

High-accuracy measurements of the vapor pressure of ice referenced to the triple point

Katarzyna Bielska,^{1,2} Daniel K. Havey,³ Gregory E. Scace,⁴ Daniel Lisak,² Allan H. Harvey,⁵ and Joseph T. Hodges¹

Received 25 October 2013; revised 21 November 2013; accepted 25 November 2013; published 6 December 2013.

[1] The vapor pressure of hexagonal (Ih) water ice was measured over the temperature range 175 K to 253.4 K and referenced to the value at the triple point of water. This experiment combined a highly accurate humidity generation system containing an ice-coated saturator (millikelvin-level temperature control) to provide humidified streams of nitrogen to a cavity-enhanced laser absorption spectrometer. The measured ice vapor pressures had relative standard uncertainties ranging from 0.4% to 0.7% over the entire temperature range. We demonstrate that these measurements validate thermodynamic correlations for ice vapor pressure based on integration of the Clapeyron equation. Moreover, they also indicate that some commonly used vapor pressure correlations are inaccurate and should be avoided. **Citation:** Bielska, K., D. K. Havey, G. E. Scace, D. Lisak, A. H. Harvey, and J. T. Hodges (2013), High-accuracy measurements of the vapor pressure of ice referenced to the triple point, *Geophys. Res. Lett.*, 40, 6303–6307, doi:10.1002/2013GL058474.

1. Introduction

[2] The saturation vapor pressure of hexagonal (Ih) water ice as a function of temperature is an important quantity in many geophysical processes, particularly in the Earth's atmosphere, and in wide-ranging terrestrial and extraterrestrial studies involving snow and ice. Examples include microphysical models of homogeneous and heterogeneous ice nucleation in clouds that depend on critical ice saturation ratios [Koop *et al.*, 2000; Wise *et al.*, 2009; Kärcher, 2003], the evaporative lifetime of cloud particles involved in heterogeneous chemical reactions [Solomon *et al.*, 1997], atmospheric water vapor transport in coupled climate models [Kremser *et al.*, 2009], washout of short-lived atmospheric substances [Aschmann *et al.*, 2009], formation of aircraft contrails [Kärcher *et al.*, 2009], the dynamics of glacial melt and ablation in glacial geology [Bliss *et al.*, 2011], and estimation of ice sublimation rates on the Moon [Andreas, 2007]. Values

for ice vapor pressure accurate to within a few percent are particularly important in atmospheric frost-point measurements [Brabec *et al.*, 2012] and studies of ice nucleation and supersaturation in clouds [Peter *et al.*, 2006; Krämer *et al.*, 2009].

[3] Unfortunately, experimental validation of the temperature-dependent formulas for the vapor pressure of ice has proven to be elusive because of difficulties in accurately measuring low concentrations of water vapor. Indeed, for more than a hundred years, numerous studies have aimed to measure this important physical property. Accounts of early literature were discussed by Scheel and Heuse [1909], while Weber [1915] performed some of the first precise measurements of ice vapor pressure over the temperature range 143 K to 250 K, primarily using a mercury manometer. More modern measurements of ice vapor pressure [Dousslin and Osborn, 1965; Jancso *et al.*, 1970; Marti and Mauersberger, 1993; Mauersberger and Krankowsky, 2003; Mokdad *et al.*, 2012] are also highly scattered, imprecise, and subject to biases. Jancso *et al.* [1970] measured the vapor pressure of ice from 195 K to 272 K using a differential capacitance manometer, referencing their results to the triple-point state and presenting a temperature-dependent correlation. Marti and Mauersberger [1993], and later Mauersberger and Krankowsky [2003], used mass spectrometry in an attempt to improve confidence in the low-temperature region of the correlation of Jancso *et al.* [1970]. Recently, Fernicola *et al.* [2012] measured the vapor pressure of ice over the range 223 K to 273.16 K with capacitance manometry and a temperature-regulated ice-containing sample cell with millikelvin-level stability. They reported relative standard uncertainties between 0.02% and 0.35%. After our work was completed, Mokdad *et al.* [2013] reported preliminary results obtained from a new static apparatus at temperatures down to 194 K; these measurements are much less scattered than the 2012 results from the same group and had relative standard uncertainties between approximately 0.025% and 1.2%.

[4] An alternative to direct measurement is integration of the thermodynamically based Clapeyron equation, starting at the triple-point temperature of 273.16 K where the vapor pressure of water has been measured accurately with a combined relative standard uncertainty of $\sim 5 \times 10^{-6}$ [Guildner *et al.*, 1976]. The calculation uses the enthalpy of sublimation, the heat capacities of vapor and solid, and the molar volumes of vapor and solid, all of which are known with low uncertainty. This approach was taken by Wexler [1977], and Sonntag [1990] produced a correlation in wide use by converting Wexler's equation to the ITS-90 temperature scale. The thermodynamic approach was refined with newer data by Murphy and Koop [2005]. An equivalent approach, based on reference-quality thermodynamic potentials

¹Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, Maryland, USA.

²Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland.

³Deceased.

⁴Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland, USA.

⁵Applied Chemicals and Materials Division, National Institute of Standards and Technology, Boulder, Colorado, USA.

Corresponding author: J. T. Hodges, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899-8320, USA. (joseph.hodges@nist.gov)

for fluid water [Wagner and Pruß, 2002] and for ice Ih [Feistel and Wagner, 2006], was used to derive the standard sublimation-pressure formula adopted by the International Association for the Properties of Water and Steam (IAPWS) [International Association for the Properties of Water and Steam (IAPWS), 2011; Wagner et al., 2011]. However, these thermodynamics-based formulations are not widely used in the geophysical community, much of which continues to use correlations fitted to scattered experimental data [Marti and Mauersberger, 1993] or other approximate equations [Buck, 1981; World Meteorological Organization (WMO), 2008]. Nevertheless, Murphy and Koop [2005] argued for the appropriateness and validity of a general thermodynamic formulation for the vapor pressure of ice, although they emphasized that no experimental measurements existed at that time that indisputably validate a single thermodynamic correlation from 160 K to 273 K. Such measurements would require relative combined standard uncertainties at the sub-1% level.

[5] In this work, we present measurements of the vapor pressure of ice Ih for temperatures from ~ 175 K to ~ 253 K. Over this temperature range, these data are of much lower uncertainty than most previous measurements (with the exception of Fernicola et al. [2012] and Mokdad et al. [2013], neither of which extend to such low temperatures) and establish clearly that the IAPWS formulation (and other formulations based on integration of the Clapeyron equation) is superior to other commonly used equations, most of which are based on semiempirical fits to experimental results.

2. Experimental Procedure and Data Reduction

[6] The details of our experiments and data analysis have been described preliminary reports of subsets of this work [Lisak et al., 2009; Bielska et al., 2012]. In brief, we used a steady-flow humidity generator comprising an ice-coated saturator at uniform temperature, T_s , and a flowing stream of high-purity nitrogen carrier gas to produce humidified streams of vapor [Hodges and Scace, 2006]. The temperature range of the saturator was adjusted over the range ~ 175 K to ~ 273 K, and the stability and standard uncertainty of the saturator temperature were 1 mK and 10 mK, respectively. With this humidity generation system at thermal equilibrium, the output water vapor concentration was determined solely by the temperature and pressure of the exiting gas mixture. Specifically, the water vapor molar fraction, x_w , was modeled by

$$x_w = p_i(T_s)f(T_s, p_s)/p_s \quad (1)$$

in which p_i is the vapor pressure of ice Ih evaluated at the saturator temperature, p_s is the total gas pressure in the saturator, and f is the enhancement factor discussed below. As described in Lisak et al. [2009] and Bielska et al. [2012], the amount of water vapor in the flowing gas mixture exiting the humidity generator was measured with the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) technique [Hodges et al., 2004; Hodges and Lisak, 2006]. In this approach, individual and nearly isolated near-infrared, rotation-vibration absorption transitions of H_2^{16}O were probed with a spectral resolution of ~ 1 MHz, using a single-frequency distributed feedback diode laser. The ring-down cavity was at room temperature and typically maintained at a pressure of ~ 13 kPa. The FS-CRDS measurements yielded rovibrationally resolved absorption spectra with transition areas that were equal to the product of water vapor number density and transition line

intensity. We extended the water vapor concentration range of these measurements by probing four transitions spanning an intensity range of $\sim 500:1$. Notably, the transition areas were obtained by fitting theoretically constrained profiles to the measured spectra. As discussed in Bielska et al. [2012], the concentration of water vapor relative to that at the triple-point reference condition was found in terms of the product of measured area ratios as well as the gas temperature and pressure within the humidity generator and cavity ring-down spectrometer. We note that this spectrum-area-ratioing approach enabled the ice vapor pressure to be determined relative to that at the reference condition independently of the absolute line intensities of the involved absorption transitions. (For completeness, we note that in our previous publication Bielska et al. [2012, Figure 3] we incorrectly switched the labels for the two curves that compared our preliminary results (200 K to 253.4 K) to the respective correlations of Wexler [1977] and Marti and Mauersberger [1993]).

2.1. Measurement Uncertainties

[7] We considered several sources of Type A (random) and Type B (systematic) uncertainty in our measurement of p_i . The principal Type A uncertainties are those involving the pressure and temperature measurements in the humidity generator and ring-down cavity as well as in the FS-CRDS determination of the spectroscopic areas. Type B components included those associated with calibration uncertainties for the pressure and temperature instrumentation, spatial nonuniformities in pressure and temperature, the temperature correction for intensities of the probed transitions, and the background signal caused by desorption of water vapor from all wetted surfaces located downstream of the humidity generator. Our analysis revealed that the most important uncertainties in p_i are from the following sources: spectrum area measurement for the transition probed when the humidity generator was near the triple-point temperature (relative standard uncertainty $u_r(p_i)$ of 0.35%), spectrum area ratios for the line pairs obtained at lower temperatures (0.1%–0.2%), pressure-and-temperature-related measurement uncertainties (0.18%), and finally uncertainty in water vapor background partial pressure which was estimated to be ~ 10 μPa . For temperatures above ~ 200 K, the water vapor background term is negligible compared to the ice vapor pressure and yields $u_r(p_i) < 0.005\%$, whereas at the minimum temperature of ~ 175 K, the background term corresponds to $u_r(p_i) \sim 0.6\%$, thus dominating the combined uncertainty in p_i . Adding all terms in quadrature, we find that the combined relative standard uncertainty in p_i ranges from 0.4% at 253 K to 0.7% at 175 K. Additional details regarding our measurement uncertainties can be found in Lisak et al. [2009] and Bielska et al. [2012].

2.2. Enhancement Factor

[8] Our technique measures the amount of water in a saturated nitrogen stream that is in equilibrium with ice Ih. For this binary mixture, the partial pressure of water vapor is not identical to the saturation pressure of pure ice. Rather, the ratio of these quantities is the enhancement factor, which is of the order of unity and depends on temperature, T , and pressure, p . The enhancement factor is primarily determined by the Poynting correction for the effect of pressure on the fugacity of a solid (which can be computed accurately since the molar volume of ice is well known) and by the deviation

Table 1. Coefficients for the IAPWS Formulation of $p_i(T)$ Given in Equation (2)

	$m=1$	$m=2$	$m=3$
a_m	-0.212144006×10^2	0.273203819×10^2	-0.610598130×10^1
b_m	$0.333333333 \times 10^{-2}$	0.120666667×10^1	0.170333333×10^1

of the vapor phase from ideal-gas behavior (which can be estimated accurately if the second interaction virial coefficients are known for all pairs of components in the system).

[9] While our preliminary report of this work [Bielska et al., 2012] utilized a correlation for the enhancement factor of H₂O in air, we chose to refine this result by calculating the enhancement factor specific to nitrogen as the carrier gas. Our analysis employs the formulation for thermodynamic properties of ice adopted by IAPWS [IAPWS, 2009; Feistel and Wagner, 2006] and second virial coefficients for pure water [Harvey and Lemmon, 2004], pure diatomic nitrogen [Span et al., 2000], and the water-nitrogen pair [Tulegenov et al., 2007].

[10] The calculated enhancement factors range from 1.0046 at the triple-point temperature to 1.0140 at our lowest temperature. The largest contribution to the enhancement factor is the vapor-phase nonideality, which is dominated by the (negative) second virial coefficient for the water-nitrogen pair. This interaction produces nonideality at our conditions that is at least 1 order of magnitude more than that for water vapor at saturation with no carrier gas. Importantly, we find that the uncertainty in the calculated enhancement factor is less than 0.001 at all points, which is negligible in the context of our data reduction.

3. IAPWS Reference Formula

[11] Our results are compared directly to the IAPWS [IAPWS, 2011; Wagner et al., 2011] formulation given by

$$p_i = p_{i,t} \exp[\theta^{-1}(a_1\theta^{b_1} + a_2\theta^{b_2} + a_3\theta^{b_3})] \quad (2)$$

in which $\theta = T/T_t$, where $T_t = 273.16$ K is the temperature of water at the triple point and where the ice vapor pressure at the triple point is $p_{i,t} = 611.657(3)$ Pa given by Guildner et al. [1976]. The constant coefficients, a_m and b_m ($m=1, 2, 3$), in equation (2) are given in Table 1. The IAPWS formula given by this equation is applicable over the temperature range 50 K to 273.16 K. Expressions for $u_i(p_i)$ covering this temperature range can also be found in IAPWS [2011].

4. Results and Discussion

[12] Table 2 gives our measured values and standard uncertainties for the vapor pressure of ice Ih as a function of temperature. In Figure 1 (top) we compare our experimental results to previous measurements of $p_i(T)$, in which all values are expressed as the relative difference with respect to that given by the IAPWS formulation. Prior determinations considered here include the work of Weber [1915], Douslin and Osborn [1965], Jancso et al. [1970], Marti and Mauersberger [1993], and Fericola et al. [2012]. The data of Mokdad et al. [2012] are not shown; they show approximately 5% scatter and are considered to be superseded by their most recent results; see Mokdad et al. [2013]. The pair of dashed red lines located symmetrically about the temperature axis corresponds to the standard uncertainty ($k=1$) of the

IAPWS reference equation. We note that, apart from the recent high-precision data of Fericola et al. [2012] which are limited to temperatures above 220 K and of Mokdad et al. [2013] which are limited to temperatures above 194 K, all previous measurements exhibit substantially larger imprecision than our results, especially for temperatures below about 200 K. Our results agree with those of Fericola et al. [2012] and Mokdad et al. [2013] to within the combined uncertainties of both measurements. For the lower temperature region below about 200 K, we find the scatter in the Marti and Mauersberger data to be more than an order of magnitude greater than our measurement uncertainty. In addition to the large scatter, the measurements of Marti and Mauersberger and Jancso et al. exhibit relatively large positive bias (many points deviating by $> 10\%$) with respect to the IAPWS values. Remarkably, we note that Weber's [1915] century-old measurements of ice vapor pressure show relatively low scatter and are in excellent agreement (1% level) with both our results and the IAPWS formulation for temperatures above 200 K.

[13] We also compare our experimental results to several analytical formulations for $p_i(T)$ found in the literature. These results, which are shown in Figure 1 (bottom), reveal that our measurements are in good agreement with the thermodynamic-based correlations of Wexler [1977] (which is almost indistinguishable from Sonntag [1990], which is not shown), Murphy and Koop [2005], and IAPWS [2011] over the entire temperature range, thus experimentally confirming their relative combined standard uncertainty to be less than $\sim 0.5\%$. The precision of our measurements is insufficient to distinguish between these three formulas. However, we find that the $p_i(T)$ formulae given by Marti and Mauersberger [1993] (based on an exponential fit to their data in Figure 1) and that of the World Meteorological Organization (WMO) [WMO, 2008] (which seems to be closely related to the semi-empirical equation of Buck [1981] and gives almost identical results) substantially disagree with our observations, with deviations exceeding several times our reported uncertainty. Mauersberger and Krankowsky [2003] also published a correlation based on new measurements and applicable to

Table 2. Ice Vapor Pressure Values and Combined Standard Uncertainties (Coverage Factor $k=1$) Obtained in This Study as a Function of Ice Temperature, T^a

T/K	p_i/Pa	$u(p_i)/\text{Pa}$	$[(p_i - p_{i,\text{ref}})/p_{i,\text{ref}}]/\%$
253.380	1.055×10^2	4.1×10^{-1}	-0.07
238.375	2.289×10^1	8.9×10^{-2}	-0.04
223.521	4.134×10^0	1.7×10^{-2}	0.28
204.937	3.395×10^{-1}	1.4×10^{-3}	-0.34
204.918	3.388×10^{-1}	1.5×10^{-3}	-0.28
204.918	3.398×10^{-1}	1.5×10^{-3}	0.03
201.230	1.959×10^{-1}	8.4×10^{-4}	-0.15
196.757	9.808×10^{-2}	4.2×10^{-4}	0.03
192.476	4.892×10^{-2}	2.1×10^{-4}	-0.18
187.065	1.952×10^{-2}	8.5×10^{-5}	0.12
183.205	9.766×10^{-3}	4.5×10^{-5}	-0.15
179.478	4.912×10^{-3}	2.7×10^{-5}	0.55
174.777	1.948×10^{-3}	1.4×10^{-5}	-0.19

^aWe have multiplied our measured relative vapor pressure values by the water triple-point vapor pressure of Guildner et al. [1976] ($p_i(T_t=273.16 \text{ K})=611.657 \text{ Pa}$, which has a specified relative uncertainty of $\sim 1.6 \times 10^{-5}$ at the 99% confidence interval, corresponding to a standard uncertainty of $\sim 3 \text{ mPa}$). Stated uncertainties account for combined Type A and Type B contributions. Here $p_{i,\text{ref}}(T)$ is the IAPWS formulation for ice vapor pressure given in equation (2).

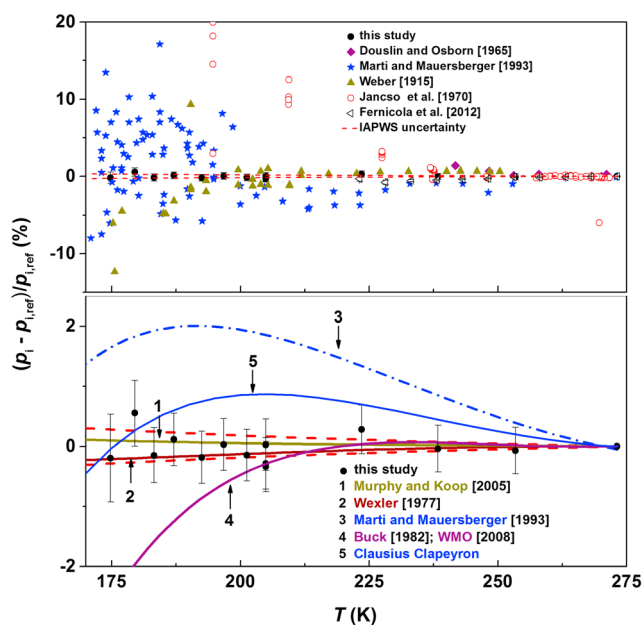


Figure 1. Relative difference between (top) measured and (bottom) calculated ice vapor pressures, $p_{i,\text{meas}}$, and those given by the IAPWS formulation, $p_{i,\text{ref}}$. The symmetric pair of dashed curves corresponds to the relative standard uncertainty ($k=1$) in $p_{i,\text{ref}}$.

the temperature range 164.5 K to 169 K. Although this work extended the range of the original correlation of *Marti and Mauersberger* [1993], we find that their 2003 correlation has a negative bias of 12% at 164.5 K and a temperature-dependent deviation of $\sim 3\% \text{ K}^{-1}$ relative to the IAPWS values. We also considered a simple thermodynamic approximation for the ice vapor pressure obtained from the Clausius-Clapeyron equation with the enthalpy of sublimation assumed to be a constant; we used the triple-point value of $2834.4 \text{ kJ kg}^{-1}$ recommended by *Feistel and Wagner* [2006]. The resulting equation for $p_i(T)$ is an exponential function of $-1/T$ and as shown in Figure 1 yields a maximum relative deviation of less than 1% over the indicated temperature range. However, at temperatures lower than those shown in Figure 1 it exhibits larger negative deviations (e.g., 3.5% at 150 K and 10% at 130 K).

5. Conclusions

[14] We have presented low-uncertainty measurements of the vapor pressure of water ice Ih over the temperature range 175 K to 253.4 K which are referenced to the value at the triple-point state. These data are consistent with two recent studies reporting fairly low uncertainties [*Fernicola et al.*, 2012; *Mokdad et al.*, 2013] but extend to lower temperatures. Our experimental results are consistent with predictions of ice vapor pressure based on rigorous thermodynamic integration, as are the other two recent studies in their more limited temperature ranges. Thus, we recommend the formulation of IAPWS [2011], which is documented by *Wagner et al.* [2011] and also given here as equation (2). Widely used correlations, such as those of *Marti and Mauersberger* [1993], *Buck* [1981], and the *WMO* [2008] deviate significantly from the recommended formulation and are especially unreliable for temperatures below ~ 200 K. Use of these semiempirical correlations for estimating the vapor pressure of ice may

therefore compromise measurements and modeling calculations that involve the vapor pressure of ice. Finally, we note that, unlike the more widely used correlations discussed here, the recommended IAPWS formulation has a specified uncertainty from 50 K to 273.16 K, thus making it applicable to relatively low temperatures.

[15] **Acknowledgments.** The authors thank Daniel M. Murphy for advice on important applications of ice vapor pressure in atmospheric studies. They also acknowledge the former NIST Office of Microelectronics Programs for partial support of this research, as well as support by the Programme of the National Laboratory FAMO in Toruń, Poland.

[16] The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

References

- Andreas, E. L. (2007), New estimates for the sublimation rate for ice on the moon, *Icarus*, 186, 24–30.
- Aschmann, J., B.-M. Sinnhuber, E. L. Atlas, and S. M. Schauffler (2009), Modeling the transport of short-lived substances into the tropical upper troposphere and lower stratosphere, *Atmos. Chem. Phys.*, 9, 9237–9247.
- Bielska, K., D. K. Havey, G. E. Scace, D. Lisak, and J. T. Hodges (2012), Spectroscopic measurement of the vapour pressure of ice, *Philos. Trans. R. Soc. A*, 370, 2509–2519, doi:10.1098/rsta.2011.0188.
- Bliss, A. K., K. M. Cuffey, and J. L. Kavanaugh (2011), Sublimation and surface energy budget of Taylor glacier, Antarctica, *J. Glaciol.*, 57, 684–696.
- Brabec, M., F. G. Wienhold, B. P. Luo, H. Vömel, F. Immler, P. Steiner, E. Hausammann, U. Weers, and T. Peter (2012), Particle backscatter and relative humidity measured across cirrus clouds and comparison with microphysical cirrus modeling, *Atmos. Chem. Phys.*, 12, 9135–9148.
- Buck, A. (1981), New equations for computing vapor pressure and enhancement Factor, *J. Appl. Meteorol.*, 20, 1527–1532, doi:10.1175/1520-0450(1981)020<1527:NEFCVP>2.0.CO;2.
- Douslin, D. R., and A. Osborn (1965), Pressure measurements in the 0.01–30 Torr range with an inclined-piston gauge, *J. Sci. Instrum.*, 42, 369–373, doi:10.1088/0950-7671/42/6/301.
- Feistel, R., and W. Wagner (2006), A new equation of state for H_2O ice Ih, *J. Phys. Chem. Ref. Data*, 35, 1021–1047, doi:10.1063/1.2183324.
- Fernicola, V., L. Rosso, and M. Giovannini (2012), Investigation of the ice-water vapor equilibrium along the sublimation line, *Int. J. Thermophys.*, 33, 1363–1373, doi:10.1007/s10765-011-1128-2.
- Guildner, L. A., D. P. Johnson, and F. E. Jones (1976), Vapor pressure of water at its triple point, *J. Res. Nat. Bur. Stand.*, 80A, 505–521, doi:10.6028/jres.080A.054.
- Harvey, A. H., and E. W. Lemmon (2004), Correlation for the second virial coefficient of water, *J. Phys. Chem. Ref. Data*, 33, 369–376, doi:10.1063/1.1587731.
- Hodges, J. T., and D. Lisak (2006), Frequency-stabilized cavity ring-down spectrometer for high-sensitivity measurements of water vapor concentration, *Appl. Phys. B*, 85, 375–382.
- Hodges, J. T., and G. E. Scace (2006), Developing advanced humidity standards to measure trace water vapor in specialty gases, *Micro*, 24, 59–66.
- Hodges, J. T., H. P. Layer, W. M. Miller, and G. E. Scace (2004), Frequency-stabilized single-mode cavity ring-down apparatus for high-resolution absorption spectroscopy, *Rev. Sci. Instrum.*, 75, 849–863, doi:10.1063/1.1666985.
- International Association for the Properties of Water and Steam (IAPWS) (2009), Revised release on the equation of state 2006 for H_2O ice Ih, available at <http://www.iapws.org>.
- International Association for the Properties of Water and Steam (IAPWS) (2011), Revised release on the pressure along the melting and sublimation curves of ordinary water substance, available at <http://www.iapws.org>.
- Jancso, G., J. Pupezin, and W. A. Van Hook (1970), The vapor pressure of ice between $+10^{-2}$ and -10^{+2} °C, *J. Phys. Chem.*, 74, 2984–2989, doi:10.1021/j100709a025.
- Kärcher, B. (2003), Simulating gas-aerosol-cirrus interactions: Process-oriented microphysical model and applications, *Atmos. Chem. Phys.*, 3, 1645–1664.
- Kärcher, B., U. Burkhardt, S. Unterstrasser, and P. Minnis (2009), Factors controlling contrail cirrus optical depth, *Atmos. Chem. Phys.*, 9, 6229–6254.
- Koop, T., B. P. Luo, A. Tsias, and T. Peter (2000), Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, *Nature*, 406, 611–614, doi:10.1038/35020537.
- Krämer, M., et al. (2009), Ice supersaturations and cirrus cloud crystal numbers, *Atmos. Chem. Phys.*, 9, 3505–3522.

- Kremser, S., I. Wohltmann, M. Rex, U. Langematz, M. Dameris, and M. Kunze (2009), Water vapour transport in the tropical tropopause region in coupled chemistry-climate models and ERA-40 Reanalysis Data, *Atmos. Chem. Phys.*, *9*, 2679–2694.
- Lisak, D., D. K. Havey, and J. T. Hodges (2009), Spectroscopic line parameters of water vapor for rotation-vibration transitions near 7180 cm^{-1} , *Phys. Rev. A*, *79*, 052507.
- Marti, J., and K. Mauersberger (1993), A survey and new measurements of ice vapor pressure at temperatures between 170 and 250 K, *Geophys. Res. Lett.*, *20*, 363–366, doi:10.1029/93GL00105.
- Mauersberger, K., and D. Krankowsky (2003), Vapor pressure above ice at temperatures below 170 K, *Geophys. Res. Lett.*, *30*(3), 1121, doi:10.1029/2002GL016183.
- Mokdad, S., E. Geogin, I. Mokbel, J. Jose, Y. Hermier, and M. Himbert (2012), On the way to determination of the vapor-pressure curve of pure water, *Int. J. Thermophys.*, *33*, 1374–1389, doi:10.1007/s10765-012-1261-6.
- Mokdad, S., E. Geogin, Y. Hermier, F. Sparasci, D. Ameer, and M. Himbert (2013), Measurement of saturation vapor pressure of pure water in the temperature range between 193.15 K and 328 K, Proceedings of the 16th International Conference on the Properties of Water and Steam, London, Sept. 1-5, 2013.
- Murphy, D. M., and T. Koop (2005), Review of the vapour pressures of ice and supercooled water for atmospheric applications, *Q. J. Roy. Meteorol. Soc.*, *131*, 1539–1565, doi:10.1256/qj.04.94.
- Peter, T., C. Marcolli, P. Spichtinger, T. Corti, M. B. Baker, and T. Koop (2006), When dry air is too humid, *Science*, *314*, 1399–1401.
- Scheel, K., and W. Heuse (1909), Bestimmung des Sättigungsdruckes von Wasserdampf unter 0° , *Annalen der Physik (Leipzig)*, *29*, 723.
- Solomon, S., S. Borrmann, R. R. Garcia, R. Portmann, L. Thomason, L. R. Poole, D. Winker, and M. P. McCormick (1997), Heterogeneous chlorine chemistry in the tropopause region, *J. Geophys. Res.*, *102*, 21,411–21,429, doi:10.1029/97JD01525.
- Sonntag, D. (1990), Important new values of the physical constants of 1986, vapour pressure formulations based on the ITS-90, and psychrometer formulae, *Meteorol. Z.*, *40*, 5–9.
- Span, R., E. W. Lemmon, R. T. Jacobsen, W. Wagner, and A. Yokozeki (2000), A reference equation of state for the thermodynamic properties of nitrogen for temperatures from 63.151 to 1000 K and pressures to 2200 MPa, *J. Phys. Chem. Ref. Data*, *29*, 1361–1433, doi:10.1063/1.1349047.
- Tulegenov, A. S., R. J. Wheatley, M. P. Hodges, and A. H. Harvey (2007), Intermolecular potential and second virial coefficient of the water-nitrogen complex, *J. Chem. Phys.*, *126*, 094305, doi:10.1063/1.2446843.
- Wagner, W., and A. Pruß (2002), The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use, *J. Phys. Chem. Ref. Data*, *31*, 387–535, doi:10.1063/1.1461829.
- Wagner, W., T. Riethmann, R. Feistel, and A. H. Harvey (2011), New equations for the sublimation pressure and melting pressure of H_2O ice Ih, *J. Phys. Chem. Ref. Data*, *40*, 043103, doi:10.1063/1.3657937.
- Weber, S. (1915), Commun. Phys. Lab. Univ. of Leiden, No. 150, 4-52. [The data are reproduced in H. Spencer-Gregory and E. Rourke, *Hygrometry* (Crosby Lockwood and Son, London 1957)].
- Wexler, A. (1977), Vapor pressure formulation for ice, *J. Res. Nat. Bur. Stand.*, *81A*, 5–20, doi:10.6028/jres.081A.003.
- Wise, M. E., K. J. Baustian, and M. A. Tolbert (2009), Laboratory studies of ice formation pathways from ammonium sulfate particles, *Atmos. Chem. Phys.*, *9*, 1639–1646.
- World Meteorological Organization (WMO) (2008), Guide to meteorological instruments and methods of observation, WMO-No. 8, 7th ed.