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A new modeling tool for the diffusion of gases in ice or amorphous binary mixture in the polar stratosphere and the upper troposphere

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Abstract

To elaborate stratospheric ozone depletion processes, measurements of diffusion coefficients of selected gas phase molecules (i.e. HCl, CH₃OH, HCOOH and CH₃COOH) in ice in the temperature range 170–195 K have been analyzed with respect to the mechanisms and rates of diffusion. It is argued that the diffusion in ice of these compounds is governed by a vacancy – mediated mechanism, i.e. H₂O vacancies are required to diffuse to lattice sites adjacent to these compounds prior to the diffusion of the corresponding molecule into the vacancy sites. In addition, we show that the diffusion coefficients of these compounds exhibit a specific interconnection, i.e. a linear relationship holds between the logarithm of the pre-exponential factor, D_o , and the activation energy E . The physical meaning of this interconnection is discussed.

1 Introduction

It is generally accepted that H₂O ice particles play a prominent role in the heterogeneous chemistry in the polar stratosphere that leads to ozone depletion (Solomon, 1988; Tabazadeh and Turco, 1993). Moreover, such particles also contribute to radiative forcing as well as to chemical conversions in the upper troposphere where they exist in form of cirrus clouds and contrails. Since the rates of heterogeneous chemical conversions depend on both surface and bulk concentrations, diffusion measurements in or on ice have attracted major interest.

When in a solid a single diffusion mechanism is operative, the diffusion coefficient, D , is often found to obey an Arrhenius type behaviour, i.e.

$$D = D_o \exp[-E/(k_B T)] \quad (1)$$

where the activation energy E and the pre-exponential factor D_o are essentially temperature independent and k_B is the Boltzmann constant. In this case, the slope of the

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linear $\ln D$ vs. $1/T$ plot leads to the value of E which – as shown by a careful thermodynamical study (Varotsos and Alexopoulos, 1979, 1986) – coincides with the enthalpy of activation ΔH_{act} of the diffusion process. Whilst such findings apply to the rate of diffusion they do not provide any information on the diffusion mechanism.

5 Early self-diffusion studies in ice have been performed using microtome sectioning and scintillation or mass spectrometric probes (H_2^{18}O , D_2O , T_2O) near the ice melting point (see Petrenko and Whitworth, 1999 and references therein). These studies led to a diversity of views concerning the mechanism of H_2O isotopic diffusion in ice (Petrenko and Whitworth, 1999). Opinions have been expressed, for instance, that for
10 $T > 223\text{ K}$ self-diffusion occurs by an interstitial-mediated mechanism, while for $T < 223\text{ K}$ a vacancy-mediated process is operative (Goto et al., 1986; Hondoh et al., 1989).

15 During the last decade, new infrared-laser resonant desorption (LRD) techniques have been employed to derive diffusion coefficients by depth profiling of ice films (Livingston and George, 1999, 2001; Livingston et al., 1997, 1998, 2000, 2002; Krasnopoler and George, 1998). These measurements revealed two different rate categories for bulk diffusion in ice. Whilst compounds such as HCl , CH_3OH , HCOOH and CH_3COOH display diffusion kinetics similar to the kinetics of H_2O self-diffusion, species such as Na and NH_3 exhibit diffusion kinetics appreciably slower than for H_2O self diffusion. Livingston et al. (2002) argued that the diffusion process of the compounds of
20 the first category occurs via a vacancy-mediated mechanism in which H_2O vacancies may be required to diffuse to lattice sites adjacent to the impurity compounds prior to the diffusion of this compound into the vacancy sites. The present paper focuses on the hetero-diffusion data of compounds of the first category. We will draw special attention to the fact that the diffusion data of these species are interconnected in a specific
25 manner.

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2 Theoretical considerations of hetero-diffusion in ice

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diffusing species according to (Varotsos and Alexopoulos, 1986):

$$v^j/v^m = (m^m/m^j)^{1/2} \quad (3)$$

where m^m , m^j denote the mass of the matrix (m) and the diffusing species (j), respectively, and v^m , v^j for the corresponding attempt frequencies.

5 The Gibbs energy ΔG_{act} can be decomposed into an entropy $\Delta S_{\text{act}} = -d\Delta G_{\text{act}}/dT|_p$ and an enthalpy $\Delta H_{\text{act}} = \Delta G_{\text{act}} + Td\Delta G_{\text{act}}/dT|_p$ term whereupon Eq. (2) turns into:

$$D = f\alpha^2 v \exp(\Delta S_{\text{act}}/k_B) \exp[-\Delta H_{\text{act}}/(k_B T)] \quad (4)$$

which can be alternatively written as:

$$D = D_o \exp[-\Delta H_{\text{act}}/(k_B T)] \quad (5)$$

10 with

$$D_o = f\alpha^2 v \exp(\Delta S_{\text{act}}/k_B) \quad (6)$$

As a consequence the temperature dependence of the diffusion coefficient follows a simple exponential behaviour, for which the pre-exponential factor D_o is associated with a dynamic (frequency) term as well as a thermodynamic (entropy) term. For the 15 same matrix therefore, low values of D_o hence reflect low attempt frequencies or low entropies of activation. It should be noted that ΔS_{act} is always positive because the diffusing species is more loosely bound or less ordered at the transition state than at the individual lattice sites.

According to the so-called $cB\Omega$ model, the Gibbs free energy of activation can be 20 further decomposed into the product of a bulk mechanical as well as a molecular property (Varotsos and Alexopoulos, 1978, 1980 1981, 1986; Varotsos et al., 1982, 1985, 1986), viz.

$$\Delta G_{\text{act},j} = c_{\text{act},j} B\Omega \quad (7)$$

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where (B) is the isothermal compression modulus, (Ω) the mean volume per atom and $(c_{act,j})$ a constant independent of temperature and pressure. The additional subscript j clarifies here that the value of this constant may be different for various diffusing species j .

5 The validity of this model has been tested for various defect processes and different categories of solids and the results were compiled by Varotsos and Alexopoulos (1986). Moreover, it was later found (Varotsos et al., 1999) that this model also holds even for more complex defect processes that e.g. are responsible for the emission of electric pulses observed upon pressurizing a solid, which may explain the detection of electric
10 signals defected before major earthquakes (Varotsos et al., 2003, 2005a, b). On the basis of Eq. (7), the corresponding entropy $(\Delta S_{act,j})$ and enthalpy $(\Delta H_{act,j})$ terms are found to be given by

$$\Delta S_{act,j} = -c_{act,j}\Omega(\beta B + \frac{dB}{dT}|_p) \quad (8)$$

$$\Delta H_{act,j} = c_{act,j}\Omega(B - T\beta B - T\frac{dB}{dT}|_p) \quad (9)$$

15 where (β) is the thermal volume expansion coefficient. Thus, by inserting Eq. (8) into Eq. (6), the pre-exponential (D_o) value for the diffusion of species j (labeled hereafter D_{oj}) is given by (when Eq. (3) is also considered):

$$D_{oj} = f\alpha^2 v^m (m^m/m^j)^{1/2} \exp[(-c_{act,j}/k_B)\Omega(\beta B + T\frac{dB}{dT}|_p)] \quad (10)$$

or

$$20 \ln\{D_{oj}/[f\alpha^2 v^m (m^m/m^j)^{1/2}]\} = [(-c_{act,j}/k_B)\Omega(\beta B + T\frac{dB}{dT}|_p)] \quad (11)$$

Together with Eq. (9), this relation reveals that for the diffusion of various species j into the same matrix material (m) , when plotting $\ln\{D_{oj}/[f\alpha^2 v^m (m^m/m^j)^{1/2}]\}$ versus

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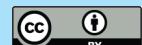
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$\Delta H_{act,j}$ a straight line should result, the slope of which is solely governed by the elasticity and expansivity properties of the host material. Since in the present case we only consider water ice as a matrix and data for other hosts are not easily available, the variation of diffusion data with these properties has yet not been tested.

5 In the present case the D_{oj} values vary by several orders of the magnitude, i.e., the D_o value for HCOOH exceeds that of HCl by as much as seven orders of magnitude (see Table 1). In view of this large variability, the mass effect associated with the frequency term $v^m (m^m/m^j)^{1/2}$ which emerged from Eq. (3) can, to a first approximation, be discarded. This explains why the plot of the $\ln D_{oj}$ versus $\Delta H_{act,j}$ or E is almost a straight line.

10 The apparent success of this analysis is, except for other potential sources, mainly due to the invariance of the diffusion mechanism. In all cases considered here this mechanism is identical, i.e. diffusion is governed by a vacancy controlled mechanism. This in turn leads to the conclusion that diffusion data that do not fall onto the line delineated here correspond to different diffusion mechanisms. This, for instance, applies 15 to NH_3 and Na .

15 The following comments, however, are worthwhile to be added. It has been argued (Domine and Xueref, 2001) that the diffusion coefficients reported by Livingston et al. (2002) were too large to be interpreted as molecular diffusion in crystalline ice. 20 This is so because in most solids, diffusion coefficients are of the order of 10^{-10} to $10^{-12} \text{ cm}^2/\text{s}$ near the melting point while Livingston et al. (2002) obtained values in that range 100 K below the melting point. Domine and Xueref (2001) have shown convincingly using IR spectroscopy that the ice samples used by Livingston et al. (2002) were not real ice, but were in fact amorphous binary mixture with a degree of disorder such 25 that diffusion could be expected to be fast. These arguments by Domine and Xueref (2001) seem to be well supported by the following fact: Livingston et al. (2002) obtained diffusion coefficient values near 180 K higher than those reported earlier by other authors in the range 240–260 K (cf. since diffusion is thermally activated, the diffusion coefficients should decrease upon decreasing the temperature). It seems therefore

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reasonable to accept that the ice samples used by Livingston et al. (2002) were in fact amorphous binary mixture rather than real ice. The interesting fact that even in this case the present analysis seems to be well obeyed (since the plot $\ln D_o$ versus ΔH_{act} , in Fig. 2 is almost a straight line) stems from the following: Eq. (11) is based on the cBΩ model, i.e., Eq. (7), which is of thermodynamic origin and has been shown (Varotsos and Alexopoulos, 1986) to be valid for amorphous binary mixtures as well (cf. the B value of such a mixture can be estimated in terms of B -values of the end constituents, see Varotsos, 1980). Irrespective of this point, however, it should be stressed that measurements of diffusion in ice are nowadays difficult and many measurements have been debated in the past.

3 Conclusions

It is well-recognised that H_2O ice particles play a key role in the ozone depletion in the polar stratosphere and contribute to radiative forcing (e.g. Chandra and Varotsos, 1995; Gernhardt et al., 1995). Temperature dependent measurements of diffusion coefficients for HCl , CH_3OH , HCOOH and CH_3COOH in ice, as studied in recent measurements (Livingston et al., 2002; Nehme, 2006) show that their D_o -values differ by several orders of magnitude. By contrast, the absolute values of the diffusion coefficients do not differ significantly (see Fig. 1), indicating that the transport of material occurs with more or less comparable rates for the same mechanism. Despite this variation, we show that the (natural) logarithm of D_o varies almost linearly with the activation energy E for diffusion which for linear $\ln D$ vs. $1/T$ plots coincides with the activation enthalpy, ΔH_{act} . If values for the the pre-exponential factors D_o could be estimated (i.e. by considering the entropy change during the diffusion process) then the correlation derived here could be of substantial predictive power for diffusion coefficients of other species in ice. The present analysis holds even if we consider convincing arguments clarifying that the samples used by Livingston et al. (2002) were in fact amorphous binary mixtures and not real ice.

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Chandra, S. and Varotsos, C. A.: Recent trends of the total column ozone-implications for the Mediterranean region, *Int. J. Remote Sens.*, 16, 1765–1769, 1995.

Domine, F. and Xueret, I.: Evaluation of depth profiling using Laser resonant desorption as a method to measure diffusion coefficients in ice, *Anal. Chem.*, 73, 4348–4353, 2001.

Gernhardt, H., Goersdorf, U., Claude, H., and Varotsos, C. A.: Possible impact of polar stratospheric processes on midlatitude vertical ozone distributions, *Int. J. Remote Sens.*, 16, 1839–1850, 1995.

Goto, K., Hondoh, T., and Higashi, A.: Determination of Diffusion-Coefficients of Self-Interstitials in Ice with a New Method of Observing Climb of Dislocations by X-Ray Topography, *Jpn. J. Appl. Phys.*, 25, 351–357, 1986.

Hondoh, T., Goto, A., Hoshi, R., Ono, T., Anzai, H., Kawase, R., Pinienta, P., and Mae, S.: Utilization of high speed x-ray topography for determining diffusion coefficients of point defects in nearly perfect crystals, *Rev. Sci. Instr.*, 60, 2494–2497, 1989.

Krasnopoler, A. and George, S. M.: Infrared resonant desorption of H_2O from ice multilayers, *J. Phys. Chem. B*, 102, 788–794, 1998.

Livingston, F. E. and George, S. M.: Effect of HNO_3 and HCl on HDO Diffusion on Crystalline D_2O Ice Multilayers, *J. Phys. Chem. B*, 103, 4366–4376, 1999.

Livingston, F. E. and George, S. M.: Diffusion kinetics of HCl hydrates in ice measured using infrared laser resonant desorption depth-profiling, *J. Phys. Chem. A*, 105, 5155–5164, 2001.

Livingston, F. E., Smith, J. A., and Goerge, S. M.: Depth-profiling and diffusion measurements in ice films using infrared laser resonant desorption, *Anal. Chem.*, 72, 5590–5599, 2000.

Livingston, F. E., Smith, J. A., and George, S. M.: General trends for bulk diffusion in ice and surface diffusion on ice, *J. Phys. Chem. A*, 106, 6309–6318, 2002.

Livingston, F. E., Whipple, G. C., and George, S. M.: Diffusion of HDO into single-crystal (H_2O)-O-16 ice multilayers: Comparison with (H_2O)-O-18, *J. Phys. Chem. B*, 101, 6127–6131, 1997.

Livingston, F. E., Whipple, G. C., and George, S. M.: Surface and bulk diffusion of HDO on ultrathin single-crystal ice multilayers on Ru(001), *J. Chem. Phys.*, 108, 2197–2207, 1998.

Nehme, R.: Diploma-thesis, University of Duisburg-Essen, edited by: Behr, P., Nehme, R., Zellner, R., in preparation, 2006.

Petrenko, V. F. and Whitworth, R. W.: *Physics of Ice*, New York, Oxford University Press, 1999.

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Solomon, S.: The Mystery of the Antarctic Ozone Hole, *Rev. Geophys.*, 26, 131–148, 1988.

Tabazadeh, A. and Turco, R. P.: A Model for Heterogeneous Chemical Processes on the Surfaces of Ice and Nitric-Acid Trihydrate Particles, *J. Geophys. Res.*, 98(D7), 12727–12740, 1993.

5 Varotsos, P.: On the temperature variation of the bulk modulus of mixed alkali halides, *Phys. Status Solidi B*, 99, K93–K96, 1980.

Varotsos, P. A. and Alexopoulos, K.: Curvature in conductivity plots of silver-halides as a consequence of anharmonicity, *J. Phys. Chem. Solids*, 39, 759–761, 1978.

10 Varotsos, P. and Alexopoulos, K.: On the possibility of the enthalpy of a Shottky defect decreasing with increasing temperature, *J. Phys. C Solid State*, 12, L761–L764, 1979.

Varotsos, P. and Alexopoulos, K.: Migration entropy for the bound fluorine motion in alkaline-earth fluorides, *J. Phys. Chem. Solids*, 41, 443–446, 1980.

Varotsos, P. and Alexopoulos, K.: Migration parameters for the bound fluorine motion in alkaline-earth fluorides II, *J. Phys. Chem. Solids*, 42, 409–410, 1981.

15 Varotsos, P. and Alexopoulos, K.: Thermodynamics of Point Defects and their relation with the bulk properties, Eds. S. Amelinckx, R. Gevers, and J. Nihoul, North Holland, 474 pp., 1986.

Varotsos, P., Alexopoulos, K., and Nomikos, K.: Comments on the pressure variation of the Gibbs energy for bound and unbound defects, *Phys. Status Solidi B*, 111, 581–590, 1982.

20 Varotsos, P., Alexopoulos, K., Varotsos, C., and Lazaridou, M.: Interconnection of point defect parameters in BaF_2 , *Phys. Status Solidi A*, 88, K137–K140, 1985.

Varotsos, P., Sarlis, N., and Lazaridou, M.: Interconnection of defect parameters and stress-induced electric signals in ionic crystals, *Phys. Rev. B*, 59, 24–27, 1999.

25 Varotsos, P. A., Sarlis, N. V., and Skordas, E. S.: Electric fields that “arrive” before the time derivative of the magnetic field prior to major earthquakes, *Phys. Rev. Lett.*, 91, 148501, doi:10.1103/PhysRevLett.91.148501, 2003.

Varotsos, P. A., Sarlis, N. V., Tanaka, H. K., and Skordas, E. S.: Some properties of the entropy in the natural time, *Phys. Rev. E*, 71, 032102, doi:10.1103/PhysRevE.71.032102, 2005a.

30 Varotsos, P. A., Sarlis, N. V., Tanaka, H. K., and Skordas, E. S.: Similarity of fluctuations in correlated systems: The case of seismicity, *Phys. Rev. E* 72, 041103, doi:10.1103/PhysRevE.72.041103, 2005b.

Varotsos, P., Varotsos, C., Hatjicontis, V., and Lazaridou, M.: On a plausible explanation of the connection of point-defect parameters with the melting-point, *J. Phys. Chem. Solids*, 47, 79–82, 1986.

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Table 1. Summary of rate parameters for the diffusion coefficients of selected compounds in ice.

	<i>E</i> (kcal/mol)	<i>D</i> _o (cm ² /s)	<i>D</i> (180 K) (cm ² /s)	<i>T</i> (K) Ref.
HCl	15.3±1.0	$1.5 \times 10^{7 \pm 0.2}$	4.83×10^{-12}	169.0–194.9 Livingston et al., 2002
HCOOH	21.8±0.9	$8 \times 10^{14 \pm 0.1}$	2.42×10^{-12}	175.1–194.9 dto.
CH ₃ COOH	17.0±0.7	$1.0 \times 10^{10 \pm 0.1}$	2.08×10^{-11}	169.9–194.9 dto.
	13.14±3.0	$0.813 \times 10^6 \pm 3.2$	8.6×10^{-11}	198–213 Nehme, 2006
CH ₃ OH	15.2±0.7	$2.4 \times 10^{7 \pm 0.3}$	7.8×10^{-12}	169.4–185.4 Livingston et al., 2002

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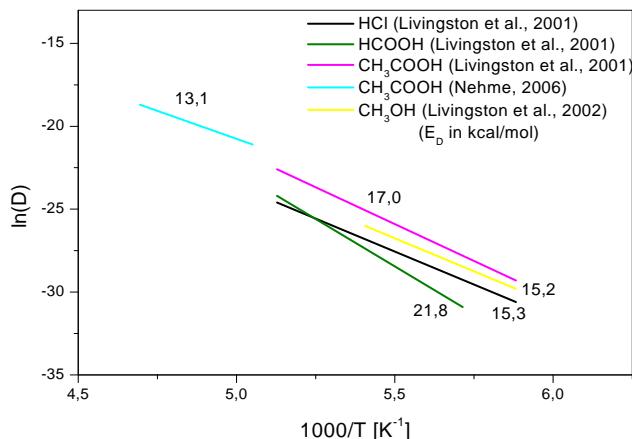


Fig. 1. Arrhenius plots for temperature dependent diffusion coefficients for various species in ice as obtained by the LRD depth-profiling technique (Livingston et al., 2001, 2002) and chemical titration (Nehme, 2006). The figures on the individual lines are activation energies (in kcal/mol) as derived by the authors.

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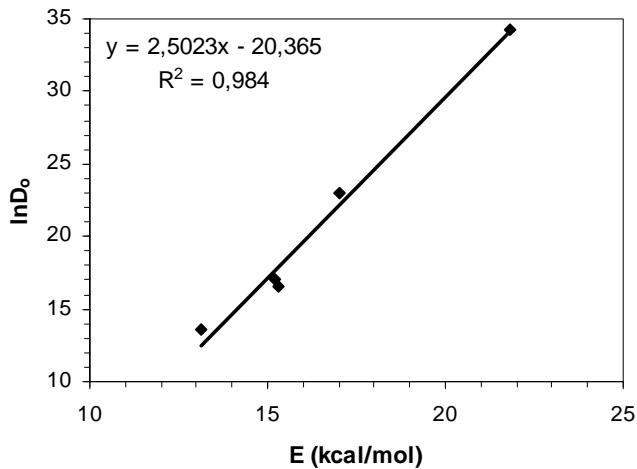
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Fig. 2. Relationship between the pre-exponential factor D_o of the diffusion coefficient and the activation energy E .

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