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VAPOUR PRESSURE OF DSC CALIBRATION SUBSTANCES

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Abstract

For a large number of DSC calibration substances the vapour pressure at room temperature or at transition temperature (whichever is the highest) is given. It is important to know the vapour pressure of substances, because a DSC measurement on a substance with a high vapour pressure requires encapsulation of the substance in a hermetically sealed crucible to prevent evaporation. Because the calibration procedure must be performed using the same type of sample pan as will be used during the actual measurements, the presented information allows one to decide which calibration substances and/or what type of sample pan should be used for calibration.

Keywords: DSC calibration, test for hermetic sealing, vapour pressure of substances

Introduction

Many reference materials for DSC calibration are mentioned in literature. A good survey has recently been given by Sabah *et al.* [1]. The German Thermal Analysis Society GEFTA (Gesellschaft für Thermische Analyse) presented recommendations for a correct and instrument independent calibration, together with substances to be used for this procedure [2, 3]. Suitable materials should not show any unwanted reactions, for instance with the sample pan [1–4]. Another problem that should be avoided is evaporation of substance from the sample pan, because this will result in a decrease of the sample mass, and therefore in a wrong value for the (specific) heat of transition [1–5].

Sabah *et al.* [1] advise the use of hermetically sealed sample holders for substances with high vapour pressures, but this can give practical problems. According to our experience, application of 'hermetically' sealed aluminium pans often does not result in real hermetic sealing: in many cases we observed mass loss. Hermetic sealing can be easily tested by filling a sample container with water and storing the filled pan for several days at room temperature; if the mass has changed after some days it is clear that the pan was not sealed hermetically. In many cases this is a better test than heating a sample container filled with water to a temperature above 100°C and observe when it bursts, because even badly closed pans can be heated above 100°C for short times without bursting.

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Of course, one can also use pans that can be better sealed (medium or high pressure pans). The high mass and the large dimensions (and the high price) are, however, disadvantages compared to the normal aluminium pans. Furthermore the calibration should be performed with the same type of pan that will be used during the actual experiments.

For these reasons calibration substances with the lowest possible vapour pressures are needed. Therefore a list of calibration substances is compiled in which, besides the usual quantities transition temperature and (specific) enthalpy of transition (taken from different sources [1–6]), also the vapour pressure data are included. For substances with transitions below room temperature, the vapour pressure at 298.15 K is important, being the temperature for storage and preparation. For substances with a transition at temperatures above room temperature the vapour pressure at the transition temperature is relevant.

Determination of the vapour pressure

Vapour pressure data have been presented in different literature sources and in different forms:

I. The Handbook of Chemistry and Physics [7, Ch. 6, p. 99] gives IUPAC recommended data in the form of a table, presenting vapour pressures as a function of temperature (10 K interval). The vapour pressure at the relevant temperature is found by interpolation (extrapolation in the case of naphthalene), making use of the linear relation between the logarithm of the pressure and the reciprocal thermodynamic temperature (expressed in Kelvin). Thus the vapour pressures are found for water (p(298.15 K)=3.17 kPa), naphthalene (p(353.39 K)=1.00 kPa) and hexafluorobenzene (p(298.15 K)=11.2 kPa).

II. A pressure – temperature table with large increments (the temperatures belonging to pressures 1, 10, 100 Pa, 1, 10, and 100 kPa) is presented in [7, Ch. 6, p. 60–87]. In this case an interpolation/extrapolation must be made from an $\ln p$ *vs.* T^{-1} plot (temperature expressed in Kelvin!). This resulted in vapour pressures of cyclopentane (p(298.15 K)= 41.7 kPa), cyclohexane (p(298.15 K)= 12.9 kPa), biphenyl (p(342.08 K)= 0.11 kPa), benzil (p(368.01 K)= 0.022 kPa), and bismuth (p(544.55 K)$<10^{-4}$ kPa).

III. Parameters of a vapour pressure equation are given that allow for the calculation of the vapour pressure as a function of temperature. The Handbook of Chemistry and Physics [7, Ch. 4, p. 124–125] contains a table for the metals. The applied equation is: $\log(p/\mathrm{atm})=A+B/T+C\log T+D/T^3$. In this equation the temperature is expressed in Kelvin and the pressure, as indicated, in atmosphere (1 atm=101.325 kPa). This was used to calculate the vapour pressure of:

mercury (A=5.116, B= –3190, C=D=0): p(298.15 K)=0.0003 kPa;
gallium (A=6.657, B= –14208, C=D=0): p(302.91 K)$<10^{-4}$ kPa;
indium (A=5.991, B= –12548, C=D=0): p(429.75 K)$<10^{-4}$ kPa;
tin (A=6.036, B= –15710, C=D=0): p(505.08)$<10^{-4}$ kPa;
lead (A=5.643, B= –10143, C=D=0): p(600.61 K)$<10^{-4}$ kPa;

zinc (A=6.102, B= –6776, C=D=0): p(692.68)=0.021 kPa;
aluminium (A=9.459, B= –17342, C= –0.7927, D=0): p(933.47)<10^{-4} kPa;
silver (A=9.127, B= –14999, C= –0.7845, D=0): p(1234.93)=0.0004 kPa; and
gold (A=9.152, B= –19343, C= –0.7479, D=0): p(1337.33)<10^{-4} kPa.

IV. Stephenson and Malinowski [8] give parameters of the Antoine vapour pressure equation for several organic compounds: $\log(p/\text{kPa})=A-B/\{C+(T/\text{K})\}$.

For diphenylether: A=8.7091; B=3351.9; C=0; this results in a vapour pressure of 0.003 kPa at 300.02 K.

For acetanilide: A=10.36243; B=4556.937; C=0; resulting in a vapour pressure of 0.04 kPa at T=387.53 K.

For benzoic acid: A=7.80991; B=2776.12; C=-43.978; this results in a vapour pressure of 0.82 kPa at 395.52 K.

V. Reiser *et al.* [9] presented the following equation for the vapour pressure of adamantane: $\ln(p/\text{kPa})=65.206-9335.6/(T/\text{K})-15.349\log(T/\text{K})$, which results in a pressure of 0.017 kPa at T=298.15 K.

VI. For 1,3-difluorobenzene only few relevant data were found:

– the boiling temperature at atmospheric pressure (p=101.325 kPa): 355.15 K [10];

– the enthalpy of evaporation for some temperatures [11]: the mean value between 298 and 355 K is: ΔH_{vap}=34.56 kJ mol^{-1}. Now using the Clausius–Clapeyron equation ([12]):

$$\ln\left(\frac{p_2}{p_1}\right)=-\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

with R=8.314472 J K^{-1} mol^{-1}, p_1=101.325 kPa and T_1=355.15 K the vapour pressure at 298.15 K can be calculated: 10.6 kPa.

VII. The vapour pressure of diphenylacetic acid was more difficult to determine. In Ref. [13], page C-86 a sublimation pressure is given: 3.33 kPa at 468.15 K. No value for the enthalpy of vaporisation was found. Therefore the enthalpy of vaporization was estimated by taking the average of the values for some corresponding substances [13, p. D 153–163 and 14, Ch. 5, p. 39–56]:

benzoic acid:	ΔH_{vap}=68.2 kJ mol^{-1}
benzil:	ΔH_{vap}=62.9 kJ mol^{-1}
acetinilide:	ΔH_{vap}=64.7 kJ mol^{-1}
naphthalene:	ΔH_{vap}=71.4 kJ mol^{-1}
diphenylether:	ΔH_{vap}=51.5 kJ mol^{-1}
Mean value:	ΔH_{vap}=63.7 kJ mol^{-1}

Now, using the same method as for 1,3-difluorobenzene, an estimated value for the vapour pressure was found: 0.5 kPa at 420.44 K.

VIII. The vapour pressure of sodium nitrate [5, 13, p. B 138] has not been measured, but will be very low. A problem is that the substance decomposes above 650 K (only 70 K above the melting temperature).

Table 1 Calibration substances for DSC and DTA. The following data are presented: temperature of transition in degrees Celsius and Kelvin, specific enthalpy of transition, type of transition, reference, relevant temperature for vapour pressure and vapour pressure at relevant temperature

Substance	T_{tr}/°C	T_{tr}/K	ΔH_{tr}/J g^{-1}	ΔH_{trans}	[Ref.]	T_{rel}/K	p/kPa
Cycopentane	–150.77	122.38	69.60	sol-sol	1, 3	298.15	41.7
	–135.09	138.06	4.91	sol-sol	1, 3		
	–93.43	179.72	8.63	sol-liq	1, 3		
Cyclohexane	–86.90	186.25	79.80	sol-sol	1	298.15	12.9
	6.66	279.81	31.50	sol-liq	1		
1,3-Difluobenzene	–85.85	187.30	7.25	sol-sol	1	298.15	10.6
	–69.07	204.08	75.21	sol-liq	1		
Adamantane	–64.53	208.62	24.78	sol-sol	5	298.15	0.017
Mercury	–38.83	234.32	11.44	sol-liq	1	298.15	0.0003
Water	0.00	273.15	333.78	sol-liq	5	298.15	3.17
Hexafluorobenzene	5.15	278.30	62.28	sol-liq	1	298.15	11.2
Diphenylether	26.86	300.01	107.10	sol-liq	1	300.02	0.003
Gallium	29.76	302.91	79.88	sol-liq	1, 3	302.91	$<10^{-4}$
Biphenyl	68.93	342.08	120.40	sol-liq	1	342.08	0.11
Naphthalene	80.20	353.35	148.70	sol-liq	1	353.39	1.00
Benzil	94.82	367.97	112.00	sol-liq	1	368.01	0.022
Acetanilide	114.33	387.48	160.20	sol-liq	1	387.53	0.04
Benzoic acid	122.35	395.50	147.90	sol-liq	1	395.52	0.82
Diphenylacetic acid	147.26	420.41	147.30	sol-liq	1	420.44	0.5
Indium	156.60	429.75	28.62	sol-liq	1, 3	429.75	$<10^{-4}$
Tin	231.93	505.08	60.40	sol-liq	1, 3	505.08	$<10^{-4}$
Bismuth	271.40	544.55	53.83	sol-liq	1, 3	544.55	$<10^{-4}$
Sodium nitrate	276.00	549.00	40.10	sol-sol	1	580.00	–
	307.00	580.00	178.00	sol-liq			
Lead	327.46	600.61	23.02	sol-liq	1	600.61	$<10^{-4}$
Zinc	419.53	692.68	107.45	sol-liq	1	692.68	0.021
Lithium sulphate	578.28	851.43	228.10	sol-sol	1, 3	851.43	–
Aluminium	660.32	933.47	398.10	sol-liq	1, 3	933.47	$<10^{-4}$
Silver	961.78	1234.93	104.73	sol-liq	3, 6	1234.93	0.0004
Gold	1064.18	1337.33	63.73	sol-liq	3, 6	1337.33	$<10^{-4}$

Lithium sulphate [5, 13, p. B 104] is stable at the transition temperature. The vapour pressure will be very low at this temperature.

The vapour pressures of the reference materials at the relevant temperatures are included in Table 1.

Discussion of the results

Some standard reference substances, as can be seen from Table 1, show very high vapour pressures. This implies that, even with the use of so-called ‘hermetically sealed’ pans, mass loss can occur during an experiment.

To be sure that during an experiment the sample did not lose any mass, it is always necessary to measure the sample mass before and after the experiment. If loss of mass is observed, it is possible that this is caused by evaporation of some substance that is stuck on the outside of the sample pan and it is advisable to run a second experiment; when the mass during this second experiment remains constant, the results obtained during this experiment are valid.

What vapour pressure is acceptable depends on the quality of the sealing of the sample pans and on the time spent in the ‘dangerous’ zone, i.e. on the heating and cooling rate. The following rules of thumb may be convenient.

For storage of the sample, in order to use it more than once, the vapour pressure at room temperature should be lower than 0.01 kPa. For adamantane, encapsulated in a normal crimped pan, we measured mass loss when stored at room temperature.

For fast runs above room temperature a pressure of 1 kPa will be acceptable, provided that the experiment is performed using a hermetically sealed pan.

Substances with a high vapour pressure at room temperature are difficult to handle. Cyclopentane, cyclohexane, 1,3-difluorobenzene and hexafluorobenzene have such high vapour pressures at room temperature that only very well closed sample pans can be applied. Even then, it is necessary to weigh carefully before and after the experiment. Sometimes it is advisable to make a hole in the sample pan after the experiment and heat to completely evaporate the sample. In this way an extra check of the sample mass is possible.

Most metals show a very low vapour pressure. For metals, however, attack of the aluminium sample holder can occur. Sometimes this reaction can be avoided by encapsulating the sample in some aluminium oxide powder [5]. The reaction of zinc with the sample holder can be stimulated by the relatively high vapour pressure (0.021 kPa) at the melting temperature.

Conclusions

- The vapour pressure of calibration substances is determined at room temperature or at transition temperature.
- Volatile samples with pressures above 10 kPa at room temperature (cyclopentane, cyclohexane, 1,3-difluorobenzene and hexafluorobenzene) should preferably be handled only in very well sealed or high-pressure sample holders.

- Volatile samples with lower pressures (water, naphthalene, acetanilide, benzoic acid and diphenylacetic acid) should preferably be measured in hermetically closed sample pans.
- Mercury should be encapsulated in a hermetically sealed pan, suitable for liquids.
- The other substances can be measured in normal crimped sample pans.
- In all cases the sample mass should be determined before as well as after the experiment. When the sample mass remains constant, the experimental results are valid. When the sample mass decreases, a second experiment can be performed in order to test whether the mass now remains constant.
- When mass-loss and reaction between sample and sample holder are not observed, it is possible to use this sample more than once for calibration.
- A simple test for checking the hermetic sealing of a sample pan is to fill such a pan with water and store it for several days at room temperature. Only if the mass remains constant, the sealing is really hermetic.

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