



Vapor Pressure Measurements Knudsen Effusion Method

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Knudsen Effusion Method approved by OECD 104 Guideline for Vapor Pressure Measurements

Introduction

The vapor pressure of materials is an important physical and chemical property that defines the amount of vapor a material generates at its surfaces. Materials have the tendency to enter the vapor phase by sublimation (solid – gas) or evaporation (liquid – gas). The vapor pressure of materials at thermodynamic equilibrium is only a function of temperature.

The knowledge of vapor pressure is highly desirable for liquids, oils, pesticides, fertilizers and various substances in order to avoid the atmospheric accumulation of toxic compounds with a low vapor pressure. The loss of additives such as plasticizers and UV absorbers from polymers by diffusion and evaporation from the surface can cause an undesirable decrease in their efficiency. However, controlled vaporization can be beneficial for pregnancies activity. Further, information about vapor pressure of pharmaceutical compounds is beneficial in understanding the stability and shelf life of these products. The vapor pressure of materials are required to be registered with the US Environmental Protection Agency (EPA)¹ or the European Chemicals Agency (ECHA)².

Knudsen cell Method

The Knudsen effusion method³⁻⁸ is a dynamic gravimetric technique based on the rate of escape

of vapor molecules through an orifice in a Knudsen cell into a vacuum at a known temperature. The rate of mass loss through the orifice is measured by UltraBalance (Surface Measurement Systems). Sample masses from 1 to 100mg can be studied typically in the temperature range from 20 to 400°C. VPA allows the direct measurement of vapour pressure using the Knudsen Vapour pressure technique. The VPA can measure vapor pressure of samples in the range of 10^{-12} Pa right through to 10^5 Pa across a wide temperature range.

In a typical experiment, the sample is sealed in a Knudsen cell made of titanium containing an orifice of known area. The Knudsen cell with the sample is then heated to a desired temperature and kept at this temperature for several hours. The orifice size is determined from benzoic acid vapor pressure measurements because its vapor pressure at different temperatures is well known (1-4). The rate of mass loss at temperature T and time t is related to vapor pressure of condensed phase, P , derived from Knudsen equation (1), where dm/dt is the rate of mass loss with time t [min], M sample molar mass [Kg/mol], R universal gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$) and A the orifice area [m^2]

$$P = -\frac{\sqrt{\left(\frac{2\pi RT}{M}\right)}\left(\frac{dm}{dt}\right)}{A} \quad (1)$$





The orifice area is calculated from orifice diameter (d) of Knudsen cell

$$A = \pi r^2 = \pi \left(\frac{d}{2}\right)^2 \quad [\text{m}^2] \quad (2)$$

The Effusion rate dm/dt needs to be converted from [mg/min] to [Kg/sec] as follow

$$-\frac{dm}{dt} = -\frac{dm}{dt} \times \frac{10^{-6}}{60} = \quad [\text{Kg/sec}] \quad (3)$$

Hence, the equation (1) can be rewritten as follow

$$P = -\frac{\sqrt{\left(\frac{2\pi RT}{M}\right)\left(\frac{dm}{dt} \times \frac{10^{-6}}{60}\right)}}{\pi\left(\frac{d}{2}\right)^2} \quad [\text{Pa}] \quad (4)$$

Equation (4) is used to calculate vapor pressure of materials from experimental data (Figure 1) generated by VPA. The dm/dt is a slope value derived from a least square regression analysis to mass data over selected period of time t at constant temperature T as shown in Figure 2 and 3. The dm/dt value is used in Equation 1 and 4 for vapor pressure calculation.

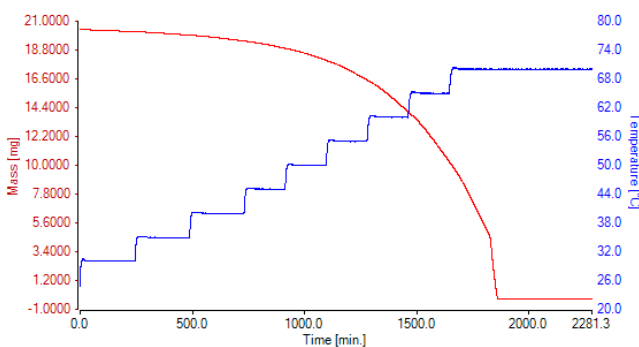


Figure 1 Change in mass (line in red) of Benzoic acid at different temperature steps (line in blue) with dwell of 180min at each step under high vacuum.

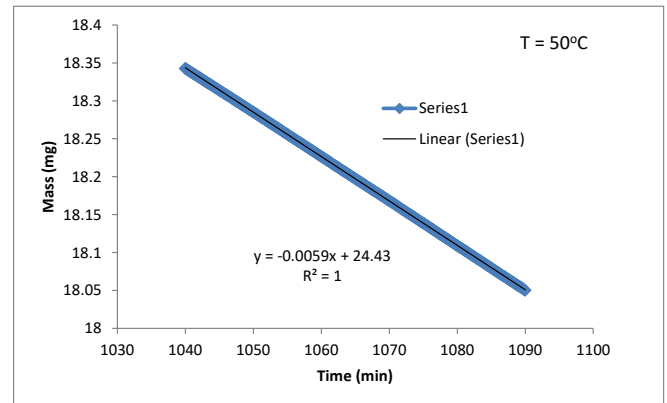


Figure 2 Last 50min of Benzoic acid mass loss (line in blue) at 50°C under high vacuum before temperature was increased to 55°C. Least square regression analysis on mass data (line in blue) was performed to derive slope value (dm/dt). The analysis yielded dm/dt value of -0.0059.

The identical automated analysis are performed in VPA analysis software. Users first enter sample molar mass (M) in (g/mol) and orifice size (micron) and then selects fitting window range by defining the upper and lower time limit. The VPA analysis software will automatically calculate vapor pressure at certain temperature as shown in Figure 3. Upon the completion of analysis for each experimental temperature, the vapor pressure values for each experimental temperature are saved. The software generates vapor pressure curves and automatically calculates heat of vaporization. All values are then reported in Vapor Pressure report as shown in Figure 4.

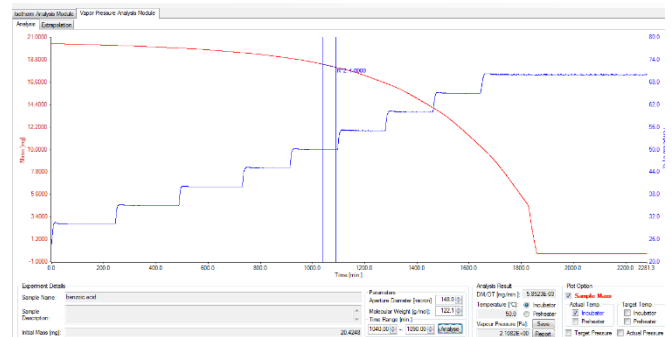


Figure 3 Screenshot of VPA analysis software showing vapor pressure calculation at 50°C by selecting fitting window range in which linear mass loss is observed. This linear fitting procedure needs to be repeat for each experimental temperature.

Line in red is mass and line in blue is temperature. Two blue vertical lines displays fitting window range which was shown in Figure 3.

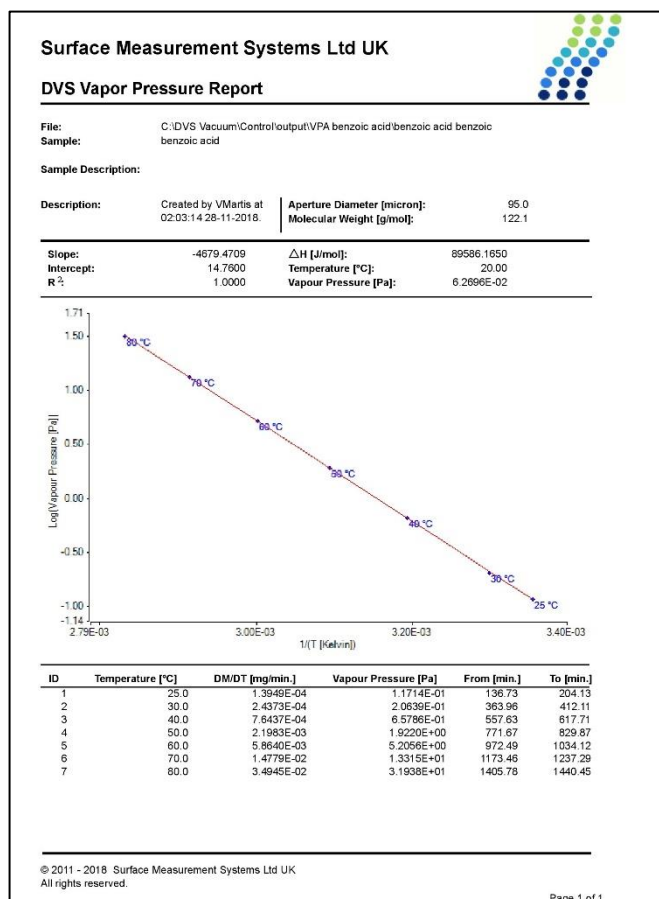


Figure 4 Vapor Pressure Report generated by VPA Analysis Software.

The series of measured vapor pressures at different experimental temperatures, as shown in Figure 4 are then used to determine the A (intercept) and B (slope) constants in Clausius-Clapeyron equation (Equation 5) to calculate enthalpy of vaporization ΔH or heat of sublimation.

$$\log_{10}(p/Pa) = A - \frac{B}{T/K} \quad (5)$$

Vapor pressure values obtained from measured experimental temperatures can be used to determine vapor pressure value at a desired temperature by plotting $\log(P)$ versus $1/T$.

Vapor Pressure Measurements of various substances

a) Vapor pressure measurements of benzoic acid

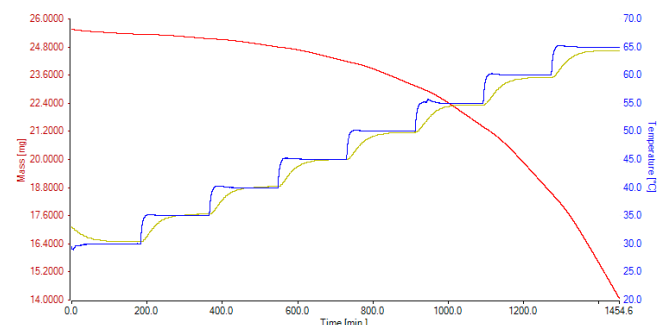


Figure 5 Benzoic acid mass loss rate in the temperature range from 30 to 65°C in 5°C steps with a dwell of 180min at each step. The mass is shown in red, the incubator temperature in blue and the preheater temperature in yellow. Note the preheater only measures the temperature close to the sample pan.

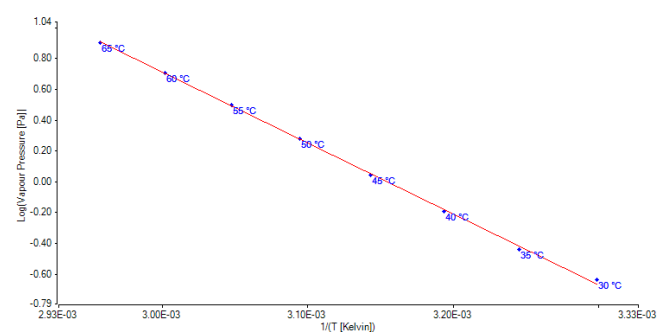


Figure 6 Clausius-Clapeyron plot of benzoic acid vapor pressures.

Table 1 Benzoic acid experimental data for vapor pressures and mass loss rates.

Temperature [°C]	DM/DT [mg/min]	Vapour Pressure [Pa]	Vapour Pressure* [Pa]
30	0.0008	0.23	0.23
35	0.0013	0.36	0.36
40	0.0023	0.65	0.65
45	0.0040	1.11	1.11
50	0.0067	1.91	1.9
55	0.0111	3.17	3.25
60	0.0178	5.11	5.16
65	0.0278	8.05	8.22

* Literature values⁴⁻⁸

Data in Table 1 shows that the experimental vapor pressures agrees with published data in literature.

b) Vapor pressure of bifenthrin

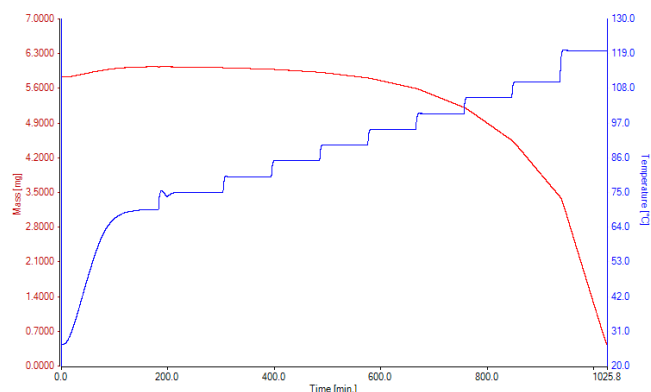


Figure 7 Bifenthrin mass loss rate (mass in red) in the temperature range from 70 to 120°C in 5°C steps (temperature in blue) with a dwell of 180min at each step.

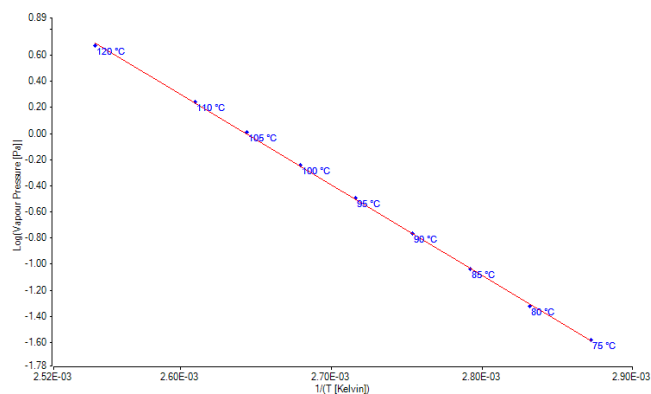


Figure 8 Clausius-Clapeyron plot of bifenthrin vapor pressures.

Table 2 Bifenthrin experimental data for vapor pressures and mass loss rates.

Temperature [°C]	DM/DT [mg/min]	Vapour Pressure [Pa]
80	0.000362	0.05
75	0.000201	0.03
85	0.000691	0.09
90	0.001288	0.17
95	0.002406	0.32
100	0.004272	0.57
105	0.007517	1.02
110	0.012730	1.74
120	0.034149	4.72

c) Vapor pressure of naphthalene

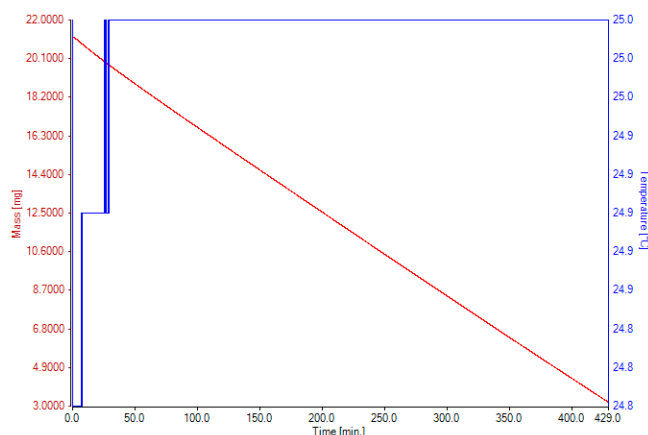


Figure 9 Naphthalene mass loss rate at 25°C. The mass is shown in red and the temperature in blue.

The vapor pressure of naphthalene determined from data in Figure 8 is 11.08Pa which is in good agreement with value of 11.6Pa reported by Environmental Protection Agency (EPA).

d) Vapor pressure of Me₂Si(OH)₂

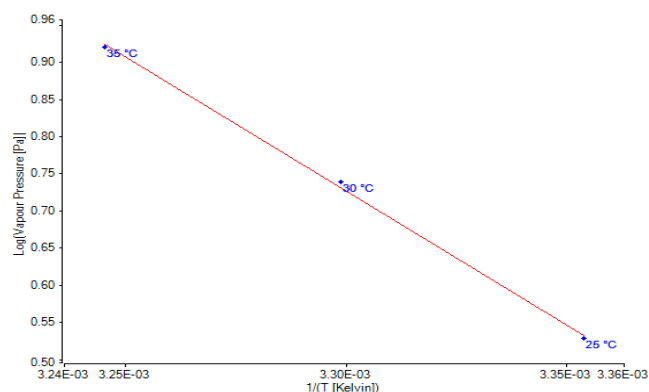


Figure 10 Clausius-Clapeyron plot of Me₂Si(OH)₂ Vapor pressures.

Table 3 Me₂Si(OH)₂ experimental data for vapor pressures and mass loss rates

Temperature [°C]	DM/DT [mg/min]	Vapour Pressure [Pa]
25	0.010799	3.38
30	0.017401	5.49
35	0.026194	8.33



e) Vapor pressure of fluorinated oil

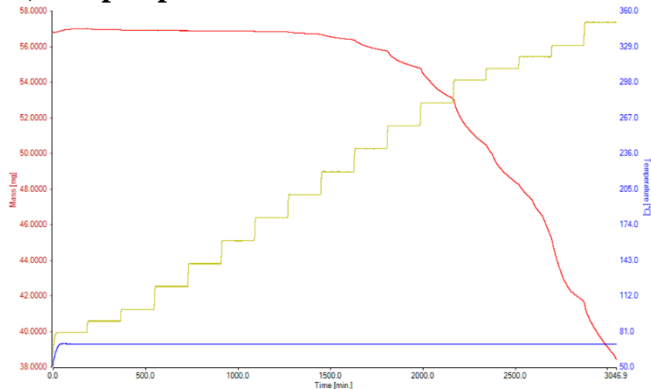


Figure 11 Fluorinated oil mass loss rate in the temperature range from 70 to 350°C in 10°C steps with a dwell of 120min at each step. The mass is shown in red, the incubator and preheater temperatures in blue and yellow respectively.

Table 4 Fluorinated oil experimental data for vapor pressures and mass loss rate. The vapor pressure value at 20°C* was extrapolated from the Clausius-Clapeyron curve shown in Figure 12.

Temperature [°C]	DM/DT [mg/min]	Vapour Pressure [Pa]
20*		4.74E-05
100	3.156E-04	0.013
110	3.969E-04	0.017
120	5.995E-04	0.026
130	9.290E-04	0.041
140	1.579E-03	0.070
150	2.538E-03	0.114
160	2.850E-03	0.130
170	3.830E-03	0.176
180	7.448E-03	0.347
190	1.129E-02	0.532
200	1.532E-02	0.729
210	2.341E-02	1.126
220	2.492E-02	1.211
230	3.479E-02	1.708

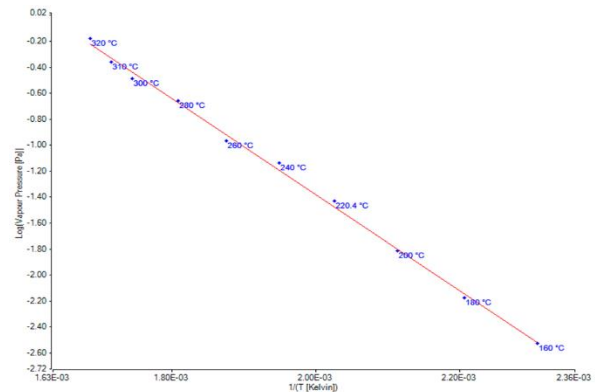


Figure 12 Clausius-Clapeyron plot of fluorinated oil vapor pressures.

f) Vapor pressure of Triisopropanolamine (TIPA)

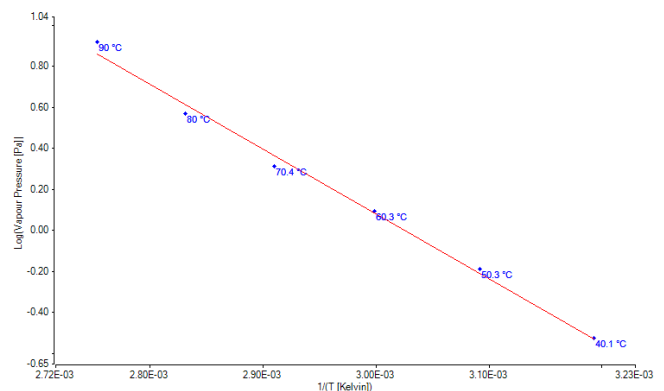


Figure 13 Clausius-Clapeyron plot of TIPA vapor pressures.

Table 5 TIP experimental data for vapor pressures and mass loss rates.

Temperature [°C]	DM/DT [mg/min]	Vapour Pressure [Pa]
40	0.0019	0.30
50	0.0042	0.65
60	0.0078	1.24
70	0.0128	2.06
80	0.0228	3.71
90	0.0505	8.31



Conclusion

This Knudsen Effusion Method is a gravimetric high vacuum method for direct vapor pressure measurements of various substances. It provides reliable and accurate experimental data that can be matched with theoretical predictions as long as the model takes into account complexity of physical and chemical properties.

Acknowledgement:

SMS thanks collaborators for providing samples for measurements.

References

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