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Compilation and evaluation of gas-phase diffusion coefficients of inorganic reactive trace gases in the atmosphere

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Abstract

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. (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.

1 Introduction

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 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 cloud droplets (Lelieveld and Crutzen, 1990) can significantly impact the budgets of NO_x, O₃, and OH radicals. These reactions can also change the

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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).

Heterogeneous interactions of trace gases with particles in the atmosphere (and with all 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, 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., 2010):

$$\frac{d[X]_g}{dt} = -k_1[X]_g = -0.25 \cdot \gamma \cdot c(X) \cdot [SS] \cdot [X]_g \quad (1)$$

where $[X]_g$ is the concentration of X in the gas phase (molecule cm^{-3}), k_1 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 ($\text{cm}^2 \text{cm}^{-3}$).

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;

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Davidovits et al., 2011):

$$\frac{1}{r_{\text{eff}}} = \frac{1}{\gamma} + \frac{1}{\Gamma_{\text{diff}}} \quad (2)$$

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 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 (Fuchs and Sutugin, 1970):

$$\frac{1}{\Gamma_{\text{diff}}} = \frac{0.75 + 0.286Kn}{Kn \cdot (Kn + 1)} \quad (3)$$

where Kn is the Knudsen number, given by

$$Kn = \frac{6D(X)}{c(X) \cdot d_p} \quad (4)$$

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. 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. (3) and (4), the diffusion coefficient determines to which extent the effective uptake coefficient is impacted by gas phase diffusion. An accurate knowledge of the diffusion coefficient is thus important to apply the uptake coefficient to

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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 illustrated in Fig. 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 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 Fig. 1a.

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 substrates 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 given by (Hanson et al., 1992; Wagner et al., 2008):

$$\Gamma_{\text{diff}} = \frac{1}{4 \times 3.66 \cdot D(X)} \frac{c(X) \cdot d_t}{1} \quad (5)$$

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 Fig. 1b as a function of pressure (N_2).

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N_2O_5 is 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 gas phase diffusion on the overall effective uptake rate. When the true uptake coefficient is close to 0.1, as shown in Fig. 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 instead of the inner wall of the flow reactor has also been 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 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 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 vs. gaseous HNO_3 , and ammonium vs. NH_3) can be minimized (Ferm, 1986). Denuders are also widely used in laboratory 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.

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For example, the widely used chemiluminescence method to measure NO₂ is based on conversion of NO₂ to NO in a 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).

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 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 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 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 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, 1969).

The diffusivities of organic species are beyond the scope of this paper (the only included organic molecule is $\text{CH}_3\text{SO}_3\text{H}$), though we note that the uptake of organics, particularly oxygenated organics, onto aerosol particles and cloud droplets can also be important in the atmosphere. Marrero and 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 Boltzmann equation, and the diffusion coefficient can be expressed as (Reid et al., 1987):

$$D(A, B, P) = \frac{0.00266T^{1.5}}{P\sqrt{M(A, B)}\sigma^2\Omega_D} \quad (6)$$

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 integral. To derive Eq. (6), 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. (6), the values of σ and Ω_D need to be calculated/estimated. Ghosal et al. (1993) used the Lennard-Jones method to

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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 Lennard-Jones method agree well with their experimentally measured values. However, to calculate σ and Ω_D , the Lennard-Jones method require molecular parameters 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 Lennard-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 ($\text{Torr cm}^2 \text{s}^{-1}$), $D(A, B)$, sometimes called as 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.

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

$$D(A, B) = \frac{1.0868 \cdot T^{1.75}}{\sqrt{m(A, B)} (\sqrt[3]{V_A} + \sqrt[3]{V_B})^2} \quad (7)$$

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

$$m(A, B) = \frac{2}{(1/m_A + 1/m_B)} \quad (8)$$

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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 $\text{Torr cm}^2 \text{s}^{-1}$.

The dimensionless 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:

$$V = \sum n_i V_i \quad (9)$$

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.

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. (9), and it is 41.8 (as listed in Table 1) which is directly calculated from extensive experimental dataset of gas phase diffusivities of SO_2 . 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 trace gases which 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., N_2) and B2 (e.g., H_2O), can be calculated as (Reid et al., 1987; Fickert et al., 1999):

$$\frac{1}{D(A, B1, B2)} = \frac{x(B1)}{D(A, B1)} + \frac{x(B2)}{D(A, B2)} \quad (10)$$

where $x(B1)$ and $x(B2)$ are the molar fraction of B1 and B2 in the mixture, $D(A,B1,B2)$, $D(A,B1)$, and $D(A,B2)$ is the diffusivity 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 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 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 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

$$D(A,B,P) = \frac{k_w r_t^2}{3.66} \quad (11)$$

where r_t is the radius of the flow tube (Zasytkin et al., 1997). This equation is only valid for conditions under which the Peclet number, Pe , is larger than 20 (Zasytkin et al.,

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1997). Pe is given by

$$Pe = \frac{2r_t v}{D(A, B, P)} \quad (12)$$

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 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 collected on the inner wall of each sections and converted to a stable absorbate, which is then quantified offline to determine the collection efficiency, E (Ferm and Sjodin, 1985):

$$E = \frac{c_i - c_{i+1}}{c_i} \quad (13)$$

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

$$1 - E = 0.819e^{-11.489\Delta} + 0.0975e^{-70.1\Delta} - 0.0325e^{-179\Delta} \quad (E14) \quad (14)$$

$$\Delta = \frac{D(A, B, P) \cdot L}{F} \quad (E15) \quad (15)$$

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).



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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; 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 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.

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 N_2/O_2 , no adjustment was made if measurements were performed in N_2/O_2 instead of air. The diffusivities of some important reactive trace gases in air (or in N_2/O_2), e.g., HO_2 , O_3 , $HOCl$, and $ClONO_2$, 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.

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 whose results appear significantly different. However, except for a few trace gases (e.g., HNO_3 and NH_3), the diffusivities of most trace gases have only been

agree very well with more recent measurements in N_2 using flow tubes (Hanson and Kosciuch, 2003) or 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 $cm^2 s^{-1}$, 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

The diffusivities of NO , NO_2 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 , 24 % for NO_2 , and 45 % for N_2O_5 , respectively. 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 ± 10 %, ± 20 %, and ± 50 % are given to the preferred diffusivities of NO , NO_2 , and N_2O_5 , respectively, 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.

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 $cm^2 s^{-1}$, is based on the measurement of Rudich et al. (1996) at 273 K and extrapolated to 296 K using Eq. (16). 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 $cm^2 s^{-1}$ at 294 K (Hirokawa et al., 2008) and (490 ± 50) Torr $cm^2 s^{-1}$ at 300 K (El Zein and Bedjanian, 2012) using flow tubes, as listed in Table 4. The two studies are in good agreement,

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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, $(96 \pm 26) \text{ Torr cm}^2 \text{ s}^{-1}$, 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 $\text{CH}_3\text{SO}_3\text{H}$

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, $(94 \pm 13) \text{ Torr cm}^2 \text{ s}^{-1}$, is the average of the values measured by Andrew (1955) and Fish and Durham (1971) at room temperature.

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, $(91 \pm 6) \text{ Torr cm}^2 \text{ s}^{-1}$, is the average of those reported by Lovejoy and Hanson (1996) and Jayne et al. (1998).

The diffusivities of H_2SO_4 in N_2 were reported to be $(85 \pm 15) \text{ Torr cm}^2 \text{ s}^{-1}$ at 295 K (Lovejoy and Hanson, 1996), $(71 \pm 5) \text{ Torr cm}^2 \text{ s}^{-1}$ at 298 K (Hanson and Eisele, 2000), and $(67 \pm 1) \text{ Torr cm}^2 \text{ s}^{-1}$ 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. (1998) and Hanson and Eisele (2000) agree with the estimated ones reasonably well (within $\sim 30\%$). The preferred diffusivity of H_2SO_4 in N_2 at 296 K,

(74 ± 10) Torr cm² 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.

The diffusivity of CH₃SO₃H in N₂ at 296 K was determined to be 60 Torr cm² 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 CH₃SO₃H in N₂, is recommended to be (60 ± 18) Torr cm² s⁻¹, and the uncertainty associated with the preferred value reflects the difference between the measured diffusivity and the estimated one.

3.4 O₃, OH, HO₂, and H₂O₂

The diffusivity of O₃ was only measured by one flow tube study, to be (410 ± 25) Torr cm² 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 O₃ in air (or N₂/O₂) has been performed and therefore no reaccommodation can be made, despite the central importance of O₃ in the troposphere and stratosphere.

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 cm² s⁻¹, is the average of values reported by Ivanov et al. (2007) and Liu et al. (2009).

The diffusivity of HO₂ 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 HO₂ radicals in He, estimated using Fuller's method, is 40 % larger than the measured values. The diffusivity of HO₂ radicals in air (or N₂/O₂) has not been measured and thus no reaccommodation

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can be made. The uptake of HO₂ 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 a factor of 1–2 larger than the measured diffusivities in H₂O, as shown in

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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. (16), it gives a value of 113 Torr cm² s⁻¹. This agrees well with the 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 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.

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 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, 1955). Though the measurement is in excellent agreement with the estimation, an uncertainty of $\pm 10\%$ is given to the preferred value at 296 K, i.e. (94 ± 10) Torr cm² s⁻¹.

5 The diffusivities of Br₂ in air was measured to be (69 ± 3) Torr cm² s⁻¹ at 293 K (Andrew, 1955) and (80 ± 3) Torr cm² s⁻¹ at 301 K (Brockett, 1966). As shown in Table 6, both measurements are in good agreement with the estimation. The preferred diffusivity of Br₂ in air at 296 K, (75 ± 6) Torr cm² s⁻¹, is the average of the values reported by Andrew (1955) and Brockett (1966). The reported diffusivities of I₂ in air at 298 K and
10 in N₂ at 273 K (Trautz and Muller, 1935) agree reasonably well with the estimated values (with $\pm 20\%$). The preferred diffusivity of I₂ in air at 298 K, (64 ± 13) Torr cm² 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 H₂O is significantly larger than
15 that in He. Similar discrepancies were also observed for HOBr and HIO in H₂O, as discussed in Sect. 3.5.1, and this may suggest that in general Fuller's method works better for diffusivities in N₂, O₂, air, and He than that in gaseous H₂O. The diffusivity of BrCl or ICl in air/N₂/O₂ has not been reported.

3.6 Temperature dependence of diffusivities

Only a few studies measured the diffusivities of atmospheric reactive trace gases at several temperatures. The diffusivities of NH₃, HCl, and HBr in N₂ 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
25 using Fuller's method. However, the temperature ranges (300–500 K) in which the diffusivities of NH₃, HCl, and HBr were determined are of little atmospheric relevance.

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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 Fig. 2 as a function of temperature. The ratios of the estimated diffusivity to the measured one (red curve, right y axis) are also shown in Fig. 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., 2010; 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.

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 gas has not been measured, Fuller's method can be used 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. 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 identify and highlight areas of uncertainty or lack of data, therefore stimulating further measurements.

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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).

molecules				
Species	N ₂	O ₂	He	H ₂ O
	18.5	16.3	2.67	13.1
Species	NH ₃	SO ₂	Cl ₂	Br ₂
	20.7	41.8	38.4	69
atoms				
Species	C	H	O	N
	15.9	2.31	6.11	4.54
Species	Cl	Br	I	S
	21	21.9	29.8	22.9

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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	117 ± 24
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.		

n.m.: no measurements available.

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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
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	

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

^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 (2003); ^l Andrew (1955); ^m Spiller (1989).

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

Trace gas	Bath gas	Reference	<i>T</i> (K)	<i>D_m</i>	<i>D_e</i>	(<i>D_e</i> − <i>D_m</i>)/ <i>D_m</i> (%)
NO	N ₂	^a	293	176	179	2
NO ₂	N ₂	^b	298	117	145	24
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

D_m: measured diffusivity (Torr cm² s^{−1}); *D_e*: estimated diffusivity (Torr cm² s^{−1}).

^a Trautz and Muller (1935); ^b Glasius et al. (1999); ^c Rudich et al. (1996); ^d Wagner et al. (2008); ^e Fero and Sjodin (1985); ^f Benner et al. (1988); ^g Hirokawa et al. (2008); ^h El Zein and Bedjanian (2012).

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**Table 5.** Summary of measured diffusivities of SO₂, SO₃, H₂SO₄, O₃, OH, HO₂, and H₂O₂, and comparison with the estimated values.

Trace gas	Bath gas	Reference	<i>T</i> (K)	<i>D_m</i>	<i>D_e</i>	(<i>D_e</i> - <i>D_m</i>)/ <i>D_m</i> (%)
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 ₂ SO ₄	N ₂	^d	295	85 ± 15	86	1
		^f	303	67 ± 1	89	33
		^g	298	71 ± 5	87	23
CH ₃ SO ₃ 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 ₂ O ₂	air	^m	333	143 ± 3	182	27

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

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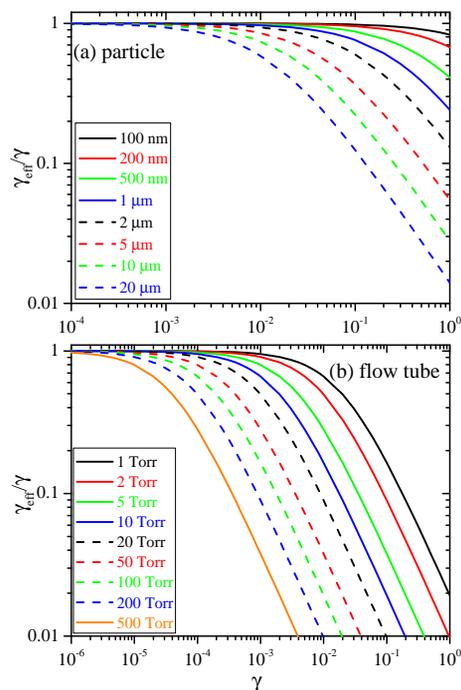


Figure 1. Influence of gas phase diffusion on the effective uptake coefficients (defined as $\gamma_{\text{eff}}/\gamma$, the ratio of the effective uptake to the true uptake coefficient) as a function of the true uptake coefficient. N_2O_5 , with a diffusion coefficient of $0.085 \text{ cm}^2 \text{ s}^{-1}$ 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 spherical 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 pressure.

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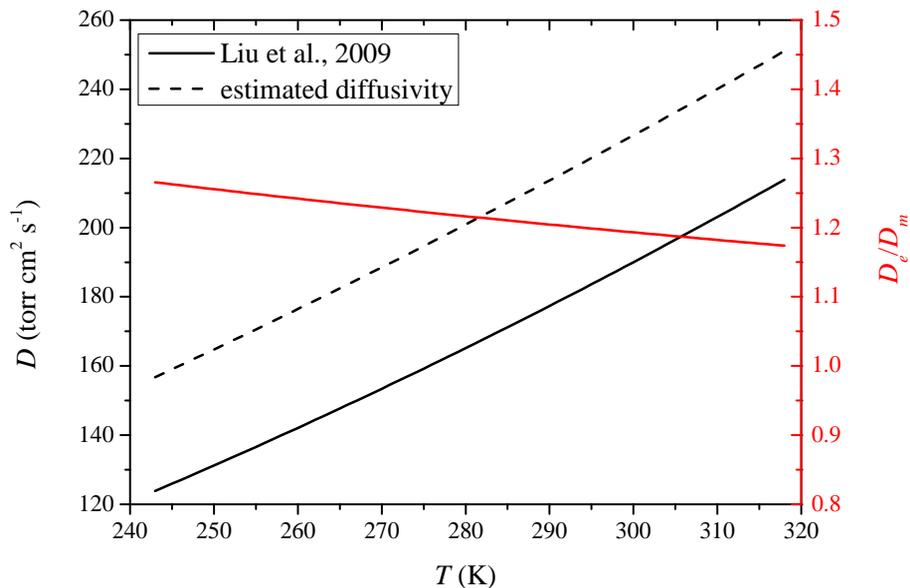


Figure 2. Temperature dependence of the diffusivity of OH radicals in air: comparison of measured diffusivities (Liu et al., 2009, black solid curve, left y axis) with estimated values (black dashed curve, left y axis). The ratios of estimated diffusivities to the measured ones (red curve, right x axis)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

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