

# The (solid + vapor) equilibrium. A view from the arc

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## Abstract

Data sets, from a variety of investigations, on the vapor pressures of the reference materials naphthalene, ferrocene, benzoic acid, and benzophenone, are combined in explanatory graphical representations, which subsequently, are used to draw conclusions about the possibilities and limitations of vapor pressure measurement and the determination of enthalpies of sublimation.

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## 1. Introduction

The slope of the equilibrium curve in the  $PT$  phase diagram is related to the substance's properties  $\Delta S_m$  the difference in entropy between the two forms, and  $\Delta V_m$  the difference in volume between the two forms:

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} \quad (1)$$

The subscript  $m$  is to indicate that the properties are taken on a molar base.

Eq. (1) is named after Emile Clapeyron (1799–1864), the spiritual father, also, of the first French railroad.

From Eq. (1) a special equation can be derived for the case where one of the forms in equilibrium is a vapor with the characteristics of the ideal gas. If so, and, moreover, with negligence of the other form's molar volume with respect to that of the vapor,  $\Delta V_m$  becomes equal to the molar volume of the vapor  $V_m^{\text{vap}}$ , which, in the ideal gas approximation, is given by  $RT/P$ .  $R$  is the gas constant ( $R = 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$ ). Furthermore, along the equilibrium curve,  $\Delta S_m$ , the other property at the right-hand side of Eq. (1), is equal to  $\Delta H_m/T$ , where  $\Delta H_m$  is the difference in molar enthalpy between the two forms.  $\Delta H_m$ , in other words, is the substance's molar heat of sublimation or vaporization. Changing the variables  $P$  and  $T$  to  $\ln P$  and  $(1/T)$ , respectively, the special equation is

$$\frac{d \ln P}{d(1/T)} = - \frac{\Delta H_m}{R} \quad (2)$$

The special equation, named Clausius–Clapeyron equation, can be regarded as an incentive

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to plot the logarithm of the equilibrium pressure against the reciprocal thermodynamic temperature (Clausius–Clapeyron plot).

The measurement of equilibrium vapor pressures, as follows from Eq. (2), is an indirect means of determining  $\Delta H_m$ , the enthalpy of sublimation or vaporization. Information on these quantities is indispensable for the theoretical modeling of intermolecular interactions. The enthalpy of sublimation is related to the lattice energy (see e.g. Ref. [1]) as

$$|U_m(\text{latt})| = \Delta H_m + 2RT \quad (3)$$

In that context, i.e. to study the relationship between molecular and crystalline structure and thermodynamic properties, a range of vapor pressure instruments have been constructed, and put into use by the Utrecht Chemical Thermodynamics Group. All of these instruments have been designed by Cornelis Gijsbertus de Kruif, who is united with Emile Clapeyron by the birthday of 26 January. The practical construction of the instruments was carried out by Tjibbe Kuipers, instrumentmaker, and the late Jan de Groot, specialist in glass-blowing. The first series of instruments constructed were based on thermal conductivity manometry (de Kruif [2], de Kruif and Oonk [3]). These instruments were followed by instruments based on the dynamic method of effusion through an orifice: torsion effusion (de Kruif and van Ginkel [4]); mass-loss effusion (van Ginkel et al. [5]); and the combination of torsion and mass-loss effusion (de Kruif and van Ginkel [6]). As a subsequent step a series of static instruments were developed, using diaphragm manometers (de Kruif et al. [7]). And, lastly, the usability of spinning-rotor friction manometry was explored (van Ekeren et al. [8]).

Among the vast number of, mainly molecular, substances that have been studied, there are four reference substances, of which the equilibrium vapor pressures over crystalline solid have been measured repeatedly—in our own laboratory and also by variety of other research groups. These substances are naphthalene, ferrocene, benzoic acid and benzophenone. In this paper a significant, representative number of data sets pertaining to the four substances is brought together—in the

form of explanatory graphical representations. It is the scope of this paper to use these representations for drawing conclusions about the possibilities and limitations of vapor pressure measurement and the determination of enthalpies of sublimation, in order to formulate a set of recommendations for future work.

## 2. Representation and processing of vapor pressure data

Usually and traditionally experimental vapor pressure data are represented by Clausius–Clapeyron plots. An example is given by Fig. 1(a), which pertains to the static data (de Kruif et al. [7]) on naphthalene. In Fig. 1(b) the same set of data is represented by the  $\ln f$  versus  $1/T$ , or ‘arc’ representation (Oonk et al. [9]; van der Linde et al. [10]), where  $\ln f$  is defined as

$$\ln f = \ln(p \text{ (Pa)}) - \alpha + \frac{\beta}{T} \quad (4)$$

In this expression  $\alpha$  and  $\beta$  are constants that are fixed such that  $\ln f$  is (close to) 0 for the two extreme  $(T, p)$  pairs of the data set. For Fig. 1 data set the values of  $\alpha$  and  $\beta$  are  $\alpha = 31.3420$  and  $\beta = 8640$  K. The change from Fig. 1(a–b) corresponds to an amplification of the sensitivity of the ordinate axis by two orders of magnitude. The result of the change is that details of the data set, that remain hidden in the traditional representation, reveal themselves in the arc representation.

The arc-like appearance, of the data set in the  $\ln f$  versus  $1/T$  representation, is due to the change of  $\Delta H_m^\circ$ , the enthalpy of sublimation, with temperature (for the use of the  $^\circ$  see below):

$$\frac{d\Delta H_m^\circ}{dT} = \Delta C_{p,m}^\circ \quad (5)$$

$\Delta C_{p,m}^\circ$  is the difference in molar heat capacity between the gaseous and the solid (or liquid) states. Generally, the heat capacity of a substance in the gaseous state is smaller than the heat capacity of the same substance in the solid (or liquid) state,  $\Delta C_{p,m}^\circ$  being negative. The effect is that vapor pressure data, in the  $\ln f$  versus  $1/T$

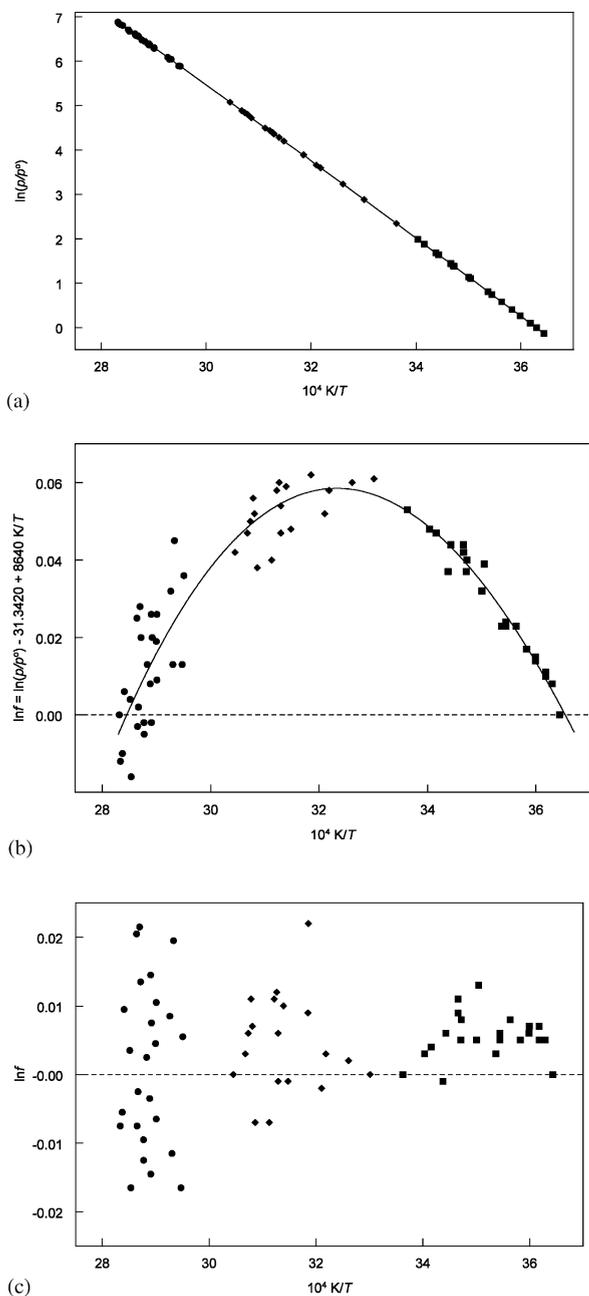


Fig. 1. Naphthalene solid. Class 1 data set from de Kruif et al. [7]. (a) vapor pressures in classical Clausius–Clapeyron representation. (b) vapor pressures in  $\ln f$  representation. Data set split up in three parts. (c) Data set split up in three parts; every part in its own  $\ln f$  representation.

representation, are giving rise to an arc with a maximum. The value of  $\Delta C_{p,m}^\circ$  is reflected by the dimensions of the arc as [10]

$$\Delta C_{p,m}^\circ \cong -8R(T_{\max}b)^{-2}h \quad (6)$$

where,  $T_{\max}$  is the temperature corresponding to the maximum of the arc,  $h$  is the height (the  $\ln f$  value at the maximum), and  $b$  the width at the base of the arc. In the case of Fig. 1(b),  $T_{\max} \cong 315$  K,  $b \cong 8 \times 10^{-4} \text{ K}^{-1}$ ,  $h \cong 0.06$ , from which  $\Delta C_{p,m}^\circ \cong -63 \text{ J K}^{-1} \text{ mol}^{-1}$ .

For the conditions under which the Clausius–Clapeyron equation, Eq. (2), is valid and neglecting any change of  $\Delta C_{p,m}^\circ$  with temperature, equilibrium vapor pressures are represented by

$$\begin{aligned} R \ln(p \text{ (Pa)}) &= \frac{-\Delta G_m^\circ(\theta)}{\theta} + \Delta H_m^\circ(\theta) \left( \frac{1}{\theta} - \frac{1}{T} \right) \\ &+ \Delta C_{p,m}^\circ \left\{ \frac{\theta}{T} - T + \ln \left( \frac{T}{\theta} \right) \right\} \end{aligned} \quad (7)$$

In Eq. (7), which is the integrated form of Eq. (2), the symbol  $\theta$  is for a selected reference temperature.  $\Delta G_m^\circ$  is the difference (vapor minus solid/liquid) in molar Gibbs energy between the gaseous and the solid or liquid states for  $p = 1$  Pa. The standard state of  $p = 1$  Pa finds expression in the ‘°’ (for homogeneity of representation, the ‘°’ is not removed from  $\Delta H_m^\circ$  and  $\Delta C_{p,m}^\circ$ , although, for the approximations made, these two quantities are independent of pressure).

In (the Utrecht) laboratory practice, Eq. (7), the Clarke and Glew equation [11], is used as the regression model for the least-squares processing of experimental data. The quantities  $\Delta G_m^\circ$ ,  $\Delta H_m^\circ$  and  $\Delta C_{p,m}^\circ$  have the function of parameters to be fitted to the experimental data. For the data set in Fig. 1, the least-squares computation, taking  $\theta = 315.00$  K, gives rise to  $\Delta G_m^\circ(\theta) = -10402 \pm 5 \text{ J mol}^{-1}$ ;  $\Delta H_m^\circ(\theta) = 71.48 \pm 0.03 \text{ kJ mol}^{-1}$ ; and  $\Delta C_{p,m}^\circ = -62 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ .

For each of the substances, naphthalene, ferrocene, benzoic acid, and benzophenone, several data sets are available on the equilibrium between solid and vapor. Details on the temperature ranges covered by the data sets and the pressures involved

Table 1

Temperature and pressure data pertaining to the equilibrium between solid and vapor; temperatures are in K, and pressures in Pa

Naphthalene	244–353	353.53	0.02–950	11.3
Ferrocene	277–368	445	0.10–300	1.02
Benzoic acid	293–391	395.52	0.06–600	0.096
Benzophenone	273–321	321.03	0.003–1.2	0.087

Columns from left to right: substance; temperature range of available experimental data; triple point temperature; pressure range involved; equilibrium vapor pressure at  $T = 298.15$  K.

are summarized in Table 1, which, in addition, gives the triple point temperatures.

For the purpose of this communication, all of the individual data sets of each of the four substances have been subjected to a visual, as well as to a statistical screening. By making  $\ln f$  versus  $1/T$  representations, and by making least-squares computations in terms of Eq. (7), respectively. It became clear that, by and large, there are two classes of data set, to be indicated, hereafter, by class 1 and 2.

A typical class 1 data set is the one shown in Fig. 1(b), it clearly displays the characteristic arc with a maximum, and additionally, through Eq. (6), it implies a realistic  $\Delta C_{p,m}^\circ$ . When subjected to a least-squares treatment, in terms of Eq. (7), it yields a  $\Delta C_{p,m}^\circ$  value, which (i) is virtually the same as the one 'read' from the arc, using Eq. (6), and (ii) has a statistical uncertainty which is less than 20% of its value. Moreover, the calculated standard deviation (between calculated and experimental pressure) of the (three-parameter) solution is two or three times lower than the one of which the parameters that have been adjusted are just  $\Delta G_m^\circ$  and  $\Delta H_m^\circ$ .

A class 2 set of data, on the other hand, does not reveal, in its  $\ln f$  representation, any arc at all. And, unlike the class 1 case, a least-squares treatment with three parameters fails to give a lower standard deviation than the treatment with two parameters.

The outcome of the screening of the data sets is visualized, for each of the four substances in Figs. 2–5. In these figures the constants  $\alpha$  and  $\beta$  are

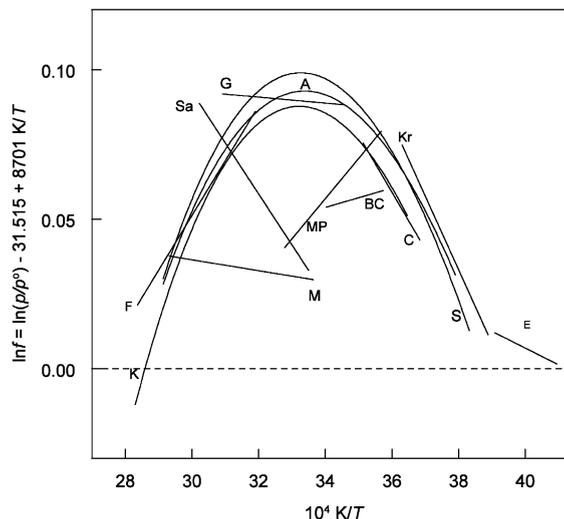


Fig. 2. Naphthalene, solid. Data sets on equilibrium vapor pressures in  $\ln f$  representation. Concave curves, class 1 data sets: (A) Ambrose et al. [12]; (K) de Kruif et al. [7]; (S) Sasse et al. [13]. Straight lines are for class 2 data sets: (F) Fowler et al. [14]; (M) Murata et al. [15]; (Sa) Sato et al. [16]; (G) Gildeblatt et al. [17]; (MP) Macknick and Prausnitz [18]; (BC) Bradley and Cleasby [19]; (C) Colomina et al. [20]; (Kr) de Kruif [21]; (E) van Ekeren et al. [22].

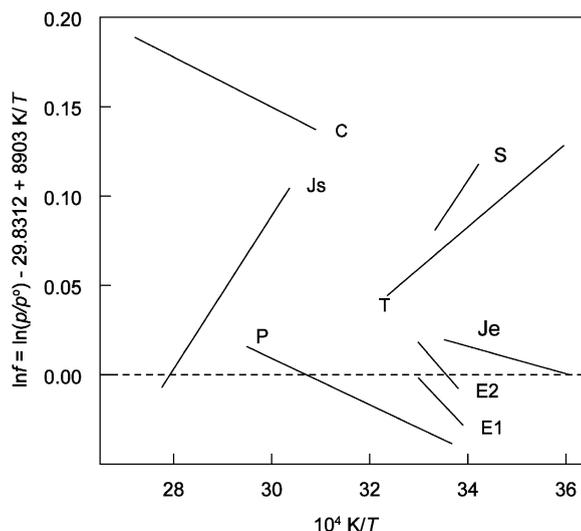


Fig. 3. Ferrocene, solid. Data sets on equilibrium vapor pressures in  $\ln f$  representation. Straight lines are for the data sets: (C) Cordes and Schreiner [23]; (Js) Jacobs et al. (static) [24]; (Je) Jacobs et al. (effusion) [24]; (P) Pelino et al. [25]; (S) Ribeiro da Silva and Monte [26]; (E1) and (E2) Edwards and Kington (series 1 and 2) [27]; (T) Torres-Gomez et al. [28].

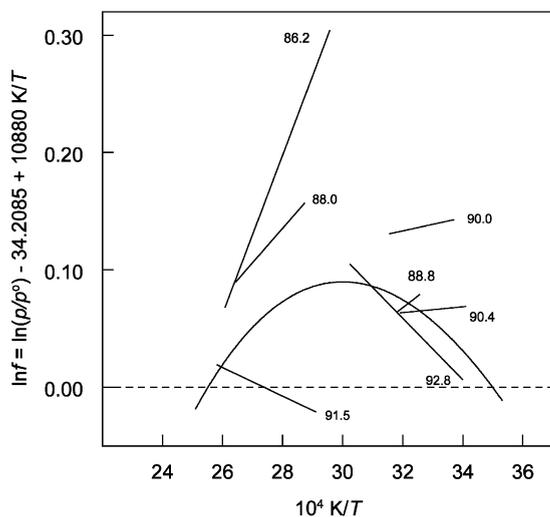


Fig. 4. Benzoic acid, solid. Data sets on equilibrium vapor pressures in  $\ln f$  representation. Concave curves, class 1 data set by de Kruif and Blok [29]. Straight lines are for class 2 data sets, indicated by the enthalpy of sublimation value they would involve: (86.2) Malaspina et al. [30]; (88.0) Mertl [31]; (88.8) Ribeiro da Silva and Monte [26]; (90.0) de Kruif [32]; (90.4) Colomina et al. [20]; (91.5) Davies and Jones [33]; (92.8) van Ginkel et al. [5].

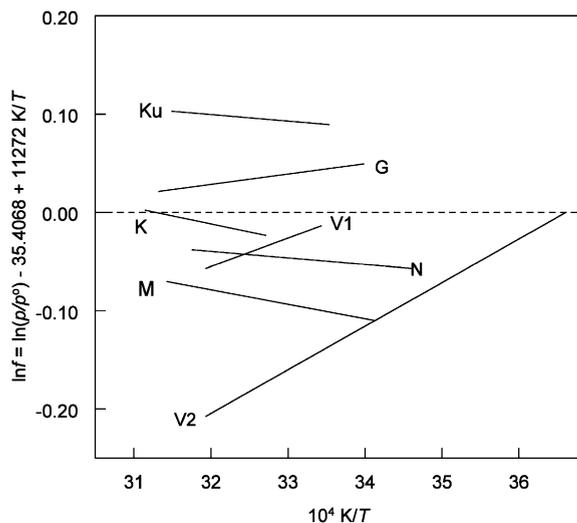


Fig. 5. Benzophenone, solid. Data sets on equilibrium vapor pressures in  $\ln f$  representation. Straight lines are for the data sets, (G) van Ginkel [34]; (K) de Kruif et al. [35]; (M) de Kruif et al. [36]; (N) Neumann and Völker [37]; (Ku) de Kruif [32]; (V1) and (V2) Volmer and Kirchhoff (series 1 and 2) [38].

fixed such that  $\ln f$  is (close to) 0 for the two extreme  $(T, p)$  pairs of all the constituting data sets. The class 1 data sets are represented by concave curves, and the class 2 sets by straight lines. The concave curves are  $\ln f$  representations of the three-parameter fits of the data; they extend over the  $(1/T)$  range of the experimental data. Similarly, the straight lines are representations of the two-parameter fits of the class 2 data sets.

### 3. Discussion

For the equilibrium between vapor and solid, data sets of class 1 are exceptional. Only in a limited number of cases the ensemble of data clearly and unambiguously reveal an arc, along with a reasonable  $\Delta C_{p,m}^\circ$  to be read from it. The four class 1 sets, three for naphthalene and one for benzoic acid, shown in Figs. 2 and 3, have been obtained by static measurements, over a wide range of temperature, about 75 K. More than by the technique applied, the appearance of the arc is the result of the wide range of temperature. To illustrate this, Fig. 1(c), the data set for naphthalene, Fig. 1(a), is split up in three parts, and each of the parts is displayed separately in its own  $\ln f$  representation. From the figure it follows that the complete data set of class 1 can be looked upon as the sum of three subsets of class 2: from right to left it becomes increasingly difficult to see the arc in the three collections of data points. This observation implies that, in terms of precision of vapor pressure, a class 2 set of data not necessarily is inferior to a class 1 set.

As was stated in the previous section, a class 1 set of data gives rise to a correct value of  $\Delta C_{p,m}^\circ$ . It implies that a like set yields the correct enthalpy of sublimation ( $\Delta H_m^\circ$ ), as a function of temperature. From the line of argument in the foregoing paragraph, it follows that correct  $\Delta C_{p,m}^\circ$  and  $\Delta H_m^\circ$  information will result from a number of combined class 2 sets of data (from different investigations), provided, also, that they span a sufficiently large range of temperature. Provided, also, that systematic errors are absent.

An important issue is the ability of an individual class 2 data set to yield an accurate value for  $\Delta H_m^\circ$ .

In the  $\ln f$  versus  $1/T$  representation of data,  $\Delta H_m^\circ$ , as follows from Eqs. (2) and (4), is given by

$$\frac{\Delta H_m^\circ}{R} = \beta - \frac{d(\ln f)}{d(1/T)} \quad (8)$$

A positive slope in the  $\ln f$  representation means that  $\Delta H_m^\circ$  is smaller than  $\beta R$ , and a negative slope corresponds to a  $\Delta H_m^\circ$  which is greater than  $\beta R$ . Keeping this in mind, one can make a number of observations. From Figs. 2–5 it follows that for a given substance at a given temperature, the calculated values of  $\Delta H_m^\circ$ , the enthalpy of sublimation, typically are in a range of 6% of their value. In other words, a range of 4 or 5 kJ mol<sup>-1</sup>. The question whether the scatter in  $\Delta H_m^\circ$  values is caused primarily by random errors or primarily by systematic errors is difficult to answer. Systematic errors may be the result of systematic errors in temperature, related to the design of the instrument [39]. Random errors, for their part, obviously, become the more influential the lower the number of data pairs and the range of temperature.

In the context of class 2 data sets and systematic and/or random errors, special attention should be given to the automated, combined torsion- and mass-loss effusion instrument designed by de Kruif and van Ginkel [6]. The instrument operates such that during a run of typically 10 h some 50 isothermal stops are made in the range of temperature where the vapor pressure increases from  $p = 0.1$  to 1.0 Pa. At each arrest, mass-loss effusion as well as torsion effusion data are collected. The raw data are processed, in a linear manner in terms of  $\ln p$  and  $(1/T)$ , and finally presented in the form of a table containing some ten data pairs (the outcome, therefore, is a class 2 data set, having  $\Delta C_{p,m}^\circ = 0$ ). For reasons not understood, when processed separately, the torsion data give rise to a  $\Delta H_m^\circ$  value which is invariably higher than the  $\Delta H_m^\circ$  value derived from the mass-loss data. The difference between the two varies from about 1.25 to 2.5 kJ mol<sup>-1</sup>. From 1983, the results published by our group are pertaining to the combined processing of torsion and mass-loss data. The same holds true for the  $PT$  data used in this communication.

It has been argued [40] that the combined torsion- and mass-loss effusion instrument has a certain disadvantage which would be related to the use of thermistors. The heat given off by the thermistor could induce a difference between the temperature measured and the temperature corresponding to phase equilibrium. Moreover, the difference would be a function of the pressure of the vapor in the effusion cell. Whether or not as the effect of thermistor heating, we have noticed that the combined torsion and mass-loss effusion data—when combined with other data and plotted in the  $\ln f$  representation, along with the optimized calculated arc—intersect the calculated arc at a certain angle. That angle is such that the effusion data have a deviation in  $\Delta H_m^\circ$  which, for the seven cases available, runs from  $-1$  to  $+2$  kJ mol<sup>-1</sup>. We will come back to this issue in a forthcoming publication.

In the paper on reference materials for calorimetry and differential thermal analysis, by Sabbah et al. [41], recommended values are given for the enthalpy of sublimation, at  $T = 298.15$  K, of the four substances, along with estimated uncertainties. The numerical values are naphthalene,  $72\,600 \pm 600$  J mol<sup>-1</sup>; ferrocene,  $73\,420 \pm 1080$  J mol<sup>-1</sup>; benzoic acid,  $89\,700 \pm 1000$  J mol<sup>-1</sup>; benzophenone,  $93\,770 \pm 3540$  J mol<sup>-1</sup>. Ignoring this information, and just pretending that Figs. 2–5 display all of the data available, one is inclined to modify these values into the following: naphthalene,  $72\,450 \pm 200$ ; ferrocene,  $75\,500 \pm 2000$ ; benzoic acid,  $92\,800 \pm 1000$ ; benzophenone,  $93\,250 \pm 2000$ . Whatever the case may be, it is obvious that, in fact, naphthalene is the only of the four which fully deserves the designation of reference material.

To continue, we will turn to the vapor pressures themselves, and use the evidence displayed by the  $\ln f$  representations to draw conclusions about accuracy and precision of vapor pressure measurements. To do so, it must be kept in mind, that a change of 0.01 in  $\ln f$  is corresponding to a change of 0.01 times  $p$  in  $p$ , i.e. a change of 1% in pressure.

In the middle part of Fig. 1, to start with, the curve which is drawn is representing the calculated result of the statistical processing of the data in

terms of Eq. (7). The standard deviation ( $s$ ) in the  $\ln f$  values of the experimental points with respect to the calculated values is about  $s = 0.01$ . For vapor pressures over molecular solids, like naphthalene, the value of  $s = 0.01$  is representative of the highest precision (the degree of absence of random errors) that can be obtained. As a matter of fact, most of the individual data sets for naphthalene, displayed in Fig. 2, have  $s < 0.02$ .

In spite of their (high) precision, the mutual coherence of the individual data sets is rather poor. Differences of 0.10 in  $\ln f$  value, i.e. 10% in pressure, are not exceptional. The accuracy (degree of absence of systematic errors) of vapor pressure measurement, apparently, is a matter of concern. The ensemble of results will now be discussed, substance by substance, to begin with naphthalene.

In the case of naphthalene, as follows from Fig. 2, there is substantial agreement between the class 1 data by Ambrose et al. [12], de Kruif et al. [7] and Sasse et al. [13]. In addition, agreement with the class 1 data is shown by the data by Fowler et al. [14], de Kruif [21] and Colomina et al. [20]. In a recent investigation [10], all of the data available for crystalline naphthalene have been used to arrive at a recommended expression, in terms of Eq. (7), for the vapor pressure of the material. The result of that investigation, valid in the range  $245 < (T \text{ (K)}) \leq 353.43$  (triple point), corresponds to  $\Delta G_m^\circ(\theta) = -5494 \text{ J mol}^{-1}$ ;  $\Delta H_m^\circ(\theta) = 72.35 \text{ kJ mol}^{-1}$ ; and  $\Delta C_{p,m}^\circ = -46 \text{ J K}^{-1} \text{ mol}^{-1}$ , for  $\theta = 296.30 \text{ K}$ , and  $R = 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$ . This result, in our view, means that crystalline naphthalene is an excellent reference material for checking the performance of vapor pressure instruments, in the range of temperature between 245 and 355 K, for pressures between 0.2 mPa and 1 kPa. Here we estimate that the accuracy of the values calculated for  $p$  is  $\pm 1\%$  over the whole range of temperature. In addition, the indication  $\pm 1\%$  is also representative of the difference between the above result and the set of pressure values proposed in 1987 by Ambrose [42].

Ferrocene, with its relatively high triple point temperature has the potential of being a suitable calibrant for vapor pressure instruments. The

information displayed in Fig. 3, and covering the range in temperature from 277 to 367 K, can be looked upon as an incentive for further work, preferably over a large range of temperature.

In the case of benzoic acid, with the availability of only one class 1 data set, it is not yet possible to recommend an expression with which vapor pressures can be calculated with an accuracy of  $\pm 1\%$ . The use of benzoic acid as a (potential) reference material has been questioned [3,41,15] because of the possibility of dimerization in the vapor phase. Even if one would know the vapor pressure at saturation as a function of temperature, one should know the degree of dimerization in order to be able to use the acid as a calibrant. The problem is that, in the case of the effusion technique, the mean mass of the molecules in the vapor phase is needed to derive the real pressure from the experimental observations. Besides, the role of molecular mass is different for mass-loss and torsion effusion. In the case of the class 1 data, read the static data, the experimental observations directly give the pressure itself.

The data available for benzophenone are in a small range of temperature, limited by the freezing point of water and the (low) melting point of the substance itself. Taking all of the data sets shown, the equilibrium pressure at  $T = 298.15 \text{ K}$ , as the arithmetic mean, is  $p = 88.4 \text{ mPa}$ . Excluding the unpublished data by de Kruif [32], the mean pressure is reduced by 2% to 86.6 in Pa, with a standard deviation of 6.5%.

In vapor pressure work, a source of systematic errors is related to the fact that the temperature of the temperature sensor deviates from the temperature of the solid in equilibrium with vapor and such that the deviation is a function of temperature. Such instrumental imperfections can be traced, even without using a reference material, simply by making an  $\ln f$  representation. Under condition that the range of temperature, in relation to the precision of the instrument, is large enough to clearly reveal the arc. An example is given by Blok et al. [39], pertaining to measurements on liquid 1,3,5-trichlorobenzene. Alarmed by an unusual asymmetric nature of the arc

(constructed after the introduction of the arc, 1998, and about 8 years after the collection of the original data), the instrument was tested by measuring the vapor pressures over liquid naphthalene in the range  $371 < (T \text{ (K)}) < 422$ . The  $\Delta C_{p,m}^\circ$  value read from the  $\ln f$  representation of the data was about five times higher than the true value. Thereafter, it became clear that the temperature, indicated by the sensor, began to deviate at  $T = 400 \text{ K}$ .

To conclude, we will address the issue of the number of significant figures to be used in publishing vapor pressures of solids. To that end, we re-examine the information contained in Fig. 1. In a sense, the complete set of data is an unusual one: from the middle part of Fig. 1 it follows that the scatter of the individual points around the calculated arc is lowest at the low-temperature part, i.e. for the squares at the right-hand side of the figure. In the bottom part of Fig. 1 this aspect is reflected by the fact that, from left to right, it becomes easier to see an arc in the  $\ln f$  representations of the subsets of data points. In line herewith, and in agreement with statements made above, the mathematical processing of the subsets of data in terms of Eq. (7) gives rise to standard deviations that decrease from left to right. For the circles,  $s = 0.012$ ; for the diamonds,  $s = 0.007$ ; and for the squares,  $s = 0.003$ . A similar trend is shown by the computed  $\Delta C_{p,m}^\circ$  values and their statistical uncertainties: for the circles,  $\Delta C_{p,m}^\circ = -125 \pm 268 \text{ J K}^{-1} \text{ mol}^{-1}$ ; for the diamonds,  $\Delta C_{p,m}^\circ = -64 \pm 55 \text{ J K}^{-1} \text{ mol}^{-1}$ ; for the squares,  $\Delta C_{p,m}^\circ = -61 \pm 21 \text{ J K}^{-1} \text{ mol}^{-1}$ . One could say that the subset of squares tends to the status of class 1. The standard deviation  $s = 0.003$ , shown by the subset of squares, is representative of about the highest precision that can be obtained. For a pressure of 100 Pa it comes down to an uncertainty of 0.3 Pa, and it asks for the use of four significant figures:  $100.0 \pm 0.3 \text{ Pa}$ . Similarly, for a pressure of 99 Pa it would come down to  $99.0 \pm 0.3 \text{ Pa}$ . However, for uniformity of representation, we suggest that, in all cases, the original observations are converted to pressure values with four significant figures. In doing so, it is avoided that the dispersion of the datapoints, in particular

in  $\ln f$  representations, is enhanced as a result of rounding off.

#### 4. Conclusion

The ensemble of vapor pressure data, displayed in Figs. 2–5, allow to draw the following conclusions.

- Accurate values for the enthalpy of sublimation, including a reliable value for the heat capacity difference, can be derived from vapor pressure data, provided that the data span an interval of temperature of at least 50 K.
- The heat of sublimation value derived from a single data set covering a range of 20–30 K, has an uncertainty of  $\pm 3\%$ .
- Out of the four substances examined, only naphthalene meets the requirements for a reference material for vapor pressure measurements, around  $T = 298 \text{ K}$  and  $p = 10 \text{ Pa}$ .
- Ferrocene has the potential of being a convenient reference material for vapor pressures of 1 Pa at 298 K; collection of independent data covering the range from room temperature to the substance's triple point is highly recommended.
- Benzoic acid and benzophenone, which have been proposed as reference materials for pressures of 0.1 Pa at 298 K, in addition to other inconveniences, still have uncertainties in their vapor pressures of about  $\pm 3\%$  and  $\pm 5\%$ , respectively.
- The arc representation corresponds to a powerful tool for checking the performance of vapor pressure instruments.

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