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Compilation and evaluation of gas phase diffusion coefficients of reactive trace gases in the atmosphere: Volume 2. Diffusivities of organic compounds, pressure-normalised mean free paths, and average Knudsen numbers for gas uptake calculations

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Abstract. Diffusion of organic vapours to the surface of aerosol or cloud particles is an important step for the formation and transformation of atmospheric particles. So far, however, a database of gas phase diffusion coefficients for organic compounds of atmospheric interest has not been available. In this work we have compiled and evaluated gas phase diffusivities (pressure-independent diffusion coefficients) of organic compounds reported by previous experimental studies, and we compare the measurement data to estimates obtained with Fuller's semi-empirical method. The difference between measured and estimated diffusivities are mostly $< 10\,\%$. With regard to gas-particle interactions, different gas molecules, including both organic and inorganic compounds, exhibit similar Knudsen numbers (*Kn*) although their gas phase diffusivities may vary over a wide range. This is because different trace gas molecules have similar mean free paths in air at a given pressure. Thus, we introduce the pressure-normalised mean free path, $\lambda_P \approx 100\,\mathrm{nm\,atm}$, as a near-constant generic parameter that can be used for approximate calculation of Knudsen numbers as a simple function of gas pressure and particle diameter to characterise the influence of gas phase diffusion on the uptake of gases by aerosol or cloud particles. We use a kinetic multilayer model of gas-particle interaction to illustrate the effects of gas phase diffusion on the condensation of organic compounds with different volatilities. The results show that gas phase diffusion can play a major role in determining the growth of secondary organic aerosol particles by condensation of low-volatility organic vapours.

1 Introduction

Organic aerosols are ubiquitous in the atmosphere and can account for a dominant fraction of submicron aerosol particles (Jimenez et al., 2009). Organic aerosols affect climate by scattering and adsorbing solar and terrestrial radiation and serving as cloud condensation nuclei and ice nuclei (Kanakidou et al., 2005; Hallquist et al., 2009). Some organic aerosol components are toxic and hazardous, causing oxidative stress upon deposition into the lung (Platt et al., 2014). For better evaluation of impacts of organic aerosols on climate and public health, it is critical to know the number concentration, particle size distribution and chemical composition of organic aerosols.

Organic aerosol particles can be directly emitted into the atmosphere, and they can also be produced by condensation of semi- and low-volatility organic vapours which are directly emitted or formed by gas phase reactions between atmospheric oxidants like OH, O_3, and NO_3 with volatile organic compounds (VOCs) of biogenic and anthropogenic precursors (Robinson et al., 2007; Kroll and Seinfeld, 2008). Photo-oxidation of parent VOCs and subsequent multigeneration gas phase chemistry produce an array of semi- and low-volatility oxidation products that can partition onto pre-existing particles (Baltensperger et al., 2005; Sax et al., 2005; Donahue et al., 2014). In addition, oxidation products partitioned into the particle phase may undergo particle-phase reactions (George and Abbatt, 2010; Shiraiwa et al., 2013), forming low-volatility products such as oligomers and other high-molecular-mass products (Kalberer et al., 2004; Ziemann and Atkinson, 2012). Recently the uptake of organic compounds (e.g. CHOCHO) onto cloud droplets followed by aqueous reactions is suggested to be an important pathway for organic aerosol formation (Volkamer et al., 2009; Lim et al., 2010; Sareen et al., 2010).

The formation and transformation of atmospheric aerosol particles occurs via multiple physical and chemical steps in and between different phases (Pöschl, 2005, 2011; Rudich et al., 2007; Pöschl and Shiraiwa et al., 2015). The combination of diffusion in gas and liquid phases, surface adsorption and reaction, bulk dissolvation and reactions makes aerosol chemistry complicated and typically nonlinear (Kolb et al., 2010; Pöschl, 2011; Berkemeier et al., 2013; Shiraiwa et al., 2014).

Over the last few decades a large number of heterogeneous and multiphase reactions have been investigated (Crowley et al., 2010; Sander et al., 2011; Ammann et al., 2013), significantly improving our understanding of many important atmospheric phenomena, e.g. stratospheric ozone depletion, acid deposition, and air quality. However, many important heterogeneous processes, such as the formation and transformation of organic aerosols, are still not well quantified, and our current knowledge is not sufficient to develop process-based modules to be included in air quality, cloud, or climate models. Process-based multiphase modules have been developed to address these challenges (Pöschl et al., 2007), and reliable thermodynamic and kinetic parameters are indispensable (Kolb et al., 2010; Abbatt et al., 2014). Therefore, it is very important to develop, disseminate and maintain evaluated databases for all the parameters which may be involved in atmospheric heterogeneous and multiphase processes.

Gas phase diffusion is the first step for the condensation of organic vapours of low- and semi-volatility to existing particles (Pierce et al., 2011; Riipinen et al., 2011; Shiraiwa et al., 2014). Therefore, the gas phase diffusion coefficient is an important parameter in kinetic models of SOA (secondary organic aerosol) formation and growth (Riipinen et al., 2011; Roldin et al., 2014; Shiraiwa et al., 2014). A few previous studies have compiled gas phase diffusion coefficients of some organic compounds to evaluate the performance of different theoretical methods used to estimate diffusion coefficients (Marrero and Mason, 1972; Reid et al., 1987; Berezhnoi and Semenov, 1997). However, most of the compounds compiled previously are of limited interest to heterogeneous and multiphase chemistry in the atmosphere. We critically reviewed the gas phase diffusion coefficients of inorganic reactive trace gases in the atmosphere in our previous work (Tang et al., 2014a), and in the present work we have compiled and evaluated the gas phase diffusion coefficients of organic species. We find that different gas molecules, including both organic and inorganic compounds, have very similar Knudsen numbers, and propose a simple equation (only as a function of particle diameter and pressure) to calculate Knudsen numbers for all gas molecules. In addition, to illustrate the effects of gas phase diffusion on organic aerosol formation, the condensation of two organic compounds with distinctive volatility onto seed aerosol particles is simulated using a kinetic multilayer model for gas-particle interactions in aerosols and clouds (Shiraiwa et al., 2012; Shiraiwa and Seinfeld, 2012).

2 Gas phase diffusion coefficients

2.1 Gas-particle interaction and gas phase diffusion

The overall kinetics of a heterogeneous or multiphase reaction, is usually described by the uptake coefficient, γ, defined as the net probability that a molecule X which collides with the surface is taken up by the surface (Crowley et al., 2010). The uptake coefficient links all the chemical and physical processes on and beyond the surface with an apparent pseudo-first-order loss rate of X in the gas phase (Ammann et al., 2013; Crowley et al., 2010):

$$\frac{\mathrm{d}[X]_\mathrm{g}}{\mathrm{d}t} = -k_I[X]_\mathrm{g} = -0.25 \cdot \gamma_\mathrm{eff} \cdot c\,(X) \cdot [\mathrm{SS}] \cdot [X]_\mathrm{g}, \tag{1}$$

where $[X]_\mathrm{g}$ is the concentration of X in the gas phase (molecule cm^{-3}), k_I is the pseudo-first-order loss rate of X (s^{-1}) in the gas phase, and γ_eff is the effective uptake coefficient of X by the surface. [SS] is the surface area concentration (cm^2 cm^{-3}). For airborne aerosol particles, [SS] is usually derived from size distribution measured by instruments such as an aerodynamic particle sizer and scanning mobility particle sizer (e.g. McNeill et al., 2006; Vlasenko et al., 2009; Matthews et al., 2014; Tang et al., 2014c). $c(X)$ is the average molecular speed of X (cm s^{-1}) in the gas phase, given by

$$c\,(X) = \sqrt{\frac{8RT}{\pi M}}, \tag{2}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), and M is the molar mass of X (kg mol^{-1}).

Significant net uptake can lead to local reduction of X in the near-surface gas phase (the distance of which from the surface is comparable to the mean free path of X) compared to the average gas phase concentration of X far from the particle; therefore, the effective uptake coefficient, γ_eff, is smaller than the true uptake coefficient, γ. Under steady-state assumptions (Schwartz, 1986), a resistance formulation can be used to describe the relation between γ_eff and γ (Davidovits et al., 1995, 2006):

$$\frac{1}{\gamma_\mathrm{eff}} = \frac{1}{\gamma} + \frac{1}{\Gamma_\mathrm{diff}}, \tag{3a}$$

where Γ_diff (sometimes called the gas transport coefficient) represents the effect of gas phase diffusion and depends on the shape and dimension of the surface and the gas phase diffusion coefficient of X (Crowley et al., 2010; Tang et al., 2014a). Alternatively, a gas phase diffusion correction factor, $C_{\mathrm{g,diff}}$, can be used to describe the influence of gas phase diffusion (Pöschl et al., 2007):

$$C_{\mathrm{g,diff}} = \frac{\gamma_{\mathrm{eff}}}{\gamma} = \frac{1}{1+\gamma/\Gamma_{\mathrm{diff}}}. \tag{3b}$$

Several methods have been developed to calculate Γ_{diff} for the uptake onto a spherical particle (Pöschl et al., 2007), such as the Fuchs–Sutugin equation (Wagner et al., 2008):

$$\frac{1}{\Gamma_{\mathrm{diff}}} = \frac{0.75+0.286Kn}{Kn \cdot (Kn+1)}, \tag{4}$$

where *Kn* is the Knudsen number, calculated by

$$Kn = \frac{2\lambda(X)}{d_{\mathrm{p}}}, \tag{5a}$$

$$\lambda(X) = \frac{3D_{\mathrm{P}}(X)}{c(X)}, \tag{5b}$$

where $\lambda(X)$ is the mean free path of X (cm), D_{P} is the gas phase diffusion coefficient of X ($\mathrm{cm^2\,s^{-1}}$) at pressure of P, and d_{p} is the diameter of the spherical particle (cm). The effect of gas phase diffusion largely depends on the particle size and the uptake coefficient, as discussed in our previous work (Tang et al., 2014a). A method to calculate *Kn* for polydisperse spherical particles has also been developed (Tang et al., 2012, 2014b). In addition, equations are available to calculate Γ_{diff} for the uptake by the inner wall of cylindrical tubes (Hanson et al., 1992; Wagner et al., 2008; Tang et al., 2014a; Knopf et al., 2015).

The effect of gas phase diffusion on the overall rate of a heterogeneous reaction, as shown in Eqs. (3–5), depends on the gas phase diffusion coefficient of X, which is a function of pressure of the bath gas (Reid et al., 1987):

$$D(X) = D_{\mathrm{P}}(X) \cdot P, \tag{6}$$

where $D_{\mathrm{P}}(X)$ is the diffusion coefficient ($\mathrm{cm^2\,s^{-1}}$) of X at the pressure P (Torr), and $D(X)$ is the diffusivity ($\mathrm{Torr\,cm^2\,s^{-1}}$), sometimes also called pressure-independent diffusion coefficient of X.

2.2 Estimation of gas phase diffusivities

In theory the gas phase diffusivity can be predicted based on molecular parameters (mainly molecular masses and collisional cross sections). However, molecular collisional cross sections are not readily available for many important trace gases in the atmosphere. Several empirical and semi-empirical methods have been developed to estimate the gas phase diffusivities. A large body of experimental diffusivities have been compared to estimated values using different modelling methods (Reid et al., 1987) and it is found that, on average, estimated diffusivities using Fuller's semi-empirical method (Fuller et al., 1966, 1969) show best agreement with experimental data. Fuller's method was used in our previous work (Tang et al., 2014a) to estimate the diffusivities of inorganic compounds and is used here to estimate the diffusivities of organic compounds.

Fuller's method (Fuller et al., 1966) suggests that the diffusivity ($\mathrm{Torr\,cm^2\,s^{-1}}$) of a trace gas A in a bath gas B at the temperature T (K) can be estimated by

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

where V_{A} and V_{B} are the dimensionless diffusion volumes of A and B, and $m(\mathrm{A,B})$ is the reduced mass of the molecular pair A–B, given by

$$m(\mathrm{A,\,B}) = \frac{2}{(1/m_{\mathrm{A}}+1/m_{\mathrm{B}})}, \tag{8}$$

where m_{A} and m_{B} are the molar masses ($\mathrm{g\,mol^{-1}}$) of A and B, respectively. The diffusion volume of a molecule can be calculated by summing the diffusion volumes of all the atoms it contains:

$$V = \sum n_i V_i, \tag{9}$$

where n_i is the number of atoms (contained by the molecule) with a diffusion volume of V_i. The atomic diffusion volume is 15.9 for C, 2.31 for H, 6.11 for O, and 4.54 for N (Reid et al., 1987). In addition, the diffusion volume should be subtracted by −18.3 if the molecule contains an aromatic or heterocyclic ring. However, alicyclic rings (e.g. cyclohexane and cyclohexene) do not have effects on diffusion volumes. For example, the diffusion volume of benzene (C_6H_6) is 90.96, but it would be 109.26 if the effect of the aromatic ring (−18.3) was not taken into account. It has not been clearly stated (Reid et al., 1987) how to calculate the diffusion volumes for compounds containing more than one aromatic rings (e.g. polycyclic aromatic hydrocarbons, PAHs). Our work presented here suggests that the estimated diffusivities agree better with experimental values when only independent aromatic rings which do not share carbon atoms with other aromatic rings are accounted. However, experimental data are only available for two PAHs (naphthalene and anthracene), and naphthalene has one independent aromatic ring while anthracene has two.

Diffusion volumes calculated using Eq. (9) do not take into account the effects of different structures of isomers, which may have different collisional cross sections and thus different diffusion volumes. The measured (Cummings and Ubbelohde, 1953; Cummings et al., 1955; Hudson et al., 1960; Altshuller and Cohen, 1960; Nagata and Hasegawa, 1970) and estimated diffusivities of four isomers (cyclohexane, methyl cyclopentane, 1-hexene, and 2,3-dimethyl-2-butene) of C_6H_{12} are listed in Table A1 in the Appendix, showing good agreement between measured and estimated values. This suggests that the effect of different isomers may be of minor importance.

The diffusion volumes for a small number of molecules (mainly used as bath gases in atmospheric chemistry research) are directly given (Reid et al., 1987). For example, the diffusion volume is 18.5 for N_2, 16.3 for O_2, 19.7 for air, and 13.1 for water vapour. A complete list of atomic and molecular diffusion volumes is given by Reid et al. (1987, Table 11-1, p. 588). It should be pointed out that atomic and molecular diffusion volumes are determined by regression analysis of experimental gas phase diffusivities of a large number of molecules using Fuller's method; thus, the differences between measured and estimated diffusivities using Fuller's method may vary with molecules.

3 Evaluation guidelines

In this work we compiled and evaluated the diffusivities of organic compounds in air, N_2, and/or O_2, and the preferred diffusivities at 298 K are recommended. We do not differentiate measurements carried out in air, N_2, or O_2, because the difference is expected to be very small. For example, the estimated diffusivities of benzene at 298 K, using Fuller's method, are 69, 71, and 70 Torr $cm^2\,s^{-1}$ in air, N_2, and O_2, respectively.

An excellent indexed collection of references which reported experimental gas phase diffusivities was published by Gordon (1977), though no data were compiled. A similar collection of references of experimental diffusivities was provided by Marrero and Mason (1972), who also evaluated the gas phase diffusivities for binary mixtures mainly consisting of small gas molecules (e.g. noble gases, N_2, H_2, CO, H_2O, CO_2, etc.). Some experimental data were also compiled by Reid et al. (1987) to test the performance of different methods used to estimate diffusivities. A limited body of experimental data were collected by Berezhnoi and Semenov (1997) to compare with the estimated values using the method they developed. We have checked these three monographs (Marrero and Mason, 1972; Reid et al., 1987; Berezhnoi and Semenov, 1997) to include studies which were not indexed by Gordon (1977). Our data compilation is limited to literature in English.

The uncertainties of experimental diffusivities reported in the literature were often not clearly stated and, if reported, the stated uncertainties (typically 1–2 Torr $cm^2\,s^{-1}$) are typically smaller than the difference between different studies on the same compounds. As a result, we do not specifically provide the uncertainties of experimental diffusivities reported by individual studies. Pressure-dependent diffusion coefficients were usually reported together with the pressure under which the measurements were performed. In present work they have been converted to pressure-independent diffusivities using Eq. (6), consistent with our previous evaluation of diffusivities of inorganic compounds (Tang et al., 2014a).

The guidelines used in our evaluation of diffusivities of inorganic compounds (Tang et al., 2014a) are also adopted here. If the diffusivity of one compound was measured by several studies, the preferred diffusivity is given as the average of the measured values at 298 K and the given uncertainty is the corresponding standard deviation. Studies whose results appear significantly different from others are not included in the average. If the measurement was not carried out at 298 K, the measured diffusivity was extrapolated to 298 K, using the temperature dependence suggested by Fuller's method, i.e.

$$D(298) = D(T) \cdot \frac{298^{1.75}}{T^{1.75}}, \quad (10)$$

where $D(T)$ is the measured diffusivities at T and $D(298)$ is the extrapolated diffusivity at 298 K. The temperature dependence of diffusivities and rationality of using Eq. (10) for extrapolation are further discussed in Sect. 4.1.

A few examples, shown in Table A2 in the Appendix, are provided here to illustrate how the data are evaluated. The diffusivities of 1-propanol were measured by four different studies (Gilliland, 1934; Lugg, 1968; Arnikar and Ghule, 1969; Nagata and Hasegawa, 1970). The measurement at 298 K by Lugg (1968) agrees well with those extrapolated to 298 K from the measurements at 299 K by Gilliland (1934), at 358 K by Arnikar and Ghule (1969), and at 363 K by Nagata and Hasegawa (1970). The preferred diffusivity at 298 K, (79±5) Torr $cm^2\,s^{-1}$, is the average of those measured at or extrapolated to this temperature, and the estimated value (75 Torr $cm^2\,s^{-1}$) using Fuller's method agrees with the preferred value within the given uncertainty.

If the standard deviation of the measurements is smaller than the difference between preferred and estimated diffusivities using Fuller's method, then the given uncertainty reflects the difference between the preferred and estimated diffusivities. For example, the diffusivity of 2-pentanol was measured by two studies (Gilliland, 1934; Lugg, 1968), and the preferred diffusivity at 298 K (54 Torr $cm^2\,s^{-1}$) is the average of the measurement at 298 K by Lugg (1968) and that extrapolated to 298 K from the measurement at 299 K by Gillaland (1934). Since the standard deviation of two measurements ($\sim$1 Torr $cm^2\,s^{-1}$) is smaller than the difference (8 Torr $cm^2\,s^{-1}$) between the preferred (54 Torr $cm^2\,s^{-1}$) and estimated (62 Torr $cm^2\,s^{-1}$) diffusivities at 298 K, an uncertainty of ± 8 Torr $cm^2\,s^{-1}$ is given to the preferred value, i.e. (54 ± 8) Torr $cm^2\,s^{-1}$.

The diffusivities of many species included in this work were only measured once. If the only measurement was carried out at 298 K, the measured value is temporarily preferred, and the given uncertainty is equal to the difference between the measured and estimated values. For example, the diffusivity of 1,3-butadiene at 298 K was measured to be 88 Torr $cm^2\,s^{-1}$, which is 10 Torr $cm^2\,s^{-1}$ smaller than the estimated value. Therefore, the preferred diffusivity of 1,3-butadiene, is recommended to be (88 ± 10) Torr $cm^2\,s^{-1}$. If

Table 1. Summary of preferred diffusivities (D, Torr cm^2 s^{-1}) at 298 K: alkanes, cycloalkanes, alkenes, alkynes, and aromatic hydrocarbons. The uncertainties given to preferred values are explained in Sect. 3.

Species	D	Species	D	Species	D
alkanes and cycloalkanes					
methane	168 ± 5	ethane	114 ± 5	propane	87 ± 5
n-butane	75 ± 3	methyl propane	71 ± 3	*n*-pentane	65 ± 2
2-methyl pentane	71 ± 6	2,2-dimethyl propane	67 ± 2	*n*-hexane	59 ± 3
2,3-dimethyl butane	60 ± 2	*n*-heptane	55 ± 2	2,4-dimethyl pentane	55 ± 2
n-octane	50 ± 4	2,2,4-trimethyl pentane	53 ± 2	*n*-nonane	44 ± 4
n-decane	44 ± 2	2,3,3-trimethyl heptane	52 ± 8	*n*-dodecane	37 ± 4
n-hexadecane	31 ± 5	*n*-heptadecane	32 ± 5	*n*-octadecane	32 ± 5
cyclopropane	97 ± 7	cyclopentane	70 ± 8	cyclohexane	63 ± 4
methylcyclopentane	62 ± 2				
alkenes and alkynes					
ethene	124 ± 5	propene	100 ± 10	1-butene	83 ± 10
cis-2-butene	83 ± 10	trans-2-butene	83 ± 10	2-methyl propene	83 ± 10
1-pentene	73 ± 6	1-hexene	61 ± 2	2,3-dimethyl-2-butene	61 ± 2
1-octene	49 ± 2	propadiene	106 ± 13	1,3-butadiene	88 ± 10
isoprene	73 ± 6	1,5-hexadiene	61 ± 2	2,3-dimethyl-1,3 -butadiene	61 ± 2
ethyne	111 ± 12	propyne	100 ± 7	1-butyne	88 ± 10
aromatic hydrocarbons					
benzene	72 ± 3	toluene	67 ± 4	ethyl benzene	57 ± 1
o-xylene	55 ± 2	*m*-xylene	52 ± 5	*p*-xylene	51 ± 6
n-propyl benzene	51 ± 2	iso-propyl benzene	51 ± 2	1,2,4-trimethyl benzene	49 ± 4
1,3,5-trimethyl benzene	50 ± 3	*p*-cymene	48 ± 1	*p*-tert-butyltoluene	43 ± 6
styrene	53 ± 5	naphthalene	46 ± 5	diphenyl	52 ± 7
anthracene	40 ± 4				

the only measurement was not performed at 298 K, the preferred value (as well as its uncertainty) is given as that extrapolated to 298 K from the measured value, using Eq. (10). For example, the diffusivity of isoprene (Table A2) at 288 K was measured to be (69 ± 5) Torr cm^2 s^{-1} at 288 K (Altshuller and Cohen, 1960), and this gives a preferred value of (73 ± 6) Torr cm^2 s^{-1} at 298 K. In addition, if the difference between the measured and estimated diffusivities is larger than a factor of 2, the compound is still listed in Tables 1–3 but without a preferred diffusivity.

Experimental methods used to measure diffusivities were reviewed by Marrero and Mason (1972), with critical discussion of the advantages and disadvantages of these methods. The two methods (i.e. coated wall flow tubes and denuders) used to measure diffusivities of inorganic compounds in the atmospheric chemistry community (Tang et al., 2014a) have not been applied to organic species yet. It is recommended for future work to use one or both of these two methods to measure the diffusivities of organic reactive trace gases important for atmospheric heterogeneous and multiphase chemistry.

4 Summary of preferred diffusivities

The preferred diffusivities at 298 K in air (or N_2 / O_2) are summarised in Tables 1–3 to provide a quick overview. Table 1 lists the preferred diffusivities of 21 alkanes, 4 cycloalkanes, 15 alkenes (including 5 dienes), 3 alkynes, and 16 aromatic hydrocarbons. Preferred diffusivities of 16 alcohols, 2 glycols, 4 ethers, 5 ketones, 8 carboxylic acids, and 9 multifunctional species (only containing C, H, and O) are provided in Table 2. Table 3 summarises the preferred diffusivities of 39 esters and 15 nitrogen-containing species. The diffusivity of CH_3SO_3H has been reviewed in our previous work (Tang et al., 2014a). The diffusivities of organic halogens are not included because their interactions with surfaces are expected to be unimportant in the troposphere and stratosphere, although some experimental data are available (Gordon, 1977).

A comprehensive and detailed 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 provided as Supplement. The supplement contains comparisons between the measured and estimated diffusivities for each measure-

Table 2. Summary of preferred diffusivities (D, Torr cm^2 s^{-1}) at 298 K: alcohols, glycols, ethers, ketones, acids, and multifunctional species. The uncertainties given to preferred values are explained in Sect. 3.

Species	D	Species	D	Species	D
alcohols and glycols					
methanol	126 ± 11	ethanol	98 ± 7	1-propanol	75 ± 4
2-propanol	79 ± 5	1-butanol	66 ± 1	2-butanol	67 ± 1
methyl 1-propanol	67 ± 2	methyl-2-propanol	66 ± 3	1-pentanol	54 ± 8
2-pentanol	54 ± 8	1-hexanol	47 ± 10	2-ethyl-1-butanol	50 ± 7
1-methyl-2-pentanol	47 ± 10	1-heptanol	42 ± 10	1-octanol	38 ± 11
prop-2-en-1-ol	78 ± 3	ethylene glycol	76 ± 10	propylene glycol	67 ± 7
ethers					
diethyl ether	70 ± 1	di-iso-propyl ether	52 ± 5	di-*n*-butylether	41 ± 8
1,4-dioxane	70 ± 3				
ketones					
acetone	81 ± 5	methyl ethyl ketone	69 ± 2	methyl *n*-propyl ketone	60 ± 3
4-methyl pent-3-en-2-one	58 ± 1	isophorone	46 ± 3		
acids					
formic acid	116 ± 4	acetic acid	94 ± 5	propanoic acid	72 ± 4
n-butyric acid	59 ± 8	2-methyl propanoic acid	60 ± 7	3-methyl butanoic acid	50 ± 10
hexanoic acid	46 ± 10	4-methyl pentanoic acid	45 ± 11		
multifunctional species					
2-methoxy ethanol	67 ± 7	2-ethoxy ethanol	60 ± 5	diethylene glycol	55 ± 8
triethylglycol	45 ± 10	2-(2-ethoxye thoxy) ethanol	46 ± 7	furfural	66 ± 4
4-hydroxyl-4-methyl-2-pentanone	49 ± 7	2-ethoxy ethyl acetate	46 ± 8	methyl salicylate	62 ± 10

ment. It is also available online (https://sites.google.com/site/mingjintang/home/diffusion) and will be updated when new data become available. Torrs per square centimetre per second (Torr cm^2 s^{-1}) is always used as the unit of diffusivities in this paper and in the Supplement. The differences between the measured and estimated diffusivities are typically $< 10\,\%$ for most of the compounds included in this work, suggesting that Fuller's method can be used to estimate the diffusivities (in air, N_2, and/or O_2) of organic species if experimental data are not available.

However, larger discrepancies also occur. For example, the diffusivities of carboxylic acids were only measured once at 298 K (Lugg, 1968). The estimated diffusivities are ∼ 5 % smaller than measured values for formic acid and acetic acid, 5 % larger than measured values for propionic acid, ∼ 13 % larger than measured values for acids containing four carbon atoms (*n*-butyric acid and 2-methyl propionic acid), and ∼ 20 % larger than measured values for acids containing five or six carbon atoms (3-methyl butanoic acid, hexanoic acid, and 4-methyl pentanoic acid). The discrepancies appear to increase with the number of carbon atoms these organic acids contain. It is not clear whether this is due to (1) that the measurement errors increase with carbon atoms, (2) that the estimation errors increase with carbon atoms, or (3) the combination of both.

The diffusivities of many (if not most) species included in this work, especially for O and N containing compounds with more than four carbon atoms which are of more interest for heterogeneous and multiphase reactions in the atmosphere, have only been measured once, and further measurements in future will help reduce the uncertainties. The estimated diffusivities of glyoxal (CHOCHO; Liggio et al., 2005; Lim et al., 2013), methyl vinyl ketone (C_4H_6O; Liu et al., 2013), trans-β-isoprene epoxydiols ($C_4H_8O_3$, Surratt et al., 2010; Nguyen et al., 2014), pinonic acid ($C_{10}H_{16}O_3$, Capouet et al., 2004), and two low-volatility compounds formed in the oxidation of α-pinene ($C_{10}H_{16}O_5$ and $C_{20}H_{32}O_{12}$, Ehn et al., 2014), which all contribute significantly to SOA formation, are 93, 73, 64, 44, 42, and 19 Torr cm^2 s^{-1}, respectively, using Fuller's method.

Temperature dependence

Temperatures of tropospheric and stratospheric interest range from ∼ 200 to ∼ 300 K. However, most of the diffusivity measurements were only carried out at around room temperature. For those studies in which the effect of tempera-

Table 3. Summary of preferred diffusivities (D, Torr cm^2 s^{-1}) at 298 K: esters and N-containing species. The uncertainties given to preferred values are explained in Sect. 3.

Species	D	Species	D	Species	D
		esters			
methyl formate	83 ± 6	ethyl formate	76 ± 2	methyl acetate	85 ± 10
propyl formate	63 ± 4	ethyl acetate	67 ± 6	methyl propionate	66 ± 1
2-methylpropyl formate	60 ± 1	propyl acetate	58 ± 2	2-methylethyl acetate	59 ± 1
ethyl propionate	61 ± 3	methyl *n*-butyrate	57 ± 3	methyl isobutyrate	57 ± 3
n-pentyl formate	50 ± 6	iso-pentyl formate	51 ± 5	*n*-butyl acetate	51 ± 5
2-methylpropyl acetate	52 ± 4	ethyl *n*-butyrate	51 ± 5	ethyl isobutyrate	51 ± 5
methyl *n*-pentanoate	51 ± 5	*n*-pentyl acetate	46 ± 6	*n*-butyl propionate	46 ± 6
iso-butyl propionate	46 ± 6	*n*-propyl *n*-butyrate	46 ± 6	*n*-propyl-iso-butyrate	47 ± 5
iso-propyl-iso-butyrate	48 ± 4	ethyl *n*-pentanoate	46 ± 6	methyl hexanonate	46 ± 6
n-pentyl propionate	42 ± 6	iso-butyl *n*-butyrate	42 ± 6	iso-butyl iso-butyrate	42 ± 6
iso-propyl *n*-pentanoate	42 ± 6	*n*-pentyl *n*-butyrate	37 ± 9	*n*-pentyl iso-butyrate	38 ± 8
iso-butyl *n*-pentanoate	38 ± 8	benzyl acetate	46 ± 4	dipentyl sebacate	n. p. r
diethyl phthalate	38 ± 4	di-*n*-butyl phthalate	26 ± 3	di-2-ethylhexyl phthalate	32 ± 4
		N-containing species			
n-butylamine	66 ± 3	iso-butylamine	68 ± 1	diethylamine	75 ± 6
triethylamine	57 ± 1	aniline	56 ± 6	ethyl diamine	77 ± 8
benzidine	n. p. r.	dimethyl formamide	74 ± 2	ethyl cyanoacrylate	54 ± 2
nitrobenzene	60 ± 5	HCN	153 ± 14	acrylonitrile	80 ± 7
benzonitrile	54 ± 8	pyridine	72 ± 1	piperidine	66 ± 3

n. p. r.: no preferred value is recommended because the difference between the measured and estimated diffusivity is larger than a factor of 2.

ture was investigated, they were usually performed at temperatures > 300 K. The measured diffusivities of 2-propanol (Gilliland, 1934; Lugg, 1968; Arnikar and Ghule, 1969; Nagata and Hasegawa, 1970), benzene (Lee and Wilke, 1954; Hudson et al., 1960; Altshuller and Cohen, 1960; Getzinger and Wilke, 1967; Lugg, 1968; Katan, 1969; Arnikar and Ghule, 1969; Nagata and Hasegawa, 1970), *n*-pentane (Lugg, 1968; Barr and Watts, 1972; Nagasaka, 1973), and ethyl formate (Lugg, 1968; Nagata and Hasegawa, 1970) are plotted as a function of temperature in Fig. 1, together with the estimated diffusivities (black curves) using Fuller's method. All the measurements show good agreement with estimations from ∼ 290 to ∼ 400 K for 2-propanol, benzene, and ethyl format. The diffusivities of *n*-pentane were measured from < 260 to ∼ 300 K (Lugg, 1968; Barr and Watts, 1972; Nagata and Hasegawa, 1970), which are of direct relevance for atmospheric chemistry, and the measured diffusivities agree very well with the estimated values. Therefore, we conclude that Fuller's method, i.e. Eqs. (7), (10), can also be used to estimate the diffusivities at different temperatures when experimental data are unavailable.

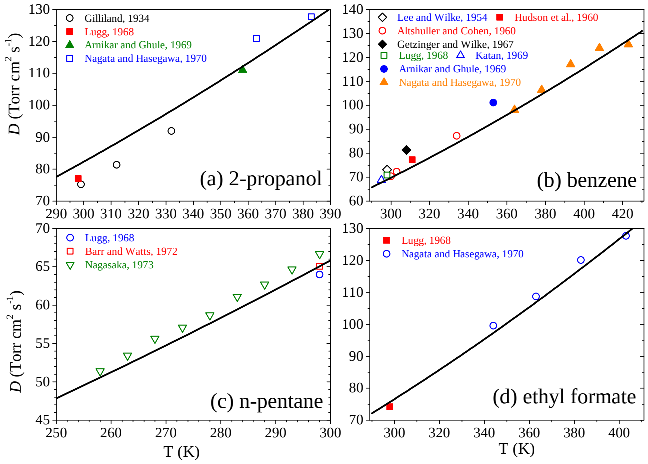

Figure 1. Comparison of measured diffusivities with estimated values (black curves) as a function of temperature using Fuller's semi-empirical method. **(a)** 2-propanol; **(b)** benzene; **(c)** *n*-pentane; and **(d)** ethyl formate.

5 Mean free paths and Knudsen numbers

Figure 2 shows the calculated Knudsen number (Kn) at 298 K and 1 atm air for the uptake of four select organic compounds onto spheric particles as a function of particle diameter using Eqs. (5a) and (5b), with gas phase diffusivities estimated using Fuller's method (Eqs. 7–9). The four organic compounds, glyoxal (Lim et al., 2013), methyl vinyl ketone (MVK) (Liu et al., 2013), and two highly oxidised and extremely low-volatility volatile organic compounds, i.e. $C_{10}H_{16}O_5$ and

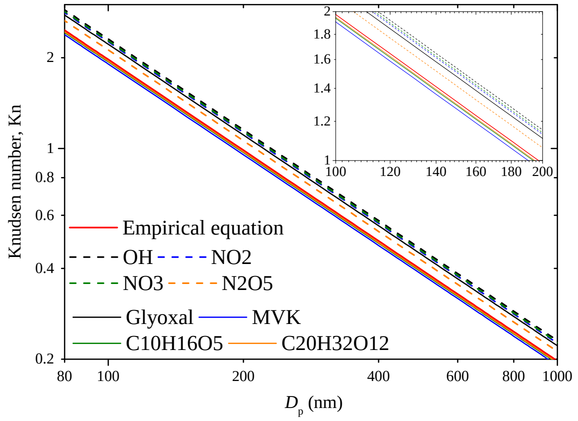

Figure 2. Knudsen numbers (*Kn*) for the uptake of four organic compounds (glyoxal, MVK, $C_{10}H_{16}O_5$, $C_{20}H_{32}O_{12}$) and four inorganic compounds (OH, NO_2, NO_3, and N_2O_5) onto aerosol particles as a function of particle diameter in 760 Torr air. Knudsen numbers calculated using the empirical equation (Eq. 11) we propose in this work are also plotted.

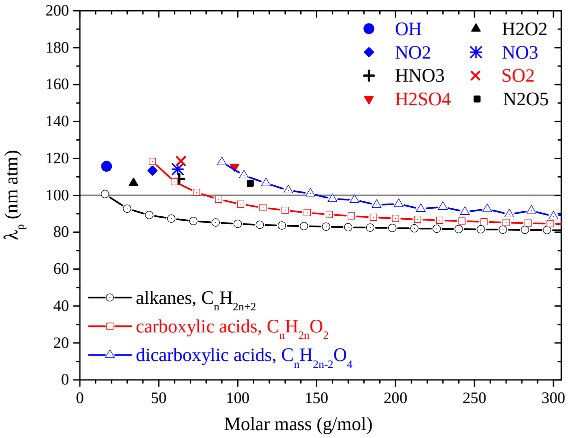

Figure 3. Mean free paths for different inorganic and organic species in 1 atm air. Three types of organic compounds (alkanes, carboxylic acids and dicarboxylic acids) containing different numbers of carbon atoms are plotted.

$C_{20}H_{32}O_{12}$ (Ehn et al., 2014), were chosen because their uptake onto aerosol particles and/or cloud droplets may significantly contribute to organic aerosol formation. For a given particle diameter, *Kn* depends on the average mean free path (Eq. 5a), which is determined by the ratio of the diffusion coefficient to the average molecular speed (Eq. 5b). The average molecular speed is proportional to the reciprocal of the square root of the molecular mass, as shown in Eq. (2). On the other hand, the diffusion coefficient also decreases with increasing molecular mass as bigger molecules move more slowly and have larger collisional cross sections (Eqs. 7–9). As a result, the effect of molecular masses largely cancels out for the mean free paths (λ) and *Kn* and, consequently, these molecules exhibit very similar λ and *Kn* values (relative deviations $< 20\,\%$) although their molecular masses vary by an order of magnitude.

As illustrated in Fig. 2, the similarity of *Kn* values for different trace gas species does not only apply to organic compounds. It also extends to inorganic species like OH, NO_2, NO_3, or N_2O_5, which are important for atmospheric heterogeneous and multiphase chemistry. At any given particle diameter, the relative deviation between the *Kn* values for both organic and inorganic trace gases considered in Fig. 2 are less than 20 %. Note that we used measured diffusivities to calculate *Kn* for these inorganic species because Fuller's method is primarily based on and aimed at organic compounds and tends to overestimate the diffusivities of small inorganic molecules (Tang et al., 2014a). Using diffusivities estimates from Fuller's method, the *Kn* values of the inorganic species would be 35–50 % higher. The reason why the performance of Fuller's method is better for organic compounds than for inorganic compounds is that the atomic diffusion volumes used in Eqs. (7)–(9) to estimate the molecular gas phase diffusivities have been generated by regression analysis of measured diffusion coefficients of many molecules, most of which are organic compounds.

We can then derive a simplified equation to calculate *Kn* as a function of particle diameter and pressure for all gas molecules. As we discussed, different gas molecules have very similar mean free paths, λ. We calculated λ for a variety of inorganic and organic molecules. As shown in Fig. 3, the mean free paths are approximately equal to 100 nm (with deviations $< 20\,\%$) at 1 atm air for all these molecules considered. As a result, we introduce the pressure-normalised mean free path, λ_P, which is equal to 100 nm atm, as a near-constant generic parameter. Equation (5a) can then simplified to

$$Kn = \frac{2}{d_p} \cdot \frac{\lambda_P}{P}, \tag{11}$$

where P is pressure of air in atm. As shown in Fig. 3, the errors in λ_P (and thus *Kn*) are estimated to be $< 20\,\%$. When the true uptake coefficient is 1, the uncertainty in the calculated effective uptake coefficient (caused by the uncertainty in *Kn*) is $< 10\,\%$ for 200 nm particles, increases to $\sim 16\,\%$ for 1 µm particles and $\sim 19\,\%$ for 10 µm particles. The reason is that the role of gas phase diffusion increases with particle diameters. The uncertainty in the derived effective uptake coefficients will decrease if the true uptake coefficients are smaller than 1. The simplified method we propose here to take into account the effect of gas phase diffusion has the potential to reduce computational expenses in atmospheric models, especially in regional or global models including process-based gas-particle interactions.

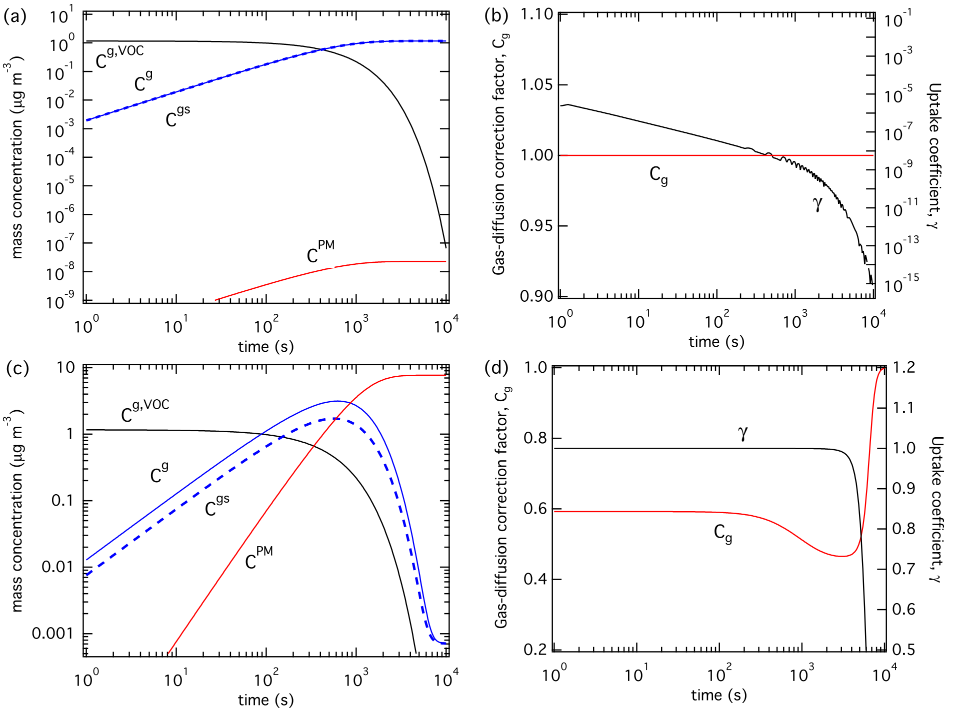

Figure 4. Temporal evolution of mass concentrations of the parent VOC in the gas phase ($C^{\mathrm{g,VOC}}$, black), the hypothesised VOC oxidation product as in the gas phase (C^{g}, solid blue), in the near-surface gas phase (C^{gs}, dashed blue), and in the particle phase (C^{PM}, red) for MVK **(a)** and $C_{20}H_{32}O_{12}$ **(c)**. Temporal evolution of gas phase diffusion correction factor ($C_{\mathrm{g,diff}}$, $\gamma_{\mathrm{eff}} / \gamma$, red curve) and uptake coefficient (γ, black curve) for MVK **(b)** and $C_{20}H_{32}O_{12}$ **(d)**.

6 Atmospheric implications

To demonstrate the effects of gas phase diffusion on organic aerosol formation, the condensation of two organic compounds onto seed aerosol particles is simulated using the kinetic multilayer model for gas-particle interaction in aerosols and clouds (KM-GAP) (Shiraiwa et al., 2012; Shiraiwa and Seinfeld, 2012). It is assumed in the simulations that the parent VOC with an initial concentration of 1×10^{10} molecule cm^{-3} (~ 0.4 ppbv) is converted to a first-generation semi-volatile product (in this study, MVK or $C_{20}H_{32}O_{12}$) with a lifetime of 10 min. The first-generation product then partitions into the seed particles, leading to particle growth. Conversion of the first-generation product to higher-generation products, particle-phase reactions and nonideal mixing are not considered here for simplicity. The initial seed aerosols are assumed to consist of mono-disperse particles with a diameter of 300 nm and a number concentration of 1×10^4 cm^{-3}. Kinetic parameters used in the simulations include surface accommodation coefficient ($\alpha_{\mathrm{s,0}}$: 1.0), desorption lifetime (τ_{d}: 1×10^{-6} s), and bulk diffusion coefficient (D_{b}: 1×10^{-5} cm^2 s^{-1}) assuming that particle phase state is liquid. The volatility is estimated to be 2×10^8 μg m^{-3} for MVK using the EVAPORATION model (Compernolle et al., 2011). Volatility of $C_{20}H_{32}O_{12}$ is highly uncertain and it is assumed to be 1×10^{-3} μg m^{-3}.

Figure 3a and b show the results of such simulation for MVK as oxidation products. The temporal evolution of mass concentration of the parent VOC ($C^{\mathrm{g,VOC}}$, black), and the oxidation product in the gas phase (C^{g}, solid blue), in the near-surface gas phase (C^{gs}, dotted blue) and in the particle phase (C^{PM}, red, i.e. SOA mass) are displayed. Mass concentrations (μg m^{-3}) are typically used for species contained in the particle phase. In this section we use mass concentrations (μg m^{-3}) instead of molecular number concentrations (molecule cm^{-3}) for species in the gas phase so that the concentrations of oxidation products in both phases have the same unit and thus are directly comparable. As the parent VOC is converted to MVK, C^{g} and C^{gs} increase simultaneously and C^{PM} increases due to condensation. $C^{\mathrm{g}} \approx C^{\mathrm{gs}}$ translates into $C_{\mathrm{g,diff}} = \gamma_{\mathrm{eff}}/\gamma \approx 1$, as shown in Fig. 3b, indicating that there is no kinetic limitation by gas phase diffusion. It results from the low value of the uptake coefficient ($\gamma < 1 \times 10^{-5}$), as the desorption (or evaporation) flux is almost as large as the adsorption (or condensation) flux due to the high volatility of MVK.

The results for $C_{20}H_{32}O_{12}$ are shown in Fig. 3c and d. Due to low volatility of $C_{20}H_{32}O_{12}$, the uptake coefficient stays at 1 during the course of SOA growth. Consequently, near-surface gas phase is depleted due to rapid uptake ($C^{\mathrm{gs}} < C^{\mathrm{g}}$) by ~ 40 % (i.e. $C_{\mathrm{g,diff}} = \sim 0.6$) during initial growth up to ~ 100 s. Afterwards, the particle diameter increases gradually to ∼ 440 nm, resulting in a lower $C_{g,diff}$ value of ∼ 0.45. Additional model simulations with different seed particle size revealed that larger particle size leads to lower $C_{g,diff}$ value. A relatively low value of $C_{g,diff}$ suggests that gas phase diffusion plays a major role in determining the overall rate of condensation of organic vapours onto seed particles, thus emphasising the importance of gas phase diffusion in the growth of organic aerosol particles.

As discussed in our previous work (Tang et al., 2014a), the effect of gas phase diffusion increases with particle size and uptake coefficients. In our simulation the uptake of compounds in the gas phase by aerosol particles is driven by their condensation onto particles. Therefore, compounds with lower volatilities exhibit larger uptake coefficients and thus the effect of gas phase diffusion becomes more important. If the uptake coefficients for high-volatility compounds (e.g. glyoxal, methylglyoxal, and aldehydes in general) are large due to reactions in the particle phase (for example, Liggio et al., 2005; Volkamer et al., 2009; Ziemann and Atkinson, 2012), gas phase diffusion may significantly influence their removal from the gas phase and the formation of secondary organic matters in the particle phase.

7 Conclusions

Gas phase diffusion coefficients of organic compounds reported in previous literature have been compiled and evaluated. The reviewed organic compounds include 21 alkanes, 4 cycloalkanes, 15 alkenes (including 5 dienes), 3 alkynes, 16 aromatic hydrocarbons, 16 alcohols, 2 glycols, 4 ethers, 5 ketones, 8 carboxylic acids, 9 multifunctional species, 39 esters, and 15 nitrogen-containing species. The experimental values are then compared with estimated ones using Fuller's semi-empirical method (Fuller et al., 1966). In general, Fuller's method can predict the diffusion coefficients with errors of $< 10\,\%$. The temperature dependence of diffusion coefficients has also been discussed, and it is found that Fuller's method can reproduce the measured diffusion coefficients very well across a wide range of temperature.

We suggest that all the compounds have very similar mean free paths and thus exhibit very similar Knudsen numbers (*Kn*) for the uptake onto particles, though they may have very different gas phase diffusion coefficients. We have introduced a new near-constant generic parameter, pressure-normalised mean free path (λ_P) to derive a simple equation, Eq. (11), which calculates *Kn* only as a function of particle diameter and pressure for all different gas molecules. This simplification could reduce the computational expense, especially for regional and global models with process-based gas-particle interactions.

We have also simulated the condensation of two organic compounds (MVK and $C_{20}H_{32}O_{12}$) with very different gas phase diffusion coefficients and volatilities onto seed aerosol particles, using the KM-GAP model. The results suggest that gas phase diffusion largely controls the condensation of low-volatility compounds like $C_{20}H_{32}O_{12}$ and thus the growth of secondary organic aerosol particles, highlighting the importance of taking into account gas phase diffusion for reliable prediction of organic aerosol formation and transformation.

It should be noted that most of the compounds for which the experimental diffusion coefficient data are available are relatively small molecules. However, the uptake of multifunctional (and thus big) organic molecules onto aerosol particles and cloud droplets is of more significance for organic aerosol formation and transformation, due to their low volatilities. Further measurements of gas phase diffusion coefficients of compounds which may directly contribute to organic aerosol formation in the troposphere is undoubtedly needed to further assess whether the simple equation we developed here to calculate *Kn* also applies to such complex organic compounds.

The preferred gas phase diffusivities (pressure-independent diffusion coefficients) at 298 K in air (or N_2 / O_2) are summarised in Tables 1–3. A comprehensive 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 provided as Supplement. It is available online (https://sites.google.com/site/mingjintang/home/diffusion) and will be updated when new experimental data become available.

Appendix A

Table A1. Measured and estimated diffusivities of fours isomers with a formula of C_6H_{12}: cyclohexane, methyl cyclopentane, 1-hexene, and 2,3-dimethyl-2-butene. The unit for diffusivities is Torr cm^2 s^{-1}.

Species	Reference	T (K)	D_m (T)	D_m (298)	D_e (T)	$D_e/D_m - 1$ (%)
cyclohexane	Cummings and Ubbelohde (1953)	289	58	61	57	−1
	Hudson et al. (1960)	289	57	60	57	1
	Nagata and Hasegawa (1970)	363	94	67	85	−10
		383	102	66	93	−9
		403	113	67	102	−10
methyl cyclopentane	Cummings and Ubbelohde (1953)	286	58	62	56	−3
1-hexene	Altshuller and Cohen (1960)	293	60	62	58	−3
2,3-dimethyl-2-butene	Cummings et al. (1955)	288	57	60	57	0

T: temperature (in K) under which the measurement was performed; D_m (T): measured diffusivity at T; D_m (298): measured diffusivity at 298 K, or extrapolated to 298 K using Eq. (10) from the measurement carried out at T; $D_e(T)$: estimated diffusivity at T using Fuller's semi-empirical method; $D_e/D_m - 1$: relative difference (in %) between the measured and estimated diffusivities at T.

Table A2. Measured and estimated diffusivities of 2-propanol, 2-pentanol, 1,3-butadiene, and isoprene, and comparison with estimated values. The unit for diffusivities is Torr cm^2 s^{-1}.

Species	Reference	T (K)	D_m (T)	D_m (298)	D_e (T)	$D_e/D_m - 1$ (%)
2-propanol	Gilliland (1934)	299	75	75	79	5
		312	81	75	85	5
		332	92	76	95	3
	Lugg (1968)	298	77	77	79	3
	Arnimar and Ghule (1969)	358	111	80	109	−2
	Nagata and Hasegawa (1970)	363	121	86	111	−8
		383	128		122	−4
2-pentanol	Gilliland (1934)	299	54	54	62	15
		312	58	53	67	16
		332	65	54	75	15
	Lugg (1968)	298	55	55	62	12
1,3-butadiene	Elliott and Watts (1972)	298	88	88	78	−11
isoprene	Altshuller and Cohen (1960)	288	69	73	64	−7

T: temperature (in K) under which the measurement was performed; $D_m(T)$: measured diffusivity at T; D_m (298): measured diffusivity at 298 K, or extrapolated to 298 K using Eq. (10) from the measurement carried out at T; $D_e(T)$: estimated diffusivity at T using Fuller's semi-empirical method; $D_e/D_m - 1$: relative difference (in %) between the measured and estimated diffusivities at T.

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