	[h]	296	60	78	30
O_3	He	[i]	296	410 ± 25	522	27
OH	He	[i]	296	663 ± 25	770	16
		[j]	296	662 ± 32	770	16
		[k]	298	662 ± 32	780	18
	air	[i]	296	165 ± 20	221	34
	[k]	298	192 ± 20	224	17	
HO_2	He	[l]	296	405 ± 50	587	45
		[i]	296	430 ± 30	587	37
H_2O_2	air	[m]	333	143 ± 3	182	27

5 D_m : measured diffusivity ($\text{Torr cm}^2 \text{ s}^{-1}$); D_e : estimated diffusivity ($\text{Torr cm}^2 \text{ s}^{-1}$).

[a] (Mason and Monchick, 1962); [b] (Andrew, 1955); [c] (Fish and Durham, 1971); [d] (Lovejoy and Hanson, 1996); [e] (Jayne et al., 1998); [f] (Pöschl et al., 1998); [g] (Hanson and Eisele, 2000); [h] (Hanson, 2005); [i] (Ivanov et al., 2007); [j] (Bertram et al., 2001); [k] (Liu et al., 2009); [l] (Bedjanian et al., 2005); [m] (McMurtrie and Keyes, 1948).

Table 6. Summary of measured diffusivities of halogen species, and comparison with the estimated values.

Trace gas	Bath gas	Reference	T (K)	D_m	D_e	$(D_e - D_m)/D_m (\%)$
HOBr	He	[a]	274	319±48	356	12
		[b]	255	237±1	314	32
	N ₂	[a]	274	84±7	92	10
	H ₂ O	[b]	255	51±1	107	110
HOI	He	[c]	253	225±12	276	23
		[c]	243	191±38	258	35
	H ₂ O	[c]	253	32±2	94	194
HCl	air	[d]	296	122	131	8
	N ₂	[e]	324	132	158	19
		[e]	373	198	202	2
		[e]	423	259	252	-3
		[e]	474	318	307	-3
		[e]	523	370	365	-1
HBr	N ₂	[e]	336	119	148	24
		[e]	391	169	193	14
		[e]	425	198	223	12
		[e]	477	241	307	13
		[e]	525	277	322	16
ClNO ₂	He	[f]	275	275±26	325	18
	N ₂	[f]	275	75±6	87	16
Cl ₂	air	[g]	293	94±2	95	1
Br ₂	air	[g]	293	69±3	70	-1
		[h1]	301	80±3	73	-9
		[h2]	298	81±1	72	-11
I ₂	Air	[i]	298	63.4	74	17
	N ₂	[i]	273	53.2	65	23
ICl	He	[j]	278	289±19	284	-2
		[j]	293	296±15	311	5
	H ₂ O	[j]	278	64±10	98	53

5 D_m : measured diffusivity (Torr cm² s⁻¹); D_e : estimated diffusivity (Torr cm² s⁻¹).

[a] (Fickert et al., 1999); [b] (Adams et al., 2002); [c] (Holmes et al., 2001); [d] (Matusca et al., 1984); [e] (Mian et al., 1969); [f] (Fickert et al., 1998); [g] (Andrew, 1955); [h1] (Brockett, 1966); [h2] (Lugg, 1968); [i] (Trautz and Muller, 1935); [j] (Braban et al., 2007).

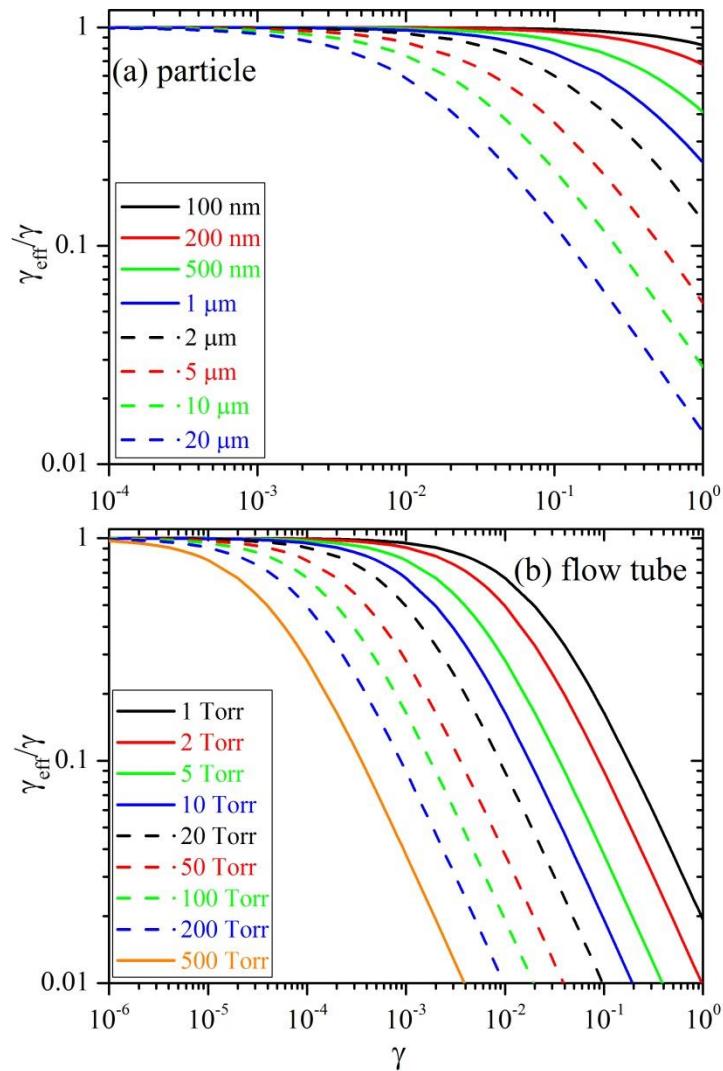


Figure 1. Influence of gas phase diffusion on the effective uptake coefficients (defined as $\gamma_{\text{eff}}/\gamma$, the ratio of the effective uptake to the true uptake coefficient) as a function of the true uptake coefficient. N_2O_5 , with a diffusion coefficient of $0.085 \text{ cm}^2 \text{ s}^{-1}$ at 760 Torr and 296 K and an average molecular speed of $24\,096 \text{ cm s}^{-1}$, is used as the representative trace gas for the calculations. (a): Uptake onto spheric particles with different diameters at 760 Torr and 296 K; (b) Uptake onto the wall of a cylindrical flow tube (inner diameter: 2.0 cm) at 296 K and at different pressures.

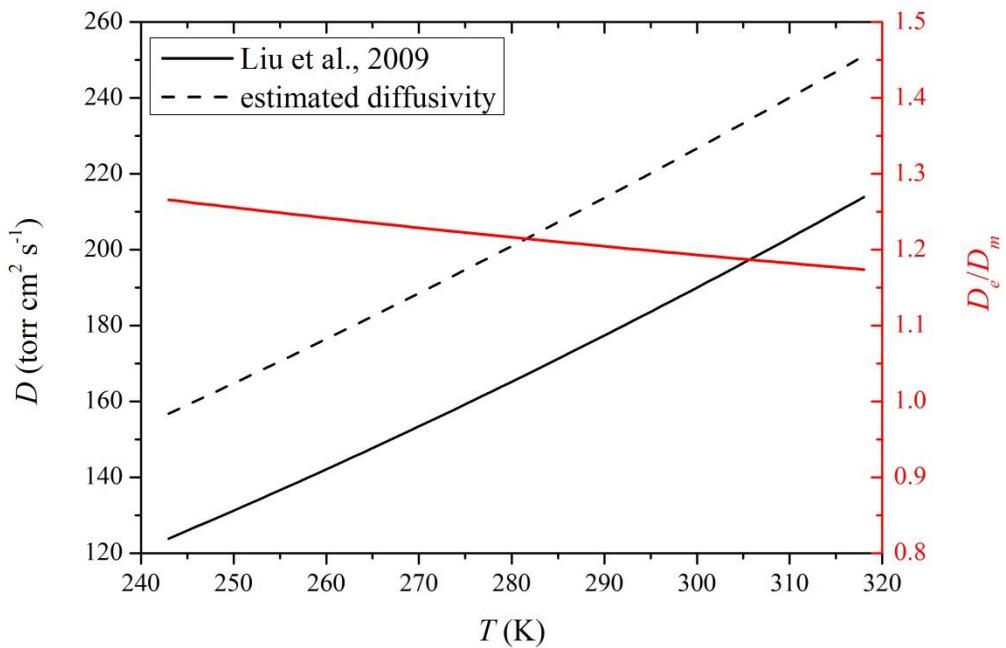


Figure 2. Temperature dependence of the diffusivity of OH radicals in air: comparison of measured diffusivity (Liu et al., 2009, black solid curve, left y-axis) with estimated values (black dashed curve, left y-axis). The ratios of estimated diffusivities to the measured ones (red curve, right x-axis) are also plotted as a function of temperature.