

***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.***

**MJR Rossi (Referee)**

michel.rossi@psi.ch

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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 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

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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.

(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  $\alpha$  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 ( $\text{molecule s}^{-1}\text{cm}^{-3}$ ) and the rate constant for condensation ( $\text{s}^{-1}$ ), respectively. Normalization of the latter on a per collision basis leads to the mass accommodation coefficient  $\alpha$ . 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).

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

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three data sets in case  $k(\text{esc})$  has not been independently determined. In the old days we have assessed  $k(\text{esc})$  from the reactor geometry and the molar mass using  $k(\text{esc}) = \langle c \rangle / 4V A(s)$  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  $R(\text{ev})$  and  $k(\text{c})$ , 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.

(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?

(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

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mounted heating element? See point (3) above.

(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.

(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).

(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

(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.

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