

Interactive comment on “Design and construction of a simple Knudsen Effusion Mass Spectrometer (KEMS) system for vapour pressure measurements of low volatility organics” by A. M. Booth et al.

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Responces to reviewers #1 Dr MJR Rossi

The present work deals with a new apparatus designed to measure the equilibrium vapor pressure of low volatile organics likely to occur in oxidized organic aerosols. The authors should be congratulated for their initiative to apply a new method to these difficult measurements that to date are far and few between. As this is the first of an expected series of publications in this field quality control issues of the results have to be

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Interactive Discussion

Discussion Paper



resolved and the absence of systematic errors has to be ascertained, or at least evaluated in their influence on the results. I point out below several areas that the authors should seriously consider by using all of their obtained results without having to resort to additional measurements. Once these issues will have been resolved I certainly will recommend publication of this work in Atmospheric Measurement Techniques as it will most likely arouse the interest of many atmospheric scientists.

- We wish to thank MJR Rossi for his valuable comments and suggestions, we have addressed them as follows.

(1) As the authors are well aware the Knudsen effusion technique measures the steady-state vapor pressure $M(ss)$ whereas it is the equilibrium vapor pressure $M(eq)$ that is desired. Depending on temperature and the value of $k(esc)$, the rate constant for physical effusion of the gas out of the Knudsen reactor, there is a discrepancy between $M(ss)$ and $M(eq)$ that may be significant. The present authors try to solve this question by calibrating the mass spectrometric (MS) signal using a compound having similar equilibrium vapor pressure. However, this only works if the mass accommodation coefficient α is identical to the molecule under investigation. I agree that oxalic acid may fall into this category, but I am less sure about ferrocene and dipenylethane. From a simple mass balance consideration $M(ss) = R(ev)/(k(c) + k(esc))$ where $R(ev)$ and $k(c)$ are the rate of evaporation (molecule $s^{-1}cm^{-3}$) and the rate constant for condensation (s^{-1}), respectively. Normalization of the latter on a per collision basis leads to the mass accommodation coefficient α . When comparing $M(ss)$ with $M(eq) = R(ev)/k(c)$ it becomes apparent that the discrepancy between $M(ss)$, the measured quantity, and $M(eq)$, the desired quantity, depends on the competition of two (unimolecular) rates, namely condensation against escape, that is $k(c)$ vs. $k(esc)$. Quantitatively speaking, the discrepancy amounts to the following relation: $1/M(eq) = 1/M(ss) - k(esc)/R(ev)$. Here one can see that this discrepancy is most serious at low temperatures where $R(ev)$ is small (exponential T-dependence) compared to $k(esc)$ (weak $T^{-0.5}$ dependence).

Interactive
Comment

I strongly suggest that the authors quantitatively assess the departure of $M(ss)$ which will always be smaller due to the pumping term $k(esc)$ from $M(eq)$ by using their data base for oxalic acid that comprises data for the 0.2, 1 and 3 mm diameter orifice. One needs two independent data sets to independently determine $R(ev)$ and $k(c)$, or three data sets in case $k(esc)$ has not been independently determined. In the old days we have assessed $k(esc)$ from the reactor geometry and the molar mass using $k(esc) = \langle c \rangle / 4V A(s)$ where $\langle c \rangle$, V and $A(s)$ are the average molecular speed, the volume and the surface of the escape orifice of the Knudsen reactor, respectively. This assumes that the Clausing factor is unity owing to the knife-edge geometry of the orifice. Moreover, the separation of the equilibrium constant into $R(ev)$ and $k(c)$, depending on the quality of the data, is interesting in its own right because even fewer values for organic compounds do exist to this day. I attribute some importance to this question in a paper presenting a novel technique that may be routinely applied in the future. The internal consistency of the three reference compounds lying within a factor of 1.5 to 2 is somewhat disappointing, and the question is whether or not this may be improved. What are the limitations of this technique? A candid assessment by the authors may be instructive for all future users.

- 1. In principle, we are in agreement with many of the considerations outlined in this comment. However, before we address the comments in detail, it should be emphasised that we are not presenting a new technique, more a novel application of a very well-established technique. KEMS has been used widely for other applications and convincing direct measurements of vapour pressures, reconciling the possible discrepancy between $M(eq)$ and $M(ss)$ have been reported. It is possible that difference in the accommodation coefficient could be important for some compounds. The discrepancy between the calibration compounds is down to Diphenylethane, Ferrocene and Benzophenone are in closer agreement. This could be due to a problem with the literature data or an accommodation coefficient effect.

We have evaluated the deviation of the steady state vapour pressure from the equi-

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librium vapour pressure using the equations above and the term for $k(\text{esc})$ and have found there is a difference for oxalic acid using the benzophenone reference using the 200 micron and 1 mm hole, possibly due to benzophenone being close to the knudsen limit. We also looked at our 2mm and 3mm hole data for malonic, succinic, glutaric and adipic acids but we see no systematic difference between pressure determined using either hole even after remeasuring with the 2mm hole size, we have recently tried measurements with very small sample sizes (0.001g) and have seen no difference vs larger samples so we conclude that the equilibrium in the cell is not significantly disturbed for the dicarboxylic acids and with these hole sizes. We therefore conclude that the steady state and equilibrium vapour pressures are indistinguishably close when the knudsen number is sufficiently high.

We have added to the text: Random errors arise from variation in the mass spectrometer signal (ioniser, and SEM / Faraday Cup detector). The error for oxalic acid is high as a result of the variation in the 3 calibration compounds used for its determination (Table 3). The adipic acid has a higher error because of its lower pressure, resulting in decreased signal to noise ratio. Systematic errors can be introduced by the choice of reference compound as measurements are relative to this and from calculation of the ionisation cross section. In all cases, the accommodation coefficient is assumed to be identical between samples. Such an assumption may introduce unquantifiable errors, but it is expected that they are minimized by appropriate choice of similar reference and sample compounds. KEMS directly measures the steady state vapour pressure but the equilibrium vapour pressure is desired. Corrections between steady state and equilibrium can be applied (Li et al., 2003; Silva and Monte, 1990), but if the Knudsen number is low enough then effusing gas does not significantly disturb the equilibrium in the cell (Li et al., 2003; Hilpert, 1991, 2001). There is no systematic difference between hole size for our dicarboxylic acid determinations so the steady state vapour pressure is indistinguishably close to the equilibrium vapour pressure for our dicarboxylic acid determinations in table 4.

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(2) Owing to the low pressures involved only heat conduction through the solids is a sufficiently rapid mechanism for temperature equilibration. What is (and is there) sufficient thermal contact between the removable cup and the shell of the Knudsen reactor? Is 10 minutes waiting period mentioned on pg. 898, line 23-24 sufficient to ascertain T-equilibration? How did you measure?

- 2. The amount of sample is typically very small (~ 0.1 g) reducing the thermal mass of the system. Conduction is through the thin walls of the k-cell which is kept in thermal contact with a tight fit against the cell holder. 10 minutes was chosen based on how long it took the mass spectrometer signal to stop increasing after a temperature step (measured with a type K thermocouple), plus a wide margin. We have added why a 10 minute equilibrium time was chosen.

(3) Owing to the fact that the effusive (thermal) molecular beam was apparently not chopped I assume that the total signal, that is the sum of both the background and the molecular beam, were recorded. Did you make any attempts to differentiate between background and molecular beam intensity using a lock-in amplifier? In case you did not, how much variation in the background did you observe between the start and the end of an experiment using a particular compound? Some compounds are “sticky” and have a long residence time on the inner metal parts such that they need long pumping times. Any memory effects in the vacuum? I think these are important practical questions to be addressed.

(4) Did you observe any interfering degassing effects when you turned on the internally mounted heating element? See point (3) above.

- 3 & 4. We determined the background signal by taking Mass spectra when the gate valve between the KEMS section and the mass spec section was closed. We saw fairly common vacuum contamination, N₂, O₂, Ar, H₂O and small amounts of CO₂. Towards the end of a run as the temperature was at its highest there was more water in the MS signal from adsorbed H₂O been driven off the k-cell.

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At the end of a run the gate valve is closed (to allow the k-cell to be changed without switching of the MS ioniser) and the molecular beam signal drops very rapidly although for a few compounds some signal from peaks which had clearly come from the sample lingered for up to several hours. This did not prove a problem as it had invariably dissipated by the time the lower chamber had been pumped down enough to start the next run.

Running the heating for the first time with no sample in the k-cell there was outgassing from the kems chamber as the heating was turned up but this was eliminated by a mild bake-out of the system. We baked the chamber with the k-cell at a higher temperature than chamber walls to ensure that any condensate coming off the walls would not contaminate the cell.

We have added a mention of vacuum background and baking to section 2.

(5) The values of the mean free path presented in Table 2 and therefore also the Knudsen numbers, depend on the concentration of the trace gas. At the fastest pumping, that is using the 3mm diameter orifice $M(ss)$ is smaller compared to pumping at the 0.2 mm orifice. This should be reflected in Table 2 rather than taking the constant $M(eq)$ except in cases where both values are indistinguishably close.

- 5. $M(ss)$ and $M(eq)$ are sufficiently close that it will not significantly affect the mean free path.

(6) I believe that the accuracy of the individual data points as well as the narrow temperature range used (30K) are insufficient to obtain accurate thermochemical parameters (pg. 901, line 2 and following).

- 6. The values reported are from linear fits of the Classius-Clayperon equation to the data points with errors derived from fitting each run separately. We agree that compared to the traditional use of high temperature KEMS to measure alloy and ceramic vapour pressures over hundreds of degrees the results will clearly not be as accurate.

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We feel however that it is appropriate to measure over such a range for organics relevant to atmospheric applications, the range is comparable to other researchers, for example Bilde et.al. covers a 24K range and Tao and McMurray a 40K range.

(7) Typo's: - Pg. 894, line 8: saturated -Pg. 896, line 20: sample Pg. 899, line 9: pressure Pg. 900, line 1: Discussion Pg. 907, Table 4: Succinic

- 7. Fixed typos

(8) I suggest to horizontally displace the different data points in Figures 5 and 6 for better readability. Many points are now overlaid and difficult to read off the figure.

- 8. Graph redrawn.

#2 Anonymous Referee

Review of "Design and construction of a simple Knudsen Effusion Mass Spectrometer (KEMS) system for vapour pressure measurements of low volatility organics" by Booth et al.

In this work a new Knudsen Effusion Mass Spectrometer (KEMS) has been build. The KEMS method is an established method in other fields of science but has not been applied before for studies of atmospherically relevant substances. There is a strong need for measurements of thermodynamic properties of semi-volatile organic molecules of atmospheric relevance and the proposed method complements existing methods nicely.

Using the new instrument the authors have measured vapor pressures of a series of dicarboxylic acids and compared with available literature data. The manuscript certainly merits publication; however a number of issues must be addressed first.

In the interactive discussion good comments have already been given. In addition the following issues should be addressed.

In general, the text can be significantly improved by more precise formulations and

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additional literature references, some suggestions are given below.

- We would like to that the reviewer for their comments and have addressed them as follows.

1) A short discussion of solid state versus sub-cooled liquid state vapor pressures and methods to come from one to the other could be given in the introduction. It should be made clear that the presented method provides solid state vapor pressures.

- 1. We've stated that although the dicarboxylic acids will exist as solids at room temperature and pressure, in the atmosphere they can exist as subcooled liquid. Also added equation from Prausnitz et al., (1986) for converting between solid state and sub-cooled liquid End 2para, 1st section

2) In the introduction it says that simple hydrocarbons are not of interest to atmospheric community – I would suggest to say “are of less interest”.

- 2. Agreed, Changed.

3) First line in section 2 is a repetition and can be deleted.

- 3. Deleted as suggested.

4) No description of the sample preparation is given– this should be done: the purity and provider of the used chemical should be given. Also it should be described how the sample was prepared and handled and it should be explained how much sample was used.

- 4. Added suppliers and purities of reference compounds and dicarboxylic acids. There was no further sample preparation, an advantage of the KEMS system.

5) a reference to the Quadstar software package should be provided.

- 5. Reference Added.

6) An example of the data obtained are given in the last figure. It would seem more

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



natural to present and discuss an example of data (Figure 7) early in the paper (as Figure 4)

- 6. Moved Figure.

7) The role and importance of the hole size should be better explained and the relevant equation(s) given

- 7. The hole size is a major factor in k , the machine constant, in eqn (1) in AMTD paper, now eqn (2). The hole size determines if the gas from the vapour phase will effuse. It should be chosen such that the Knudsen number is > 10 for whatever compound is under investigation. A further consideration for the KEMS system is that the minimum hole size is limited by the detection limit of the mass spectrometer, and the maximum hole size should not be high enough to burn out the electron impact filament. This has been clarified in the text.

8) Page 898, line 22 – please discuss the uncertainties – is the agreement using different references satisfactory?

- 8. The sources of random error between the reference compounds are due to variation in the mass spec signal (ionisers, and SEM/faraday). There are also systematic errors introduced by the choice of reference compound, this was why we used 3 reference for the initial determination of oxalic acid, and also why the references were checked against each other. Also refer to reply to comment 1. of Rossi review. We have also discussed the uncertainties in the text.

9) Page 899, line 15 and Table 4, caption: the text is unclear. Why is suddenly malonic acid mentioned as a reference, what does it mean “with SEM detection”? How were the errors given in Table 4 determined? In Table 4 it says that the variation for the oxalic acid is largely due to the use of 3 different calibration compounds – please explain and justify in the text – was the average used? The vapor pressure variation for adipic acid is also high ?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



- 9. Any compound can be used to calibrate the system once the vapour pressure is known. For the remaining dicarboxylic acids we used Oxalic acid to calibrate the system as (from table 2) the Knudsen number is too low for the original 3 calibration compounds with the 3mm hole, We also used malonic acid as a calibration to check we could use any compound once we had determined its VP. SEM detection should read SEM detector, as opposed to using the faraday cup. The errors were the standard deviation of the runs. The adipic acid has a higher error because of its lower pressure, resulting in decreased signal to noise ratio. The Text is amended to clarify this.

10) In the discussion the authors write that their method tend to give higher values compared to the TDMA method – this does not seem right to me – it is only the case for succinic and malonic acid as far as I can see – for glutaric and adipic acid the KEMS method gives lower vapor pressures?

- 10. Agreed, have changed to higher values compared to Bilde and Tao & McMurry for Malonic and Succinic acid and lower for Glutaric and Adipic acid

11) Why does the evaporation of some sample “inadvertently” explain the lower vapor pressure obtained by Cappa et al. 2007?

- 11. Cappa et.al. Used a preheating step in their TPD measurements to drive off residual solvents, this could also have driven off some sample, which would explain the lower pressure they measured compared to other techniques.

12) References: I suggest the authors go carefully through the manuscript and check that they include the relevant references. Below some suggestions: Page 894, line 25: Johnson et al. is only concerning aromatic hydrocarbons – some reference to other types of hydrocarbons would be appropriate Page 895, line 1 – please give some references illustrating that some estimation methods give erroneous results Page 895 Line 18: the authors site Cappa et al. 2007 for the TPD method – they should also site Chattopadhyay and Ziemann 2005. SOA compounds are likely to have vapor pressures upwards of 10⁻⁴ Pa – please provide some references for this statement. The

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authors should use the name of the first author when citing literature, for example: Ravishankara -> Cappa et al. 2007 In the conclusion references to TDMA type measurements on aqueous mixtures should be given (e.g. Riipinen et al. 2006).

- 12. references added

13) Notation– use consistent notation in equations and in the text and explain – e.g. page 898: dH_{sub} (in equation) and dH in text. Notation in abstract should correspond to notation in text

- 13. Changed to consistent use of dH_{sub}

14) Figure 4: In Vapor pressure – please explain better and use same notation as in equations, also give the unit of vapor pressure. In the caption an open symbol is given, in the figure a closed symbol.

- 14. Changed to consistent use of $P(298\text{K})$

15) The authors write that the technique could be improved by increasing the sensitivity of the mass spectrometer – what is it now? – and how large an improvement is reasonable to expect?

- 15. For a pressure of $1\text{e-}5$ Pa (e.g. succinic acid) in the k-cell we have 10^{11} molecules striking the ioniser per second. More sensitive ionisation such as Li-attachment could improve upon this.

Technical: Page 894, line 25: sentence not complete “hydrocarbons” missing after oxygenated Page 895 Line 15: they have -> these vapor pressures : : : would sound better Page 901: dicarboxylics -> dicarboxylic acids Page 897: no “.” after cell Some References: Chattopadhyay, S. and Ziemann, P. J. Aerosol Sci. Technol., 2005, 39, 1085. Riipinen, K. E. J. Lehtinen, B. Svenningsson, M. Bilde, A. Gaman, M. Kulmala Atmospheric Research 2006, 82, 579-590.

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