“Gas-ice partitioning coefficients of carbonyls during diffusional ice crystal growth”

By J. Seymore et al. (2025) for EGUsphere

Reviewed by Jeff Snider, University of Wyoming

Overall

The authors describe a laboratory setup and use it to characterize the amount of organic vapor incorporated into ice grown by deposition. This reviewer participated in a similar study ~ 20 years ago. These are not easy measurements to make. Interpreting the results is also difficult.

One of my major critiques concerns the tentative conclusion that a surface layer is the “single dominant influence” on uptake. This runs counter to the discussion of how uptake might be controlled by accommodation or affinity within bulk ice.

The authors should consider my critiques and reply with a revised manuscript.

Major Critiques:

On L276, you say that "Positive values of DG indicate the analyte favors the gas phase while negative values of DG indicate the analyte favors the ice phase. Even lower, more negative values of DG would indicate more efficient uptake of the analyte into the ice phase." Also, on L330, you say "Values of K > 1....indicate net uptake of the compound into the ice phase. Conversely, values of K<1…indicate negligible uptake and that the compound favors remaining in the gas phase." And, on L376, you say that "…DG>0 indicates unfavorable uptake of the species into the ice phase while DG<0 indicates favorable uptake in the ice phase."

As I demonstrate below, your statements are illogical for a system with an amount of ice which is magnitudes smaller than the amount of gas. I will symbolize these amounts as volumes (Vs and Vg) and will insist that Vg/Vs >> 1. Also, I note that Vg>>Vs is the situation within clouds. With these constraints, and assuming sufficient time for equilibration, the K you report allows for determination of analyte amount (as a mole count) within the solid (KCgVs), within the gas (CgVg), and the fraction of analyte within the solid.

Fraction of analyte within the solid = KCgVs / (KCgVs+ CgVg) = K / (K + Vg/Vs)

My point is this: Since K is not large compared to 1 (Fig. 4), and Vg/Vs >> 1 is the situation within clouds, it does not make sense to say that "negative values of DG indicate the analyte favors the ice phase", or that "Values of K > 1....indicate net uptake of the compound into the ice phase", or that "DG<0 indicates favorable uptake in the ice phase." Also, while it is logical to say that "Positive values of DG indicate the analyte favors the gas phase", and that "Conversely, values of K<1…indicate negligible uptake and that the compound favors remaining in the gas phase", and "DG>0 indicates unfavorable uptake of the species into the ice phase", these last statements are also true for a K that is magnitudes larger than 1.

In summary, you need to rewrite these sections of text. A suggestion: Think of DG is a placeholder for K, and not as an indicator of how uptake alters the partitioning of the analyte within clouds. If you do not want to focus on clouds please recognize that it is an unusual experimental setup that allows for Vg/Vs ~ 1 while also assuring time for equilibration.

Related to the previous comments and critique:

1) Since partitioning is strongly on the side of gas-phase, I don't accept your assertion that uptake into ice "…may be relevant as an influence on vertical tracer transport" in the Conclusion.

2) My formulation of partitioning comes from Brimblecombe and Dawson (https://doi.org/10.1007/BF00127265). As far as I can tell, they were the first to put the concept into the literature.

3) There is a treatment of partitioning in the atmospheric chemistry textbooks. One of these is Lamb and Verlinda (Physics and Chemistry of Clouds, Cambridge University Press, 2011; see pp. 166-168).

4) I recommend that you report your ice uptake coefficient with dimension of mol m-3 Pa-1. This is your framework for the Henry Law discussion (Equations 5 and 6). With this change you can eliminate a confusing sentence (L210-L211). It would also eliminate the need for a translation from a dimensionless K to dimensional K, in the Conclusion.

L134 says that S_i = 1.5 was a constraint in all experiments. This implies that either deposition or condensation can occur. I checked my assertion here:

T,[K]	Si,[-]	ei(T),[Pa]	e,[Pa]	es(T),[Pa]	RH,[%]
253.15	1.50	103.	155.	125.	123.
243.15	1.50	38.	57.	51.	112.
233.15	1.50	13.	19.	19.	101.

Note that the relative humidity (relative to saturation over liquid water) exceeds 100 % at all temperatures (-20, -30, and -40 °C). Since you are using “tank” air, it is unlikely that droplets formed, impacted, and contributed to the ice deposit via riming.

I recommend that you consider the following as a process that may have occurred in your experimental setup:

Provided some regions on the glass are clean (i.e., no ice nucleating particles) you may be condensing liquid directly from the vapor. Freezing would then occur, for example, once a liquid domain touches an ice domain. The latter could have been previously frozen or previously deposited. In either case, the existence of liquid water would rationalize your exothermic uptake coefficients. Here, I’m assuming that Henry’s law uptake (into the liquid) increases with decreasing temperature below 273 K.

Related Recommendations:

1) I recommend that you refer to your measurements as an uptake coefficients, as sorption coefficients, or as an ice-gas partitioning coefficients. You complicate the reading by using all of these. The place to do this is in the Introduction not in Section 2.6.

2) Since the cloud chemistry community uses “partitioning” to describe analyte mass continuity, within an element of cloud, I recommend that you not use partitioning to modify the coefficient you are evaluating. Similarly, I encourage that you do not use “partitioning” as a place holder for the process you are investigating.

3) I do not think you need Equation 2. There are tables of saturation pressure in the textbooks. E.g., Rogers and Yau, Third Edition, Elsevier, 1989; Table 2.1. The important thing is that you check your Equation 2 for dimensional consistency and for adequate numerical precision compared to tabulated data.

4) There is no reason to report the gas constant with six-digit precision or to report the reciprocal temperatures (p. 14) with four-digit precision.

5) The density of ice can be taken to be a constant.

Your discussion on L175-L187 should be revised. You are using aqueous solutions to generate a prescribed amount of gas-phase analyte within the flowtube. The $[X]_{aq}$ (Equation 6) is what's required to produce a specified gas-phase mixing ratio (10 ppbv). So, I recommend that you put the target gas-phase mole fraction ($10.x10^{-9}$), and your pressure, into Equation 6.

Please note:

L179. You are producing a partial pressure, within the flowtube, not a "gas concentration." This should be corrected here and elsewhere.

It's not clear why you have the superscript "cp" in Equation 6. Also, it's quite common to use Kh, not H, for the Henry solubility, at least in the cloud chemistry community.

About "breakthrough." I don't understand your statement that Kahnt et al. (2011) observed larger breakthrough, at lower relative humidities, but your absolute humidity is much lower. Do you mean that Kahnt et al. (2011) observed larger breakthrough at _low_ relative humidities? Additionally, relative humidity and absolute humidity are related, but it is not clear how to compare your humidity condition (absolute) to the humidity condition in Kahnt et al. (2011) (relative).

Please note the title of Kahnt et al. (2011): "Denuder sampling techniques for the determination of…derivatization methods." There are places where you use the modifier "derivation" instead of "derivatization." Please check throughout.

The word “massed” is used. Do you mean weighed? It seems that the mass of the ice was derived by weighing together with additional information. On L225-233 you say that the flow tube was rinsed (methanol), that the extract was “massed”, and that the solution was evaluated in a refractometer. The acquired information is sufficient for determining the mass of H_2O that was extracted from the tube.

1) Please correct/change all instances of “massed”.

2) You refer to the “collected ice mass” on L159. Should this be “sampled ice mass” or “extracted sample mass”? There are other instances of “ice mass”. You should consider changing these, for clarity.

3) On L305-L309, you report the calculated ice mass (Equation 3) and you compare to the collected ice mass (aka, the “yield.”). In your procedure, it seems, the methanol does not capture all the ice. Hence, the expectation is calculated > measured. Looking at data from the -30 and -40 °C, that expectation is verified. In our paper (Huffman and Snider 2004), a calculation overpredicts the observed ice mass. Splintering of the ice sample, during the uptake experiments, was suspected. In your experiments, do you have evidence of splintering?

4) Your visual observations (L318-319) are contradictory. The coatings were “either over the entire surface” or “not evenly distributed.” Which of these best represents what you saw?

5) All one can visualize is a macroscopic ice deposit, not the (microscopic) nucleation sites. Accordingly, I recommend that you revise L321.

Contamination during the processing of the samples (the H_2O samples and the cartridge samples) is a possibility. You addressed this on L325-L328. Your approach is to process blank ice samples grown from liquid.

1) Why not collect/process “blank” ice samples taken from the flowtube when it’s operated with no analyte?

2) You say that the blank signals were in the same range as analytical blanks, which were all below detection limit. It’s my opinion that you should tabulate the analytical blank values - or tabulate their average and standard deviation – and tabulate the same for the blanks ice samples.

I may have missed this. Did you do an analysis of analyte amount in denuder #1, denuder #2, and in the flowtube and use that information to quantify error in K coming exclusively from the chemical analysis method? This seems like a useful thing to do….mass must be conserved.

L39 - Neither Gautam et al. (2025) Seymore et al. (2025) are in the bibliography.

L502 – Neither Gautam et al. (2024) Seymore et al. (2024) are in the bibliography.

Regarding your tentative conclusion that a surface layer is the “single dominant influence” on uptake. This was examined by Valdez et al. (https://doi.org/10.1029/JD094iD01p0109). This reference is not in your bibliography.

Less-than-major Corrections and Less-than-major Critiques:

“ACN", define where this acronym is first used.

L144. Remove “using the hygrometer.”

L150. Remove “which is equivalent to the diffusive flux.”

L153. A cloud physics textbook (Rogers and Yau; Third Edition, Elsevier, 1989) says that the diffusivity is 20% smaller at -40 °C compared to -20 °C.

L157. Please see my earlier comment about condensation and deposition. You are interpreting t_k as the time for “deposition”, correct?

L202-L204. Is “hydrazone” different from “hydrazine” in DNPH?

L262-L267. I recommend that you not use “Cice” for the absolute mass of analyte in ice. Also, is the modifier “absolute” implying something? Recommend that you remove “absolute.”

L275 You say: “These values describe the energy available for the uptake process.” I do not agree with this. Think of DG is a placeholder for K. Also see my first critique.

L361 “…and water”. Do you mean “…and ice”?

L411 “Endothermically” or “nonexothermically”? Be consistent.

L416-L417 I don’t understand how photodegradation of MVK, within the atmosphere, can be the cause of the weak correlation with inverse temperature, in your laboratory study.

L430 “artifactully”. Is there a better way to say this?

L435 The letter “H” is being used to represent several properties. There is the Henry solubility (Equation 5), the enthalpy of solution (BTW, some refer to this as the enthalpy of gas-to-liquid transfer), and the enthalpy change you derive via the van’t Hoff regression. You can avoid introducing another “H.” Do that by acknowledging that the enthalpy change you derive for a rather cold experimental temperature may be significantly different from the reference-state enthalpy. Related to this, why not represent the Henry Solubility (Equation 5) with Kh? That is common, and it would eliminate one of the “H” symbols.

L480 Which “solubility”? I think you are referring to the Henry Law solubility, but I’m not sure.

L456 Is this the first occurrence of “additivity”? It is not clear what you are implying by “additivity”

L457 I recommend something like this: “…could help to generalize descriptions of the uptake process in models”

L539 It is not clear what you are implying by “..void space.”

L711 Check the format of the Warhaft reference.