IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.6. HI6

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H_2O + ice

Uptake and accommodation coefficient data

Parameter	Temp./K	Reference	Technique/Comments
Accommodation coefficients (α)			
0.37 – 0.94	133-158	Koros et al., 1966	(a) gravimetric
6.0 x 10^{-2}	193-223	Isono and Iwai, 1969	(b) micro photographs
1.0 (α)	≤ 193	Davy and Somorjai, 1971	(c) gravimetric
0.8 ± 0.08	208		
0.5 ± 0.05	228		
0.55 ± 0.05	268 ± 2	Bonacci et al., 1976	(d) total pressure
$\gamma_{ss} > 0.3$	195	Leu, 1988	CWFT (e)
0.65 ± 0.08	185	Haynes, Tro and George, 1992	UHV inter ferometry (f)
(1.0 ± 0.1)	160	Speedy et al., 1996	UHV-MB (g)
0.97 ± 0.10	80-220	Brown et al., 1996	UHV-MB (h)
0.14; (single crystal D_2O ice)	140	Chaix, van den Bergh and Rossi, 1998	Knud (i)
0.13	170		
0.11	190		
0.27; (frozen liquid D_2O ice)	170		
0.25;	190		
0.17	200		
0.19 (vapor deposited D_2O ice)	170		
0.17;	190		
0.11	210		
0.60 (cubic ice D_2O)	140		
0.15 (artificial D_2O snow)	170		
0.15	190		
0.07	210		
1.0 – 0.45	130-170	Fraser et al, 2001	TPD in UHV reactor (j)
0.19 - (8.5 ± 1) x 10^{-2}	170-230	Delval and Rossi, 2003; 2005	SFR/FTIR (k)
0.15 ± 0.05	175	Smith, Livingston and George, 2003	HeNe inter-ferometry (l)
0.18 ± 0.07	180		
0.26 ± 0.08	190		
0.7 ± 0.3 (average value)	251-273	Sadtchenko et al., 2004	Ice filament evaporation (m)
0.48	251		
0.42 ± 0.05	173-193	Delval and Rossi, 2004	SFR/QCMB (n)
0.42 -0.18	193-223		
0.25 ± 0.05 (bulk = frozen liquid H_2O ice)	180	Pratte, van den Bergh and Rossi, 2006	Knud (o)
0.35 ± 0.10 (vapor-condensed ice)			

0.30 ± 0.05 (artificial snow)			
0.15 ± 0.05 (single crystal ice film)	130		
0.58 ± 0.08 (cubic ice film)			
$(6 \pm 2) \times 10^{-3}$ (single ice particles of 5.3 to 7.8 μm diameter)	223	Magee, Moyle and Lamb, 2006	Electrostatic levitation (p)
0.88 ± 0.10 (single crystal ice)	258 - 273	Lu et al., 2006	Filament evaporation (q)

Comments

(a) Gravimetric measurements of targets impinged by a supersonic (SS) molecular H_2O beam as a function of time. Direct measurement of α after correction for the loss of H_2O from the multiple collision target. Values of α in the range 133 to 233 K lie between 0.37 and 0.94 which represent averages of individual measurements at each temperature.

(b) Evaporation in vacuum and deposition of spherical H_2O ice crystals onto tipped Cu-substrate in the range 193 to 223 K. From the linear increase in ice crystal radius with time the mass change of each ice crystal was determined from photomicrographs at a measured H_2O supersaturation ratio. Below 193 K α increases with decreasing temperature.

(c) Kinetics of vacuum sublimation of ice single crystals monitored by gravimetric measurement using an electromicrobalance in the temperature range 183 to 233 K resulted in a negative T-dependence of the evaporation coefficient, and by microscopic reversibility, of the condensation coefficient α. The sublimation rates of the different samples were reproducible to within ± 10%, and were independent of crystal orientation and crystallinity (single crystal vs. polycrystalline). Dopants such as NH_4OH, $NaOH$, HF, HNO_3 and NH_4F significantly lowered the sublimation rate when ice is either grown from 0.01 to 0.1 M solutions or exposed to the dopant gas in the range 1.3 to 13 mbar.

(d) Measurement of both condensation and evaporation coefficient of liquid water (278 ± 3 K) and ice in a static chamber by recording the total pressure and the liquid or solid temperature transient upon perturbation of the gas-condensed phase equilibrium by pumping or adding H_2O vapor to the liquid or solid sample. α for ice was time invariant in contrast to liquid water that was dependent on the observation period 0.2 to 10 s. However, the instantaneous value for liquid water and the steady-state value for ice were numerically equal within experimental uncertainty.

(e) Fast flow tube reactor with MS detection. A diffusion correction was applied to γ, using the measured diffusion coefficient of H_2O in He scaled to 195 K.

(f) Interferometric observation of the growth and evaporation of H_2O from a vapor-deposited ice film. No barrier for the adsorption of H_2O onto ice was found because the desorption activation energy was equal to $\Delta H_{sub} = (49.4 \pm 0.8)$ kJ mol^{-1} within experimental uncertainty. No dependence of the kinetic parameters on the various ice morphologies were observed.

(g) Measurement of the free molecular evaporation, J_{ev}, of a recrystallized cubic ice 1 film (deposited on Ru(001) from the vapor) using mass spectrometry under UHV conditions. The 30-1000 molecular layer thick ice film was deposited as amorphous film at 85 K and was annealed *in situ* up to 162 K. The rates of evaporation for D_2O were also measured and resulted in J_{ev} smaller by a factor of two.

(h) Molecular beam and optical interference techniques at 632.8 nm were both used to measure the H_2O condensation coefficient on ice multilayers grown on Ru(001). α was measured from 80 to 220 K and was consistent with a value α of unity. The H_2O desorption flux follows zero-order kinetics and is expressed as $J_{des} = (4.0 \pm 1.0) \times 10^{15} \exp(-(48.25 \pm 0.80)/RT)$ monolayers s^{-1}. Earlier results on α obtained by optical interference measurements obtained by Haynes et al. (1992) (see (f)) were reinterpreted using temperature dependent values of ρ_{ice} and n_{ice} to result in $\alpha = 1.0$ independent of temperature.

(i) Time-resolved uptake measurement in a Knudsen flow reactor using $D_2^{18}O$ as a probe interacting with $D_2^{16}O$ ice. Using reaction vessels of different gas phase residence times the kinetics of adsorption and desorption could be separated leading to condensation and evaporation coefficients (α). Different types of ice substrates led to different α values which were all significantly smaller than unity and show a significant negative temperature dependence implying a precursor-mediated reaction mechanism.

(j) TPD using m/e 18 of H_2O using line-of-sight residual gas MS in the range 130-170 K. The ice sample was deposited on a Au substrate at 10 K and corresponded to a high-density amorphous phase. However, a phase change (120 to 140 K) from amorphous to the crystalline hexagonal form preceeded the evaporation so that the parameters given correspond to the I_h crystalline phase. The desorption was found to obey a zero-order rate law and was expressed as J_{ev} (molecule cm^{-2}s^{-1}) = $10^{30 \pm 2}$ exp ((-5773 $\pm$ 60)/T). J_{ev} measured at 130K corresponds to $\alpha = 1.0$ beyond which it significantly deviates from unity.

(k) Uptake experiment of H_2O vapor on temperature-controlled Si window monitored by FTIR in transmission, HeNe interferometry and residual gas MS inside a stirred flow reactor (SFR) that also could be used as a static reactor. Ice was generated from vapor phase condensation at 190 K. Thermochemical closure between evaporation and condensation was checked by the measurement of the vapor pressure in the static reactor. The following Arrhenius expressions for the evaporation flux and the condensation rate constant k_c in the range 200-240K were obtained for pure ice: $J_{ev} = 1.6 \times 10^{(28 \pm 1)}$ exp (-(85.6 $\pm$10.0)/RT) molec cm^{-2} s^{-1}, $k_c = 1.7 \times 10^{-(2\pm1)}$exp((13.3$\pm$12.5)/RT) s^{-1} with R in J mol^{-1}K^{-1}.

(l) Study of the evaporation rate of 6 μm thick crystalline hexagonal ice deposited on a thermostatted Ru(001) single crystal at 160 K using HeNe interferometry at 594 nm with a temperature-independent refractive index of ice $n = 1.31$. The evaporation rates of $H_2^{18}O$ and D_2O are smaller by 9% and by a factor of two, respectively. A transition state model was used to explain these results which, however, predicts only 50% of the rate decrease in going from H_2O to D_2O.

(m) Transient evaporation of H_2O and D_2O from thin ice film deposited on a 10 μm tungsten filament. Measurement of transient voltage and resistance across the filament and ion current (ion gauge and and TOF MS). These observables wnabledthe rate of evaporation and the temperature of the evaporating H_2O molecules in the range 251 – 273K to be determined. The vaporization rate follows Arrhenius behaviour and results in an activation energy of 50 $\pm$ 4 kJ/mol which corresponds to the low-temperature enthalpy of evaporation of pure ice at < 200K. The extrapolation of the low-temperature molecular precursor model of Davy and Somorjai (1971) (see (c)) to 273K greatly underpredicts α relative to this measurement. However, the α at 251K seem to be smaller than the given average value of $\alpha = 0.7$.

(n) Same experiment as in (k) except that the mass loss of ice using a quartz crystal microbalance (QCMB) was recorded as a function of time in the stated temperature range. The rate constant for H_2O condensation, k_c, was measured in two series of experiments from the net rate of evaporation, once under stirred flow conditions and once under fast pumping conditions where no condensation occurred. A break of the Arrhenius plot at T = 193 $\pm$ 2 K separates evaporation and condensation into two regimes with $J_{ev} = 2.2 \times 10^{30}$ exp (-(50.2 $\pm$ 2.1)/RT) for 173 < T/K < 193, and $J_{ev} = 1.6 \times 10^{28}$ exp (-(42.7 $\pm$2.1)/RT) for 193 < T/K < 223, with R = 8.314 J mol^{-1} K^{-1}.

(o) Knudsen flow reactor study using pulsed valve admission of H_2O, which was monitored using MS. Except for (artifical) snow a negative temperature dependence in the range 140 to 210 K was observed, consistent with a precursor-mediated adsorption mechanism. Both rate (flux) of evaporation and α are significantly different for different types of ice whereas the enthalpy of sublimation is the same, namely (50.2 $\pm$ 5.9) kJ/mol. Thermochemical closure of evaporation and condensation rate (activation energies) is achieved with thermochemistry (ΔH^0_{subl}).

(p) Observation of the mass change of single frozen H_2O droplets in a electrodynamic levitation cell at temperatures between 213 and 233 K during several evaporation and condensation cycles. Variable H_2O saturation ratios are determined at an accuracy of 5% using a calibration

technique based on growth of H_2SO_4 droplets as a function of rh. No significant temperature dependence of α was observed over the given range. The typical uncertainty for α is in the range 4.5 to 7.5 x 10^{-3} using a standard growth model. Total pressure is not reported.

(q) Filament evaporation in high vacuum chamber (see (m)) using MS. Vapor-deposited $H_2^{18}O$ tracing layers of typically 50–100 nm thickness were "sandwiched" between two polycrystalline $H_2^{16}O$ layers of total thickness of typically 3 μm at 150 K. From the tracing layer position and the time of appearance of $H_2^{18}O$ absolute H_2O evaporation rates were measured in the range 258–273 K. Evaporation rates as a function of time revealed two processes, one from single crystallites and the other from disordered H_2O trapped inside grain boundaries. In comparison to polycrystalline samples (see (m)) single crystal evaporation rates are on average slower by a factor of two.

Preferred Values

Parameter	Value	T/K
α	9.72 x 10^{-2} exp(232/T)	130-190
α	1.52 x 10^{-3} exp(1022/T)	190-230
α	0.7	250-273

Reliability

$\Delta \log (\alpha)$	0.3
$\Delta \alpha$	± 0.3

Comments on Preferred Values

Results on both evaporation (sublimation, desorption) and condensation (adsorption) rates have been used to derive the mass accommodation coefficient α, assuming the principle of microscopic reversibility applies under identical experimental conditions. It has been verified experimentally (Haynes, Tro and George, 1992) despite certain reports to the contrary (Marek and Straub, 2001).

Gas kinetic theory provides a maximum rate R or flux F of evaporation and condensation for the simple process $H_2O(g) \Leftrightarrow H_2O(s)$ (k_c, R_{ev}), with $H_2O(s)$ corresponding to ice. The maximum rate of evaporation (and condensation) is given by the Hertz-Knudsen equation $J^{max}_{ev} = (2\pi MRT)^{-0.5}P_{eq}$, where P_{eq} corresponds to the equilibrium vapor pressure of H_2O over ice; rate and flux are related through $V \cdot R = J \cdot A$, with V and A being the volume and geometric surface area of the system. The condensation and evaporation coefficients are given by the following expressions depending on the observable, that is either the rate or flux of evaporation or condensation:

for H_2O condensation experiments: $\alpha = k_c/\omega$

where k_c is the measured first order rate constant for condensation and ω is the calculated gas-kinetic collision frequency ($\omega = (<c>/4V)/A$ with $<c>$ being the average molecular velocity),

for evaporation experiments $\alpha = J_{ev}/Jmax_{ev}$ or R_{ev}/R^{max}_{ev}

Representative kinetic results are displayed in the Table above in terms of α (and γ_{ss}). Those that are expressed as J_{ev} and J^{max}_{ev} as a function of temperature in the range 140 to 230 K have been converted to α using the vapor pressure data of Marti and Mauersberger (1993) and of Mauersberger and Krankowsky (2003). Apart from a few exceptions the consensus obtained from recent experiments seems to be that α for H_2O on ice significantly less than unity for T > 160 K. Moreover, a decreases to 0.13 at 230 K, after which it increases again towards 273 K to attain a $\alpha = 0.8 \pm 0.2$ at 260 K (Sadtchenko et al., 2004; Lu et al., 2006). The low temperature data of Sack and Baragiola (1993) seem to be out of line as their measured evaporation fluxes J_{ev} consistently exceed J^{max}_{ev} by a factor of up to ten at 140 K and by a factor of two at 160 K for no obvious reason thus leading to α exceeding unity.

In general, the preferred values for α pertain to those for vapor-condensed ice. According to the measured temperature dependence of α we have split it into three ranges, namely 130 – 190, 190 – 230 and 230-260 K, each with its own temperature dependence.

The preferred values for α over the range 130 – 190 K are given by the Arrhenius fit to the weighted average data of Haynes et al. (1992), Chaix et al. (1998), Fraser et al. (2001), Delval et al. (2004) and Pratte et al. (2006). Although less relevant for the atmosphere, the low temperature data have been considered here as a benchmark as α must converge towards unity at T ≤ 130 K according to most experimental results.

For the range 190 – 230 K the data of Chaix et al. (1998), Delval et al. (2003; 2004) and Pratte et al. (2006) have been used to determine the preferred value of α. The data of Davy et al. (1971) have the same temperature dependence in this range although the absolute value of α is larger by a factor of 3.5.

The preferred value of α in the temperature range (250 – 273 K) is based on the work of Bonacci et al. (1976), Sadtchenko et al. (2004) and Lu et al. (2006). In the temperature range (230 – 250 K) α increases substantially although the data do not define well the form of the temperature dependence and no recommendation is made. This increase may be associated with the known presence of a significant "quasi-liquid" layer on pure ice for T ≥ 233 K. It is likely that α is unity at T = 273 K although it has not yet been measured at this temperature.

From a plot of α vs. T of the data (not shown) displayed in the Table one concludes that out of 13 independent measurement of α over varying T-ranges all except one (Smith et al., (2003)) show a negative temperature dependence. Haynes et al. (1992) do not observe a temperature dependence and prefer to state a T-independent value of α in the range 172 to 205 K. However, the condensation coefficient of Haynes et al. (1992) steadily decreases from $\alpha = 1.06$ at 20 K to 0.68 at 185K as do the α values of Fraser et al. (2001) in the range 130 to 170 K. Interestingly enough, Brown et al.(1996) "reanalyse" the data of Haynes et al. (1992) in the framework of their combination of molecular beam and interferometric experiments and come to the conclusion that $\alpha = 0.97 \pm 0.10$ for all investigated temperatures in the range 90 to 145 K when allowing both the density of ice and its index of refraction to linearly vary over the given T-range. Tolbert and Middlebrook (1990) agree with this proposal for the growth of thin films of ice at T < 145 K. Later interferometric work by the same group (Smith et al. (2003)), relaxes this restrictive condition and obtains an α value that is smaller than unity over the narrow range 175 to 190 K, albeit with a positive temperature dependence.

Support for the negative temperature dependence comes form the work of Davy et al. (1971), Chaix et al. (1998) (for D_2O condensation and evaporation kinetics), Delval et al. (2003, 2004) and Pratte et al. (2006) using a vacuum microbalance technique, a Knudsen reactor or a stirred flow reactor, the latter equipped with both gas and condensed phase diagnostics, respectively.

The separation of condensation and evaporation kinetics (k_c and R_{ev}) is performed using multiple data sets as well as steady-state and transient experimental techniques. In order to avoid confusion, the incorrectly used term "uptake coefficient" used by Chaix et al. (1998), Delval et al. (2003, 2004) and Pratte et al. (2006) corresponds to mass accommodation in terms of either the condensation or evaporation coefficient, because the condensation rate was taken into account when studying the evaporation rate, and vice versa. The corrected "uptake coefficient" therefore corresponds to α.

The "direct" measurement of k_c in transient supersaturation experiments has been validated by Pratte et al. (2006) using two steady state techniques, namely the CFM (Compensated Flow Method) and TASSM (Two Aperture Steady State Method). Pratte et al. (2006) also examined the condensation/evaporation kinetics of different types of ice and found significant differences ranging from $\alpha = 0.67$ for cubic ice at 130 K to $\alpha = 0.19$ for single crystal ice at T = 145 K as did Chaix et al. (1998). However, the equilibrium vapor pressure P_{eq} is invariant from one type of ice to another when evaluated according to $[H_2O]_{ss} = P_{eq}/RT = R_{ev}/k_c$ and is consistent with the heat of sublimation $\Delta H^0_{sub} = 51.5 \pm 6.7$ kJ mol^{-1}. Thermochemical closure is only afforded when considering negative activation energies for H_2O condensation (k_c) because activation energies for evaporation (R_{ev}) by themselves significantly fall short of the accepted thermochemistry for H_2O sublimation (Pratte et al., 2006). The Arrhenius plot for k_c in the range 130 to 210 K shows a discontinuity equal to a "break" or change in slope of the straight line at 193 $\pm$ 2 K with a concomitant change in the corresponding plot of J_{ev} (Delval et al., 2004; Pratte et al., 2006) which is the temperature at which the T-dependence of α changes (see preferred values). This observation has been made in both the Knudsen as well as the stirred flow reactor, the latter of which used both the gas phase (MS) as well as the mass loss of the thin ice film (QCMB) as a function of time. The data beyond 225 K of the stirred flow reactor (Delval et al., 2004) have not been taken into account in the evaluation because of possible systematic errors owing to heating/cooling effects of the ice surface due to excessive rates of condensation/evaporation at these higher partial pressures of H_2O.

The results of Bonacci et al. (1976), obtained in the high-temperature range, are similar, albeit a bit lower than Sadtchenko et al. (2004). The α values reported for single crystal ice by Lu et al. (2006) seems to be larger than for vapor-phase polycrystalline ice (Sadtchenko et al., 2004) at 260 K which is unexpected in light of results obtained at lower temperatures (Chaix et al. (1998); Pratte et al. (2006)).

In conclusion, the H_2O/ice system presents several complexities despite the fair number of experimental investigations which are summarized as follows:
- The measured temperature dependence in the range 130 - 260 K is the consequence of a complex mechanism consisting of several elementary steps. Despite this complexity, measured rates of condensation are first order in H_2O and rates of evaporation are zero order under all conditions examined (Flückiger et al. (2003).
- A span in α of up to a factor of 4.5 exists between vapor-condensed and quasi single crystal H_2O ice samples, comparable to the temperature variation of α in the range 130-260 K. This span is even larger (factor of 6.5) when including results on cubic ice in the range 130 - 140 K.
- Several experiments point towards two singularities in log α vs. 1/T over the range 130 – 260 K, namely at T = 190 $\pm$ 5 and 230 $\pm$ 5 K. This manifests itself in a change of slope at these temperatures.

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