

Interactive comment on “Deposition mode ice nucleation reexamined at temperatures below 200 K” by E. S. Thomson et al.

MJR Rossi

michel.rossi@psi.ch

Received and published: 15 October 2014

The present paper is one of the rare new experimental studies on ice nucleation and therefore caught my attention when reading it. I congratulate the authors at gathering high quality elementary kinetic/thermodynamic information on this important, yet still poorly understood physical atmospheric process. Theories come and go, but solid observational data withstand the test of time, and this what we need in this field. I have a “burning” question and a few remarks as well as a suggestion at streamlining the present report in order to make the issue stand out crisp and clear for better audibility by the interested community. I bristled when reading “. . .the steady-state vapour pressure over the ice. . .” on line 22/23 on pg. 23715. What is that: steady-state or

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equilibrium? A flowing gas experiment always deals in steady-state partial pressures, whereas equilibrium vapour pressures are encountered in static systems, and invariably steady-state are smaller than equilibrium values because steady-state is the equilibrium value perturbed by the pumping term. It is true, that sometimes steady-state partial pressures are close to the (calculated) equilibrium vapour pressures. However, as I gather from Figure 1 the present case is probably not one of them. Usually, you have to obtain two independent kinetic data sets in order to separate the rate of evaporation Rev and the accommodation coefficient α for H₂O vapor (see Iannarelli and Rossi, *acp* 14, 5183 (2014) for a recent example). I assume that the ice crystal housing where the interaction of the H₂O gas with the functionalized graphite surface is taking place, may be understood as a stirred flow reactor (SFR) under molecular flow conditions, an assumption that is valid up to 10⁻² mbar before going into the transition region where the gas-kinetic formulas retain their physical meaning. The ratio between the equilibrium and steady-state concentrations or pressures (at fixed temperature) is given by:

$$r = (H_2O)_{eq}/(H_2O)_{ss} = 1 + k_{esc}/(\omega \cdot \alpha(H_2O)) \quad (1)$$

where ω and $\alpha(H_2O)$ are the H₂O - graphite collision frequency and accommodation coefficient for H₂O at T, respectively. In order to put some life into these formulas I made “reasonable” assumptions based on the dimensions of the SFR displayed in Figure 1 (the authors easily may obtain numbers closer to the real dimensions of the equipment). I used the average thermal velocity $\langle c \rangle$ of H₂O vapor at 300 K effusing out of one of the two small feeder tubes (5.9×10^4) cm s⁻¹, $k_{esc} = (\langle c \rangle / 4V) A_h$ and $\omega = (\langle c \rangle / 4V) A_s$ s⁻¹ using $V = 66$ cm³, $A_s = 1$ cm² and $A_h = 0.6$ cm² with a 50 mm diameter of the cylindrical chamber, from which roughly 1/3 is cut off, and three apertures whose diameters are 5 mm each. A_s is the active area of interaction with the cold substrate, and A_h is the effective area across which the gas effuses, respectively, leading to $k_{esc} = 134$ and $\omega(H_2O, 300 K) = 223.5$ s⁻¹. Using these numbers we obtain $r = 3.00$ and 7.00 with α being 0.3 and 0.1, respectively (See Iannarelli

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and references cited therein). This range has been measured for different atmospheric ices depending on the type of ice and temperature. This shows that both steady-state and equilibrium concentrations or partial pressures are very different, thus fully warranting a correction, unless I grossly misunderstand. There is no direct relationship between measured pressure and the elementary fluxes J_{back} , J_{nuc} and J_{eq} unless you separate Rev and the rate constant for H_2O deposition, that is $\omega \cdot \alpha(\text{H}_2\text{O})$. Therefore, the authors must be careful with such seemingly “robust” statements as expressed on line 14, pg. 23715. Perhaps they are not that robust!! What is the pressure in the sample chamber at the highest flow rates? Is there a beam-gas interaction with the He beam?

A few remarks follow:

- The discussion of surface wetting properties or the classification of hydrophobic and hydrophilic nature of a surface is certainly misplaced in a molecular interpretation of surface properties. The bulk thermodynamic parameters are easy to measure, but do not reveal any molecular information (lines 16 and 18, pg. 23718, and beyond). How many “hydrophobic surface groups does it take to make a surface macroscopically hydrophobic? It turns out, that for instance on soot there is a specific balance of polar and non-polar groups, every soot sample has them, but in different proportions which will lead to different macroscopic wetting behaviour as revealed for instance through the contact angle. So far, there is not a single molecular theory that I know of that would explain the wetting behaviour from molecular parameters or potentials. - Concerning results of Figure 5 vs. 6: All that one may say is that a two-parameter fit is far superior to a one-parameter fit, which is not exactly earthshaking! Temperature has a given functional form, but nobody can be sure that T is a causal parameter. - What is the relationship between capital “V” and lower case “v” on pg. 23719? What is “v” in equation (4) and (6)? Is it “vee”(volume) or “vue ” (vibrational frequency)? - Concerning the logarithmic A-factor mentioned on line 12, pg. 23721 of $10^{(-13)}\text{s}^{-1}$: This is a postulate, and numbers of that magnitude are rarely observed, although they are in

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some cases!. There is no theory behind it, this number just “works”. See A factors that are three to four orders of magnitude lower in H_2O adsorption to different soot samples at 190 K (Alcala-Jornod and Rossi, JPC A 108, 10667-10680 (2004)). - The discussion of the f -parameter (Section 3.3) may be left out without loss of information, and the Discussion and Atmospheric Implications may be cut down to a large extent because they don’t deserve the title: What are the atmospheric implications? After reading it, it was not clear to me.

Michel J. Rossi PSI Paul Scherrer Institute Laboratory of Atmospheric Chemistry

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 23711, 2014.

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