New Static Apparatus and Vapor Pressure of Reference Materials: Naphthalene, Benzoic Acid, Benzophenone, and Ferrocene

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A new static apparatus, capable of measuring vapor pressures in the range (0.4 to 133) Pa and in the temperature range (243 to 413) K, is fully described. The performance of the new apparatus was checked by measuring the vapor pressures of four compounds recommended as reference materials for the measurement of vapor pressure—naphthalene, benzoic acid, benzophenone, and ferrocene. A recommended value for the enthalpy of sublimation of benzophenone, $\Delta_{cr}^{g} H_{m}^{0}(298.15 \text{ K}) = (95.1 \pm 1.9) \text{ kJ·mol}^{-1}$, is suggested.

Introduction

Vapor pressure is a fundamental physicochemical property indispensable for many important studies and applications including separation processes, development of models to simulate the behavior of chemicals in the environment, etc. Vapor pressure results are also important for the calculation of other important physicochemical properties, such as the enthalpies and the entropies of vaporization or of sublimation, activity coefficients, etc. The accurate determination of vapor pressures, however, is not an easy task, in particular in the low-pressure region and literature data coming from different authors often show a significant scatter and/or are influenced by systematic errors.

There are several methods for measuring vapor pressure described in the literature.[1] Our laboratory has been already equipped with two Knudsen effusion apparatuses that enable the measurement of sublimation pressures below 1 Pa.[2,3] To extend the measured pressure range, a new static apparatus was constructed. This apparatus, based on a capacitance diaphragm gage, is capable of measuring vapor pressures of either crystalline or liquid samples in the pressure range (0.4 to 133) Pa and in the temperature range (243 to 413) K. To test the performance of the new apparatus, it was decided to measure the vapor pressures of four compounds recommended as reference materials (naphthalene,[4–9] benzoic acid,[7,9] benzophenone[7,9] and ferrocene[9]) although the vapor pressure data for some of these compounds are not yet accurately established—this is why new collections of vapor pressure results of these compounds are still highly required.[9]

The newly constructed apparatus is equipped with modern digital measuring and reading devices, namely, with a new type of absolute Baratron manometer with self-controlling temperature system working at a higher temperature ($T = 423$ K) than previous models. The internal diameter of tubing is relatively large, favoring the complete degassing of samples after a few cycles of measurement and significantly decreasing the possible influence of thermal transpiration on low vapor pressure

measurements. So, it is expected that this apparatus will allow the measurement of vapor pressures with high accuracy.

Experimental Section

Materials. Naphthalene ($C_{10}H_8$, CASRN 91-20-3) was purchased from Aldrich (mole fraction purity $x = 0.99$) and further purified by zone refining with $x = 0.9999$. Benzoic acid ($C_7H_6O_2$, CASRN 65-85-0) NIST standard reference material 39i ($x = 0.99997$, determined by freezing point measurements) was used without any further purification. Benzophenone ($C_{13}H_{10}O$, CASRN 119-61-9) was supplied by Aldrich ($x = 0.99$) and was purified by sublimation at reduced pressure. The mole fraction purity of the sample used for vapor pressure measurement was $x = 0.9999$. Ferrocene ($C_{10}H_{10}Fe$, CASRN 262-20-4) was obtained from Jansen Chemica ($x = 0.99$) and was further purified by sublimation at reduced pressure. Final purity achieved was $x = 0.9999$. The purity of the samples used for vapor pressure measurements was determined by gas chromatography using Hewlett-Packard 4890 gas chromatograph equipped with a column HP5 cross-linked 5 % PH ME Siloxane, length 30 m, film thickness 0.25 μm, 0.32 mm i.d., and FID detector.

Experimental Apparatus. The newly constructed apparatus is schematically shown in Figures 1 and 2. It is constructed of stainless steel tubing of internal diameter $\phi = 17$ mm with connections ConFlat DN 16 CF and includes all metal angle valves, VAT series 57 high-temperature range for UHV, operated pneumatically.

The pressure is measured by a capacitance diaphragm absolute gage MKS Baratron 631A01TBEH. Its measuring upper limit is 133 Pa, and the uncertainty is 0.25 % of the reading pressure as stated by the manufacturer. The temperature of the pressure sensor is kept at $T = 423$ K by the self-controlling temperature system. The pressure gage has been calibrated at 423 K by the manufacturer at seven equally spaced pressures from 0 to 133 Pa with a maximum deviation of 0.23 %. This calibration is traceable to the National Institute of Standards and Technology (NIST).

The sample is placed inside a cylindrical metal (stainless steel) cell that is connected to the tubing system by a VCR8 connection ($\phi_{ext} = 12.7$ mm). The cell is placed inside the cylindrical cavity

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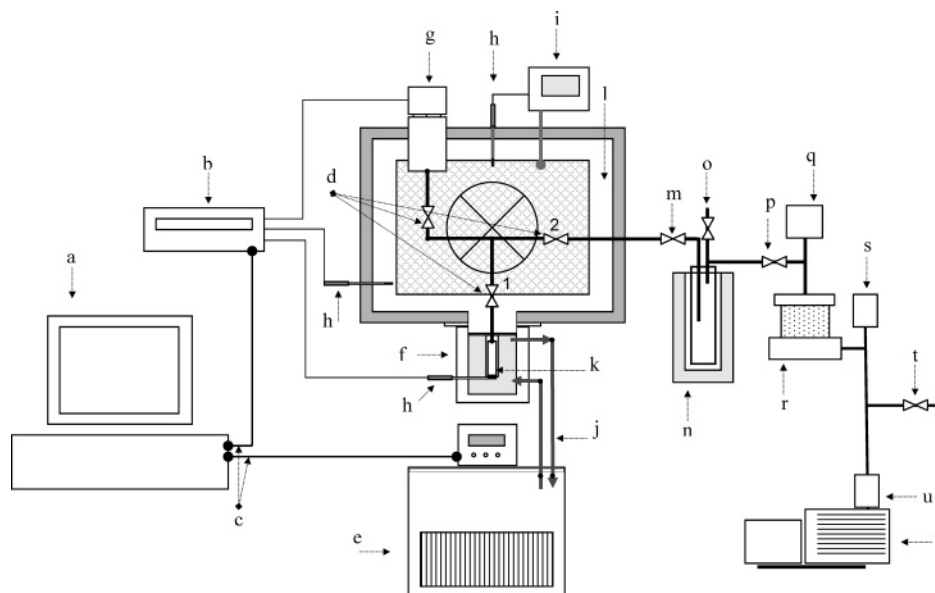‡ Academy of Sciences of the Czech Republic.

Figure 1. Schematic representation of the measuring system: a, computer; b, data logger Keithley 2700; c, RS 232C; d, high-temperature all metal electro pneumatic valves VAT series 57; e, temperature-controlled bath JULABO model F33-MW; f, heat exchange tube cavity; g, pressure transducer, MKS Baratron model 631A01TBEH; h, temperature sensor, Pt 100; i, PID temperature controller; j, bath fluid circulation tubes; k, sample cell tube; l, forced air convection oven; m, Teflon greaseless valve J. Young SPOR/20; n, glass liquid nitrogen trap; o, Teflon greaseless gas admittance valve J. Young ALS1; p, isolation valve VAT series 010; q, wide range vacuum gage Edwards WRG-S; r, turbomolecular vacuum pump system Edwards model EXT70; s, Pirani gage Edwards APG-M; t, air admittance valve; u, foreline trap Edwards FL20K; v, rotary pump Edwards RV3.
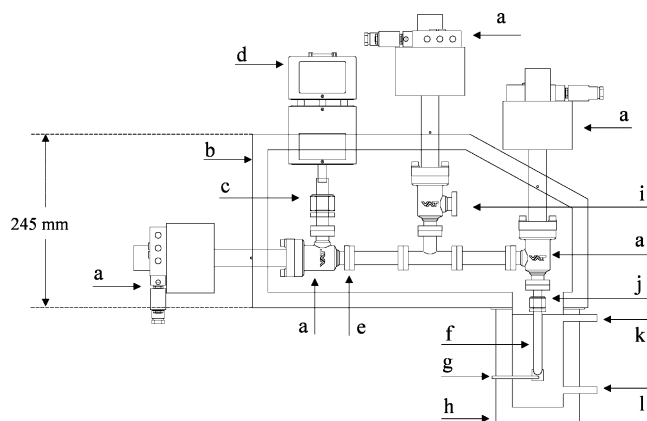

Figure 2. Schematic representation of the temperature-controlled vacuum line: a, high-temperature all metal electropneumatic valves VAT series 57; b, temperature-controlled forced air convection oven; c, VCR8 connection to the pressure transducer; d, pressure transducer, MKS Baratron model 631A01TBEH; e, ConFlat DN 16 CF vacuum connections; f, sample cell tube; g, PT100 temperature sensor; h, heat exchange sample cell tube cavity; i, connection to the high vacuum pumping system; j, VCR8 connection to the cell sample tube; k, bath fluid circulation connection (liquid out); l, bath fluid circulation connection (liquid in).

of a thermostated vessel consisting of a closed double-jacked copper cylinder (see Figure 2) with a circulating fluid from a thermostatic bath, Julabo F33-MW, which allows adjusting the temperature of the sample from 243 K up to 473 K with a stability of ± 0.01 K. The internal cavity is 120 mm long and has an internal diameter $\phi = 13$ mm. The temperature of the sample is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four wire connection) located in the bottom of the tube cavity (a silver-based thermal contact paste is used in the inter-space between the sample tube and the cavity in order to ensure a good thermal contact between the thermometer and sample). This thermometer was calibrated by comparison with a SPRT (25 Ω; Tinsley, 5187A). The uncertainty of the temperature measurements is estimated to be better than ± 0.01 K. All temperatures reported here are based

on the international temperature scale ITS-90.

The tubing between the cell and the pressure gage is placed in an insulated metallic box thermostated at a temperature higher than that of the sample in order to avoid condensation of its vapor. The box is thermostated by using air convection forced by means of a ventilator and is controlled by a PID temperature regulator Eurotherm 2116 connected to a Pt100 thermometer to ± 0.1 K.

The data acquisition system consists of a Keithley $6^1/_2$ digits data logger K2700 and a program developed in HP-VEE, which monitors the analogue output of the pressure transducer, the temperature of the sample, and the temperature of the thermo-stated box. The temperature of the circulating fluid is programmed and monitored using the software application EasyTemp, supplied by Julabo Lobortechnik GmbH. Both the Keithley data logger K2700 and the Julabo F33-MW thermo-static bath are connected to a computer using a RS-232 C interface.

The vacuum pump used to evacuate the system between the measuring cycles is a turbomolecular pump Edwards model EXT70. The primary vacuum is assured by a rotary pump Edwards model RV3. A cold trap cooled by liquid nitrogen is placed between the measuring system and the turbomolecular pump.

In a typical measuring experiment, the sample is placed inside the thermostated sample cell, and the system is evacuated to a pressure of 10^{-5} Pa (with valve number 1 closed). Prior to the measurement of the vapor pressure, the absence of materials adsorbed on the inner surface of the metal tubing is checked by closing the valve number 2 for some minutes. If any desorption is detected valve 2 is opened, and the metal tubing is heated to a higher temperature and baked out until no pressure increase (after closing valves 1 and 2) with time is observed. Then the sample is cooled to a temperature where the vapor pressure is expected to be very low, and the whole system is pumped out for 0.5 h.

After the above-described procedure, a measurement run starts by closing the valve 2 and opening the valve 1. Then the
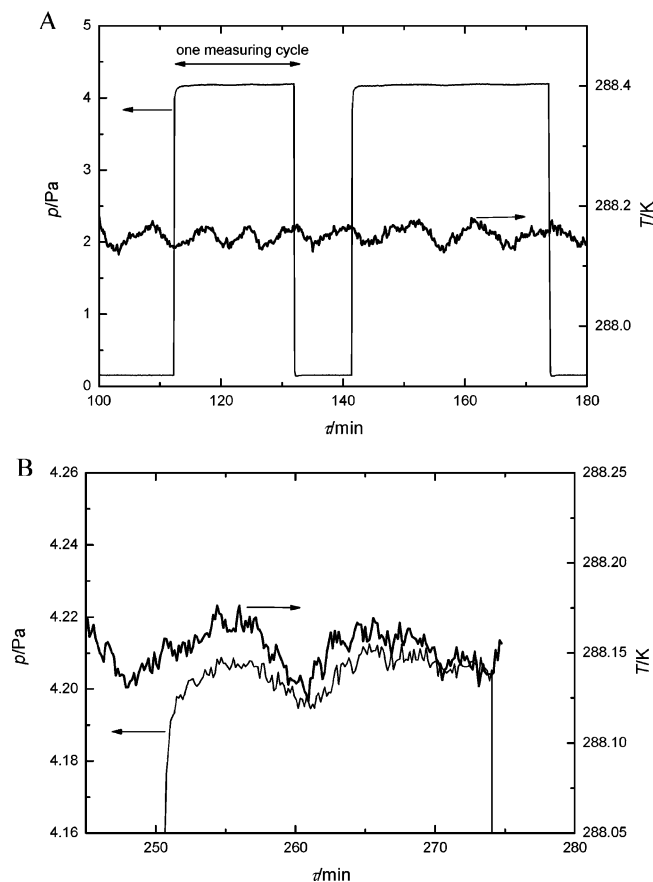
Table 1. Experimental Data on Vapor Pressure of Naphthalene[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
262.24*	0.182	−0.011	273.17	0.746	0.000	288.15	3.972	−0.015
262.25*	0.181	−0.012	274.18	0.843	0.003	288.15	4.010	0.023
263.24*	0.213	−0.007	274.19	0.842	0.000	288.17	3.980	−0.016
263.24*	0.213	−0.007	275.19	0.959	0.013	288.19	3.992	−0.012
264.23*	0.241	−0.008	276.14	1.061	0.005	293.18	6.699	−0.023
264.23*	0.244	−0.005	276.15	1.059	0.002	293.20	6.768	0.032
264.24*	0.244	−0.006	277.17	1.191	0.002	293.20	6.757	0.021
265.22*	0.279	−0.004	277.19	1.200	0.008	298.18	11.10	0.01
265.22*	0.277	−0.005	278.14	1.331	0.002	298.19	11.16	0.06
266.21*	0.315	−0.005	278.15	1.338	0.008	298.19	11.09	−0.01
266.21*	0.314	−0.005	278.17	1.334	0.001	298.20	11.20	0.09
266.21*	0.313	−0.007	278.19	1.331	−0.005	303.15	17.94	0.01
267.16	0.359	−0.001	279.19	1.490	−0.007	303.15	17.97	0.04
267.16	0.355	−0.005	279.19	1.490	−0.007	303.16	17.98	0.04
268.15	0.407	0.000	280.19	1.671	−0.004	303.18	17.97	−0.01
268.17	0.407	−0.001	280.19	1.668	−0.007	308.14	28.68	0.13
269.18	0.464	0.002	281.19	1.860	−0.013	308.15	28.64	0.06
269.18	0.462	0.000	281.20	1.862	−0.014	308.27	28.90	0.00
270.16	0.517	−0.003	281.21	1.860	−0.018	313.15	45.03	0.18
270.16	0.519	−0.001	282.17	2.078	−0.011	313.15	45.08	0.23
270.17	0.525	0.004	282.19	2.083	−0.010	313.18	45.01	0.04
271.20	0.591	0.001	283.18	2.367	0.033	318.21	69.70	0.01
271.20	0.592	0.002	283.19	2.342	0.005	318.22	69.62	−0.13
272.17	0.663	0.001	283.19	2.318	−0.019	318.25	69.75	−0.18
272.20	0.667	0.003	283.19	2.360	0.023	323.19	105.8	−0.2
273.17	0.751	0.005	283.20	2.323	−0.017	323.24	105.9	−0.5
273.17	0.748	0.002	288.14	3.968	−0.015			

[a] $\Delta p = p - p_{calc}$, where p_{calc} is calculated from the Clarke and Glew eq 3 with parameters given in Table 5. An asterisk (*) indicates that the data are not included in the fit.

Figure 3. (A) Record of the measurement. (B) Detail of the pressure and temperature reading indicating a good thermal contact between the thermometer and sample (fluctuations in sample temperature correspond to those in measured pressure).

pressure above the condensed phase is recorded during some minutes until a stable value is obtained (see Figure 3A). After that period the valve 1 is closed, and the valve 2 is opened allowing a new evacuation of the system after which the pressure is measured again. If subsequent measuring cycles yield a constant value for the measured pressure, the sample is considered to be sufficiently degassed, and the measured value is considered the equilibrium pressure at the temperature of the sample. It was found advisable to pump the sample (valve 1 opened) for a short time before each measuring cycle. The experimental runs are carried at several different temperatures over a chosen temperature interval. The temperature of each run follows a random sequence in order to detect systematic errors caused by possible decomposition or insufficient degassing of the sample.

Results

Naphthalene. Naphthalene has been suggested as a reference compound for vapor pressure measurements below $p = 1000$ Pa[4−9] as well as for enthalpy of sublimation and heat capacity measurements.[7,10] The measurements of vapor pressure of crystalline naphthalene were performed in the temperature range from $T = 262$ K up to $T = 323$ K, corresponding to a pressure range between $p = 0.2$ Pa and $p = 106$ Pa. The experimental results of the vapor pressure of naphthalene listed in Table 1 were fitted by the Clarke and Glew equation[11] (eq 3) with three parameters (only data above 0.4 Pa were included) which was found to be the most adequate equation for correlating vapor pressures measured in a temperature interval of about (50 to 80) K and in the pressure range of the new apparatus (0.4 to

130) Pa. Parameters of the Clarke and Glew eq 3 obtained by fitting experimental data for naphthalene and for the other compounds studied are given in Table 5.

Benzoic Acid. Benzoic acid has been recommended as a calibrant for measurements of the enthalpy of sublimation of substances having a vapor pressure of approximately 0.1 Pa at 298.15 K[7,10] or (10 to 360) Pa in the temperature range (338 to 383) K[7] although its use has been questioned due to the possibility of association of the compound in the vapor phase.[12,13] Despite the uncertainty of about ± 3 % on vapor pressure data, benzoic acid was also recommended as a reference material for vapor pressure measurements.[9]

Vapor pressures of benzoic acid were determined in the temperature range from 310 K to 362 K, corresponding to a pressure range of (0.4 to 69) Pa. Experimental data on vapor pressure of benzoic acid are listed in Table 2.

Benzophenone. Benzophenone has been used to test experimental equipment for the measurement of vapor pressures in the pressure range of 0.3 Pa to 130 Pa with a corresponding temperature interval of (307 to 385) K.[14,15] The recommendation as a reference material was made with reservations, which involved a reported metastable crystalline phase.[7,14,16] No evidence for any metastable crystalline phase, however, was found in a recent work by Chirico et al.[17] Liquid benzophenone supercools easily by more than 50 K (to below 270 K).[17] This permits to perform measurements on both the liquid and crystalline phases over a common temperature interval. As concluded by van Genderen and Oonk,[9] vapor pressure data of benzophenone have still uncertainties of approximately ± 5 %.

The vapor pressure measurements of benzophenone were performed in the temperature interval (308 to 385) K, corresponding to a pressure range from 0.4 Pa to 129 Pa. The vapor pressures were measured above the crystalline as well as above the liquid phase. The vapor pressures of the undercooled liquid were measured down to 308 K (the reported triple-point temperature of benzophenone being 321.19 K).[17] Experimental data on vapor pressure of benzophenone are listed in Table 3.

Table 2. Experimental Data on Vapor Pressure of Benzoic Acid[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
310.19	0.449	−0.010	323.13	1.861	−0.015	333.13	5.159	0.015
310.20	0.448	−0.012	323.14	1.856	−0.022	338.09	8.217	−0.068
311.65	0.550	0.009	323.15	1.855	−0.025	338.10	8.222	−0.071
311.66	0.535	−0.007	323.16	1.865	−0.017	343.07	13.08	−0.19
311.67	0.541	−0.001	325.12	2.333	0.028	343.09	13.01	−0.03
313.10	0.621	−0.016	325.13	2.286	−0.022	343.11	13.19	−0.10
313.12	0.650	0.012	325.15	2.295	−0.017	348.06	20.57	−0.01
313.13	0.650	0.011	326.59	2.706	0.027	348.06	20.66	−0.07
315.60	0.852	0.013	326.60	2.681	−0.001	348.07	20.62	0.21
315.62	0.852	0.011	326.63	2.726	0.036	348.08	20.92	0.11
318.10	1.123	0.022	328.08	3.115	−0.001	353.04	32.08	0.14
318.11	1.120	0.018	328.08	3.145	0.029	353.05	32.14	0.04
318.12	1.102	−0.001	328.10	3.159	0.036	353.06	32.06	0.05
320.10	1.363	−0.001	330.13	3.801	−0.026	358.04	48.94	0.02
320.13	1.368	0.000	330.13	3.807	−0.020	358.07	49.03	0.15
321.59	1.618	0.021	333.06	5.193	0.084	362.03	68.14	0.12
321.62	1.612	0.010	333.07	5.088	−0.026	362.03	68.11	−0.19
323.12	1.911	0.037	333.07	5.110	−0.004			

[a] $\Delta p = p - p_{calc}$, where p_{calc} is calculated from the Clarke and Glew eq 3 with parameters given in Table 5.

Table 3. Experimental Data on Vapor Pressure of Benzophenone[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
				Crystalline Phase				
310.09	0.394	0.000	314.08	0.634	0.004	319.04	1.108	0.000
310.09	0.395	0.001	314.08	0.632	0.002	319.05	1.109	0.000
310.10	0.396	0.002	315.07	0.709	0.003	319.06	1.110	−0.001
311.09	0.444	0.001	315.07	0.708	0.002	319.54	1.171	−0.001
311.10	0.441	−0.003	315.07	0.708	0.002	319.55	1.172	−0.001
311.12	0.442	−0.003	316.07	0.799	0.007	319.55	1.173	0.000
312.09	0.500	0.001	316.07	0.797	0.005	320.04	1.239	0.000
312.09	0.495	−0.004	316.07	0.795	0.003	320.05	1.239	−0.002
312.09	0.495	−0.005	317.05	0.886	0.000	320.06	1.241	−0.001
312.10	0.497	−0.003	317.06	0.885	−0.001	320.54	1.310	0.000
313.09	0.559	−0.002	317.06	0.886	−0.001	320.54	1.310	0.000
313.09	0.561	0.000	318.02	0.987	−0.001	320.54	1.308	−0.002
313.10	0.563	0.001	318.03	0.987	−0.002			
314.08	0.636	0.007	318.04	0.987	−0.003			
				Liquid				
308.18*	0.414	−0.002	328.06	2.546	−0.002	362.97	34.46	0.11
308.18*	0.418	0.002	328.07	2.551	0.001	362.98	34.49	0.12
313.42*	0.699	0.010	328.21	2.573	−0.007	367.85	47.26	0.20
313.43*	0.689	−0.001	333.03	3.844	−0.003	367.95	47.42	0.07
318.15*	1.076	0.008	333.11	3.886	0.014	367.96	47.38	0.00
318.15*	1.076	0.008	338.03	5.697	−0.039	373.07	65.15	0.02
321.14	1.387	−0.011	338.03	5.691	−0.045	373.07	65.13	0.00
321.14	1.391	−0.007	343.02	8.481	0.057	378.04	87.58	−0.23
321.15	1.393	−0.007	343.03	8.433	0.002	378.04	87.68	−0.13
321.15	1.396	−0.004	348.01	12.25	0.05	383.32	119.1	−0.2
322.14	1.520	−0.008	348.09	12.33	0.06	383.32	119.1	−0.2
322.15	1.525	−0.004	352.99	17.42	−0.02	384.80	129.4	−0.4
323.13	1.664	−0.003	352.99	17.41	−0.03	384.80	129.3	−0.5
323.13	1.661	−0.006	357.95	24.55	−0.02	384.81	129.4	−0.4
323.15	1.664	−0.006	357.96	24.53	−0.06			
323.21	1.676	−0.003	362.97	34.45	0.10			

[a] $\Delta p = p - p_{calc}$, where p_{calc} is calculated from the Clarke and Glew eq 3 with parameters given in Table 5. An asterisk (*) indicates an undercooled liquid.

The triple point of benzophenone calculated as an intersection of the vapor pressure equations for the crystalline and liquid phases is $T_{tp} = (321.1 \pm 0.7)$ K and $p_{tp} = (1.4 \pm 0.1)$ Pa. The enthalpy of fusion at the triple point calculated from $\Delta_{cr}^{l} H_m^0 = \Delta_{cr}^{g} H_m^0 - \Delta_{l}^{g} H_m^0$ is (18.4 ± 0.2) kJ·mol^{-1}.

Ferrocene. Ferrocene has been recommended and used as a calibrant for enthalpies of sublimation measurements exhibiting a vapor pressure of approximately 1 Pa at 298.15 K or (0.1 to 300) Pa in the temperature interval (277 to 368) K,[7] but the collection of independent data covering the range from room temperature to the triple point is still highly recommended.[9]

Table 4. Experimental Data on Vapor Pressure of Ferrocene[a]

T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa	T/K	p/Pa	Δp/Pa
288.16	0.357	0.008	305.16	1.951	−0.023	333.03	22.28	−0.05
288.17	0.341	−0.008	305.19	1.968	−0.011	333.04	22.34	−0.01
288.18	0.356	0.006	308.15	2.613	−0.007	333.04	22.27	−0.08
290.67	0.450	−0.007	308.16	2.641	0.018	338.02	33.25	0.33
290.67	0.454	−0.003	308.16	2.614	−0.009	338.02	33.27	0.35
290.68	0.456	−0.001	313.15	4.171	0.017	343.01	47.85	−0.08
293.18	0.597	0.002	313.17	4.156	−0.005	343.01	47.86	−0.07
293.20	0.595	−0.001	318.09	6.401	−0.046	343.01	47.68	−0.25
295.68	0.779	0.008	318.15	6.504	0.023	348.08	69.42	0.07
295.69	0.774	0.002	323.07	9.955	0.062	348.09	69.43	0.03
298.17	0.991	−0.003	323.08	9.948	0.047	353.06	97.48	−1.08
298.17	0.991	−0.003	323.08	9.948	0.047	353.07	98.19	−0.43
298.20	1.006	0.010	328.05	15.01	0.04	353.08	98.08	−0.61
300.71	1.296	0.016	328.05	15.19	0.22	355.93	120.8	0.7
303.14	1.613	−0.011	328.05	14.95	−0.02	356.05	121.2	0.1
303.15	1.661	0.035	328.06	14.89	−0.09	356.06	121.2	0.0
303.15	1.616	−0.010	328.06	14.85	−0.13			

[a] $\Delta p = p - p_{calc}$, where p_{calc} is calculated from the Clarke and Glew eq 3 with parameters given in Table 5.

The vapor pressures of ferrocene were measured from the temperature $T = 288$ K to the temperature $T = 356$ K, corresponding to a pressure interval of (0.4 to 121) Pa. The experimental data on vapor pressure of ferrocene are listed in Table 4.

Discussion

Usual Main Problems during Measurement of Vapor Pressure by a Static Method. The main sources of systematic errors during measurement of vapor pressure by a static method are the following: the influence of thermal transpiration in the low-pressure region (measured pressure will be higher than vapor pressure); the adsorption of the measured gas on the internal walls of the tubing (measured pressure will be lower than vapor pressure); poor thermal contact between the sample and the thermometer (resulting in an incorrect measurement of the sample temperature); leakages through the vacuum connections (resulting in a permanent drift of pressure during vapor pressure measurement); insufficient degassing of samples (resulting in a higher value of measured vapor pressure); insufficient purity of the sample.

All the above-mentioned problems except the purity of samples were solved by a suitable construction of the static apparatus. The relatively large internal diameter of tubing (17 mm) diminishes the possible influence of thermal transpiration. This effect was not observed during measurement of naphthalene even at lowest pressures ($p = 0.4$ Pa). In addition, no positive systematic deviation of our results as compared to those recommended by Růžička et al.[18] and to those obtained by effusion and by saturation methods was detected. For the other compounds, the measurements at the lowest pressures did not indicate any systematic positive deviation compared to those measured at higher pressures. The stainless steel tubing electrochemically polished (internally) minimizes the adsorption of vapors on the internal walls of the system components. Moreover, the use of a turbomolecular pump, instead of an oil diffusion pump, avoids the deposition of any oil film on the inner surface of the apparatus, which would favor the adsorption of vapor of the measured compound. The measurements of the vapor pressure show a very short thermal time response—the fluctuations in pressure correspond immediately to appropriate oscillations in temperature (see Figure 3B) identifying a good thermal contact. The connections ConFlat DN 16 CF and all metal angle valve VAT series 57 ensure a low leakage in the vacuum system. Samples are degassed by direct pumping at a

convenient temperature (no significant vapor pressure), and the efficiency of the outgassing process is checked during the first cycles of measurement.

Uncertainty of the Vapor Pressures Measured in the Apparatus. From the measurements performed with naphthalene the following conclusions about the performance of the apparatus were assumed. The lower pressure limit of the apparatus is $p = 0.4$ Pa. Below this limit, the data tend to be systematically lower than the majority of data available for naphthalene (identical finding was observed by Růžička et al.[18] after performed measurements on crystalline naphthalene by a static method using a capacitance manometer MKS Baratron 690A11TRA). The uncertainty in the pressure measurements increases linearly with the pressure, being adequately described by the expression

$$\sigma(p/\text{Pa}) = 0.01 + 0.0025(p/\text{Pa}) \quad (1)$$

Data Correlation. For naphthalene all thermodynamic data related to the equilibrium between crystalline and vapor phases (heat capacities of crystalline phase and of perfect gas, enthalpy of sublimation) are known with sufficient accuracy. Therefore, the obtained data on vapor pressure of crystalline naphthalene were also used to select the most suitable correlating vapor pressure equation to fit vapor pressure data obtained using the new static apparatus (i.e., generally for a temperature interval of about (50 to 80) K and for a pressure range (0.4 to 130) Pa). The tested correlating vapor pressure equations are listed below (although Wagner equation[19] is often used for fitting vapor pressures of liquids, it was not tested for fitting these results since it is constrained to the critical point, which is often unknown for low volatile organic compounds):

Antoine equation:

$$\ln(p/\text{Pa}) = A - \frac{B}{(T/\text{K}) + C} \quad (2)$$

where p is the vapor pressure; T is the temperature; and A, B, and C are correlation parameters.

Clarke and Glew equation:[11]

$$R \ln \frac{p}{p^0} = -\frac{\Delta_{cd}^g G_m^0(\theta)}{\theta} + \Delta_{cd}^g H_m^0(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \\ \Delta_{cd}^g C_{p,m}^0(\theta)\left(\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right) + \\ \left(\frac{\theta}{2}\right)\left(\frac{\partial \Delta_{cd}^g C_{p,m}^0}{\partial T}\right)(\theta)\left(\frac{T}{\theta} - \frac{\theta}{T} - 2\ln\left(\frac{T}{\theta}\right)\right) + ... \quad (3)$$

where p is the vapor pressure, p^0 is a selected reference pressure, θ is a selected reference temperature, R is the molar gas constant, $\Delta_{cd}^g G_m^0$ is the difference in molar Gibbs energy between the gaseous and the crystalline or liquid phases (condensed phase) at the selected reference pressure (the gaseous phase is supposed to have characteristics of ideal gas at the pressure p^0), $\Delta_{cd}^g H_m^0$ is the difference in molar enthalpy between the gaseous and the condensed phase, and $\Delta_{cd}^g C_{p,m}^0$ is the difference between the heat capacities of the perfect gas and of the condensed phase. As one of its main advantages, this equation enables the determination of $\Delta_{cd}^g C_{p,m}^0$ when the experimental range of data is wide enough. The Clarke and Glew equation was often used by the Thermodynamic Group of the University of Utrecht,[14,20−22] although sometimes only two parameters were used (i.e., $\Delta_{cd}^g C_{p,m}^0$ is supposed zero), which is equivalent to use the
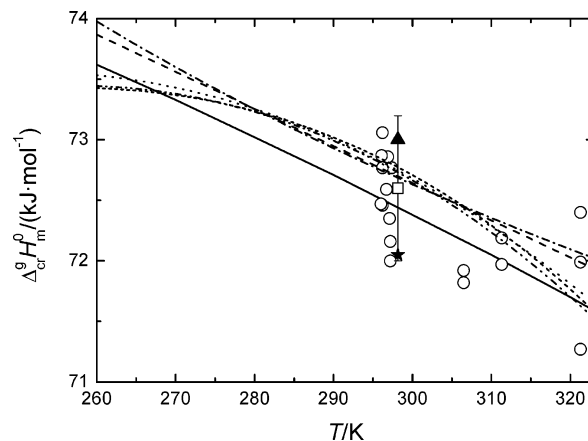

Figure 4. Comparison of the enthalpy of sublimation of naphthalene calculated from different vapor pressure equations (using vapor pressure data from this work) with recommended enthalpy of sublimation given by Růžička et al.,[18] ICTAC,[7] and with calorimetric values:[32−34] —, Růžička et al.;[18] □, ICTAC;[7] ▲, Irving;[33] ★, Morawetz;[34] ○, Murata et al.;[32] calculated using vapor pressure data from this work: − · −, Antoine eq 2; − −, Clarke and Glew eq 3 with three parameters; ···, Clarke and Glew eq 3 with four parameters; − ··, Cox eq 4 with three parameters and $T^0 = T_{tp} = 353.37$ K[26] and $p^0 = p_{tp} = 993.5$ Pa;[25] - - -, Cox eq 4 with four parameters and $T^0 = T_{tp} = 353.37$ K[26] and $p^0 = p_{tp} = 993.5$ Pa.[25]

Clausius−Clapeyron equation. We tested the Clarke and Glew eq 3 with three and four parameters.

Cox equation:[23]

$$\ln\frac{p}{p^0} = \left(1 - \frac{T^0/\text{K}}{T/\text{K}}\right)\exp\left(\sum_{i=0}^{n} A_i(T/\text{K})^i\right) \quad (4)$$

where p^0 and T^0 represent the pressure and temperature, respectively, of a chosen reference state. The Cox eq 4 was considered to be the most adequate equation for describing vapor pressure as a function of temperature down to and below the triple point.[24] Although less or more parameters can be used, the value $n = 2$ is commonly employed; in this work we used the Cox equation with two, three, and four adjustable parameters (i.e., with $n = 1$, 2, or 3, respectively) and with p^0 and T^0 being set to the triple point of naphthalene, $p^0 = p_{tp} = 993.5$ Pa[25] and $T^0 = T_{tp} = 353.37$ K.[26]

All the equations mentioned (except the Cox eq with $n = 1$) above described satisfactorily the measured vapor pressures of crystalline naphthalene. From the graphs presented in Figures 4 and 5 (where enthalpy of sublimation $\Delta_{cr}^g H_m^0$ and the difference of heat capacities $\Delta_{cr}^g C_{p,m}^0$ are plotted as a function of temperature) and from comparison with calorimetrically determined $\Delta_{cr}^g H_m^0$ and $\Delta_{cr}^g C_{p,m}^0$ (obtained from heat capacities of crystalline phase $C_{p,m}^0(cr)$ given by Chirico et al.[26] and from the perfect heat capacities $C_{p,m}^0(g)$ given by Frenkel et al.),[27] it is clear that the most reasonable description of vapor pressure and related thermal data is achieved by the Clark and Glew eq 3 with three parameters. Additionally, as mentioned before, the parameters of Clarke and Glew eq 3 have a physical meaning over the studied low-pressure region. Vapor pressure data in this work were thus fitted by Clarke and Glew eq 3 with three adjustable parameters for all the compounds studied (see Table 5).

Comparison with Literature Data

Naphthalene. Review papers on existing data of vapor pressure of crystalline naphthalene were published by Delle

Table 5. Parameters of Clarke and Glew Equation 3 for Naphthalene, Benzoic Acid, Benzophenone, and Ferrocene at the Reference Temperature θ = 298.15 K and Pressure p^0 = 10^5 Pa

compound	phase	$\Delta_{cd}^{g}G_{m}^{0}$ J·mol^{-1}	$\Delta_{cd}^{g}H_{m}^{0}$ J·mol^{-1}	$\Delta_{cd}^{g}C_{p,m}^{0}$ J·K^{-1}·mol^{-1}	σ^b Pa
naphthalene	crystalline	22 583 ± 2	72 698 ± 38	−30.7 ± 3.8	0.089
benzoic acid	crystalline	34 009 ± 25	91 363 ± 488	−36.5 ± 13.3	0.065
benzophenone	crystalline	34 531 ± 9	95 871 ± 162	−47[a]	0.003
ferrocene	crystalline	28 562 ± 5	74 488 ± 134	−45.4 ± 6.8	0.238
benzophenone	liquid	33 263 ± 9	78 781 ± 139	−107.2 ± 2.9	0.107

[a] Inserted value ($C_{p,m}^{g0}$ from Benson's group contribution method,[42] $C_{p,m}^{s}$ from Chirico et al.[17]). [b] σ is the standard deviation of the fit defined as $\sigma = [\sum_{i=1}^{n}(\Delta p)_i^2/(n-m)]^{1/2}$ where Δp is the difference between the experimental and the fit values, n is the number of experimental points used in the fit, and m is the number of adjustable parameters of Clarke and Glew eq 3.
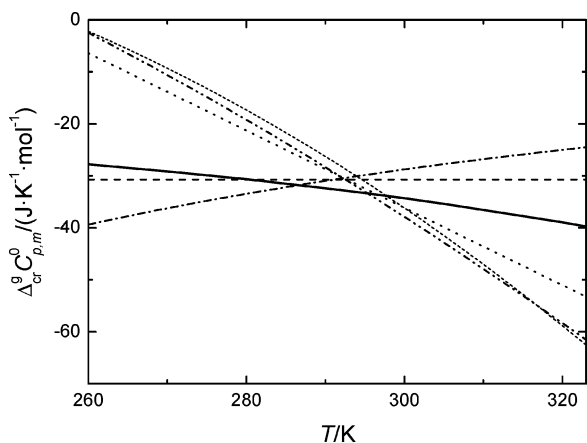

Figure 5. Comparison of differences $\Delta_{cr}^{g}C_{p,m}^{0} = C_{p,m}^{0}(g) - C_{p,m}^{0}(cr)$ of naphthalene calculated from different vapor pressure equations (using vapor pressure data from this work) with values obtained from perfect heat capacities $C_{p,m}^{0}(g)$ given by Frenkel et al.[27] and heat capacities of crystalline phase $C_{p,m}^{0}(cr)$ given by Chirico et al.[26] —, calculated using $C_{p,m}^{0}(g)$[27] and $C_{p,m}^{0}(cr)$;[26] calculated using vapor pressure data from this work: − · −, Antoine eq 2; − −, Clarke and Glew eq 3 with three parameters; ···, Clarke and Glew eq 3 with four parameters; − ··, Cox eq 4 with three parameters and $T^0 = T_{tp}$ = 353.37 K[26] and $p^0 = p_{tp}$ = 993.5 Pa;[25] - - -, Cox eq 4 with four parameters and $T^0 = T_{tp}$= 353.37 K[26] and $p^0 = p_{tp}$ = 993.5 Pa.[25]

Site,[28] Shiu and Ma,[29] Chickos and Acree,[30] and very recently, Růžička et al.[18]

Several recommendations for vapor pressure of crystalline naphthalene can be found in the literature.[4,8,18,21,25,31] Their characterization and mutual comparison is reported in the work by Růžička et al.[18] The present measured data on vapor pressure of crystalline naphthalene were compared with the above-mentioned recommendations. Comparison is shown in Figure 6 using a deviation plot. Data recommended by Růžička et al.[18] were used as a reference. All recommended values mutually agree within 3 %. The agreement of the data obtained in this work (above p = 0.4 Pa) with literature recommendations[4,8,18,21,25,31] is satisfactory.

The value $\Delta_{cr}^{g}H_{m}^{0}$(298.15 K) = (72.70 ± 0.04) kJ·mol^{-1} derived in this work is also in excellent agreement with the values of enthalpy of sublimation at 298.15 K derived from recommended vapor pressure data by Ambrose et al.,[4] (72.50 ± 0.25) kJ·mol^{-1}; by de Kruif et al.,[21] (72.51 ± 0.14) kJ·mol^{-1}; by Chirico et al.,[25] (72.7 ± 0.2) kJ·mol^{-1}; by van der Linde et al.,[31] 72.26 kJ·mol^{-1}; and by Růžička et al.,[18] 72.44 kJ·mol^{-1}, and also with selected calorimetric values (see Růžička et al.[18]) reported by Murata et al.,[32] (72.4 ± 0.7) kJ·mol^{-1}; by Irving,[33] (73.00 ± 0.25) kJ·mol^{-1}; and by Morawetz,[34] (72.05 ± 0.25) kJ·mol^{-1}. The value of $\Delta_{cr}^{g}H_{m}^{0}$(298.15 K) recommended by ICTAC (The International Confederation for Thermal Analysis and Calorimetry)[7] is (72.6 ± 0.6) kJ·mol^{-1}.
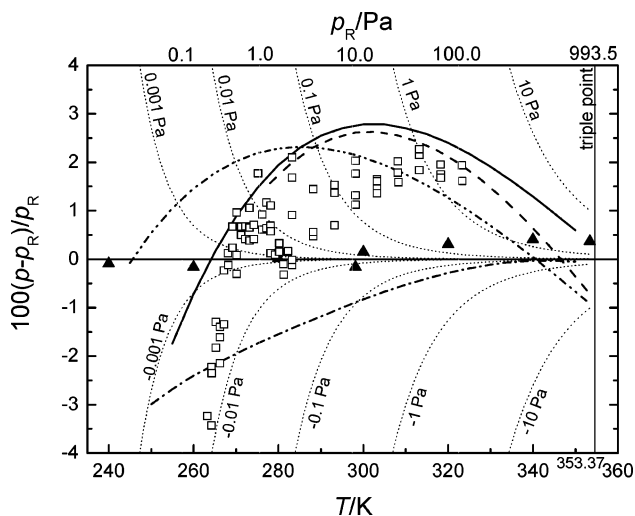

Figure 6. Comparison of vapor pressure of naphthalene obtained in this work with recommended data: □, this work; ▲, Sinke;[8] —, Ambrose et al.;[4] − −, de Kruif et al.;[21] − · −, Chirico et al.;[25] − ··, van der Linde et al.[31] p_R is taken from recommendation given by Růžička et al.;[18] ···, absolute errors (0.001 Pa, 0.01 Pa, 0.1 Pa, 1 Pa, 10 Pa).

There is also a good agreement between the constant value $\Delta_{cr}^{g}C_{p,m}^{0} = (-30.7 \pm 3.8)$ J·K^{-1}·mol^{-1} derived from our vapor pressure data, using eq 3, and that obtained from $C_{p,m}^{0}(g)$ and $C_{p,m}^{0}(cr)$ given by Frenkel et al.[27] and Chirico et al.,[26] respectively (see Figure 11).

Benzoic Acid. A number of data sets on vapor pressure and enthalpy of sublimation of benzoic acid, summarized for example in the papers by Sabbah et al.,[7] by van Genderen et al.,[9] and by Ribeiro da Silva et al.[3] can be found in the literature, but recommendations on vapor pressure data of benzoic are not available to our knowledge. Only one data set on vapor pressure of benzoic acid, reported by de Kruif and Blok,[20] covers a wide temperature range. These last data were used as a reference in comparison with those obtained in this work. From Figure 7, where data are compared using a deviation plot, it can be seen that our data are systematically higher than those obtained in the reference[20] deviating by 0.20 % up to 5.21 %. All other vapor pressure data[2,3,35−37] displayed in the Figure 7, except those given by Davies and Jones,[38] show also positive systematic deviations from the values obtained from the vapor pressure equation given by de Kruif and Blok.[20] Comparison between other vapor pressure data published prior to 1982 can be found in ref 20.

Data on the enthalpy of sublimation of benzoic acid were very recently reviewed by Ribeiro da Silva et al.[3] The mean value $\Delta_{cr}^{g}H_{m}^{0}$(298.15 K) = (90.2 ± 1.9) kJ·mol^{-1}, reported in that work, was derived from 22 values reported in the literature. ICTAC[7] recommended the value of $\Delta_{cr}^{g}H_{m}^{0}$(298.15 K) = (89.7
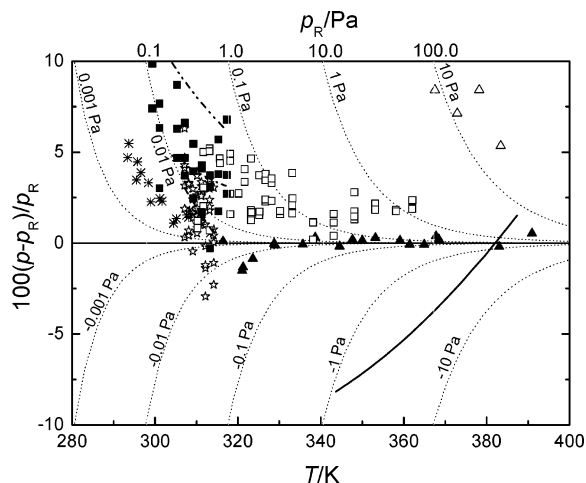
Figure 7. Comparison of vapor pressure of benzoic acid obtained in this work with literature data: □, this work; ▲, de Kruif and Blok[20] (static method); ☆, Ribeiro da Silva and Monte[2] (mass effusion); *, Colomina et al.[35] (mass effusion); △, Malaspina et al.[36] (masss effusion, partially displayed); ■, Ribeiro da Silva et al.[3] (mass effusion); —, Davies and Jones[38] (mass effusion); − −, Ribeiro da Silva et al.[37] (mass effusion, Oporto); - · -, Ribeiro da Silva et al.[37] (mass effusion, Utrecht); - ··, Ribeiro da Silva et al.[37] (torsion effusion, Utrecht). p_R is calculated using vapor pressure equation reported by de Kruif and Block;[20] ···, absolute errors (0.001 Pa, 0.01 Pa, 0.1 Pa, 1 Pa, 10 Pa). Data by Ribeiro da Silva et al.[37] (spinning rotor) are not displayed since they deviate by more than 10 % from p_R.

± 1.0) kJ·mol^{-1}. In this work the obtained value $\Delta_{cr}^g H_m^0$(298.15 K) = (91.4 ± 0.5) kJ·mol^{-1} is in reasonable agreement with both values and in excellent agreement with the value derived by de Kruif and Blok,[20] $\Delta_{cr}^g H_m^0$(298.15 K) = (92.1 ± 0.2) kJ·mol^{-1}, using a similar static method.

The value $\Delta_{cr}^g C_{p,m}^0$ = −(36.5 ± 13.3) J·K^{-1}·mol^{-1} derived from our vapor pressure data, using eq 3, is in reasonable agreement with that calculated from $C_{p,m}^0$(g) and $C_{p,m}^0$(cr) reported by Stull et al.[39] and Sabbah et al.,[7] respectively (see Figure 11).

Benzophenone. The vapor pressure data of benzophenone have been measured by several investigators. However, the discrepancy between those data does not allow the recommendation of reliable values, and collection of new data is required.[9] We chose extensive data given by de Kruif et al.[14] as a reference. Vapor pressure data are compared in Figures 8 and 9 using deviation plots. Our data for the crystalline phase are in good agreement with those published previously.[14,15,40,41] Data obtained in the present work are slightly higher than those obtained from vapor pressure equation reported by de Kruif et al.[14] (relative deviation is within the interval 1.90 % to 3.95 %). The absolute deviation of the two data sets (ranging from 0.009 Pa, at T = 311.12 K, to 0.037 Pa, at T = 320.54 K) is very small and inside experimental uncertainty. As it is seen from Figure 8, our data show higher precision than that obtained on other determinations.[14,15,40,41] Vapor pressure data measured above the liquid phase (undercooled liquid below T = 321.1 K) are in satisfactory agreement with those reported by de Kruif et al.[14] (our data are systematically higher deviating by 1.7 % up to 5.9 %). Comparison between other vapor pressure data published prior to 1983 can be found in ref 14.

ICTAC[7] recommends $\Delta_{cr}^g H_m^0$(298.15 K) = (93.77 ± 3.54) kJ·mol^{-1}. In the present work the value $\Delta_{cr}^g H_m^0$(298.15 K) = (95.9 ± 0.2) kJ·mol^{-1} was derived. Sabbah et al.[7] calculated the recommended value as an arithmetic mean of literature published values including data which differ significantly from the calculated mean. In Table 6, available literature data for
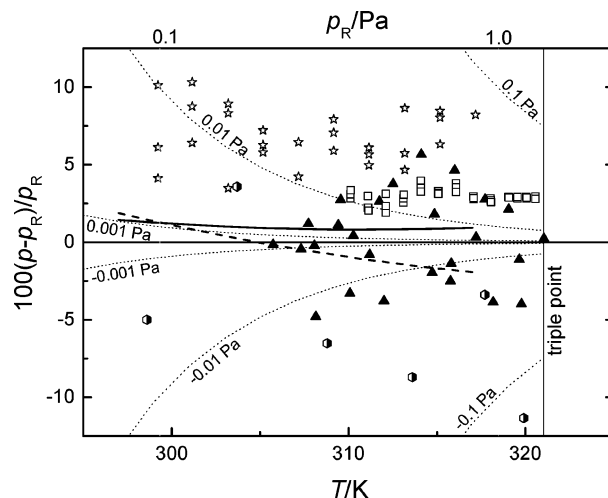

Figure 8. Comparison of vapor pressure of crystalline benzopenone obtained in this work with literature data: □, this work; ▲, de Kruif et al.[14] (static method); —, de Kruif and van Ginkel[15] (torsion effusion); − −, de Kruif and van Ginkel[15] (mass effusion); half-open/half-closed hexagon, Verevkin[41] (gas saturation); ☆, Lipovská et al.[40] (mass effusion). p_R is calculated using vapor pressure equation reported by de Kruif et al.;[14] ···, absolute errors (0.001 Pa, 0.01 Pa, 0.1 Pa).
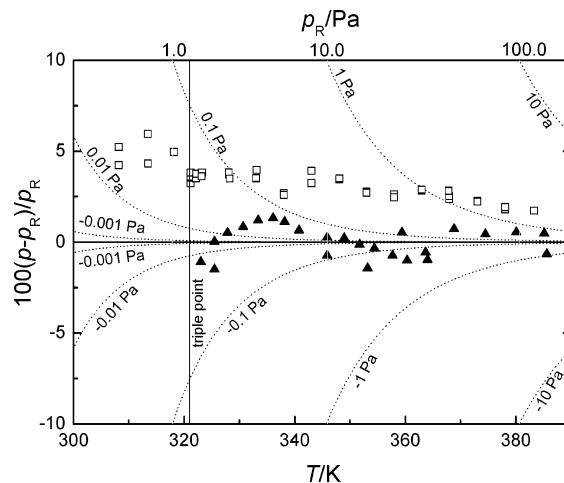

Figure 9. Comparison of vapor pressure of liquid benzophenone obtained in this work with literature data: □, this work; ▲, de Kruif et al.[14] (static method). p_R is calculated using vapor pressure equation reported by de Kruif et al.;[14] ···, absolute errors (0.001 Pa, 0.01 Pa, 0.1 Pa, 1 Pa, 10 Pa).

the enthalpy of sublimation of benzophenone are summarized. Enthalpies of sublimation reported at the mean temperature of the measurement $\Delta_{cr}^g H_m^0(T_{mean})$ were corrected to $\Delta_{cr}^g H_m^0$(298.15 K) using the following formula:

$$\Delta_{cr}^g H_m^0(298.15K) = \Delta_{cr}^g H_m^0(T_{mean}) + \int_{T_{mean}}^{298.15\,K} \Delta_{cr}^g C_{p,m}^0 \, dT \quad (5)$$

where $\Delta_{cr}^g C_{p,m}^0$ was calculated using perfect gas heat capacity $C_{p,m}^0$(g) estimated by Benson's group contribution method,[42] and heat capacity of crystalline phase $C_{p,m}^0$(cr) was taken from Chirico et al.[17] The temperature dependence of $\Delta_{cr}^g C_{p,m}^0$ was adequately described by the quadratic equation:

$$\Delta_{cr}^g C_{p,m}^0/(J·K^{-1}·mol^{-1}) = -2.91·10^{-3}(T/K)^2 + 1.56(T/K) - 253.91 \quad (6)$$

The corrections calculated using eq 5 are slightly higher than those obtained from the estimating equation suggested by Chickos et al.,[43] which were used in the work of Sabbah et al.[7]

Table 6. Review of Enthalpies of Sublimation of Benzophenone[a]

T_{mean}	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^0(T_{\text{mean}})$	$\int_{T_{\text{mean}}}^{298.15\ \text{K}} \Delta_{\text{cr}}^{\text{g}} C_{p,\text{m}}^0\ dT$	$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^0(298.15\ \text{K})$		
K	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	method	ref
313	95.1 ± 1.0	0.71	95.8	static	14*
308	95.2 ± 0.8	0.48	95.7	TE	15*
308	93.9 ± 0.4	0.48	94.4	ME	15*
298	94.6 ± 0.8	0.00	94.6	TCM	12*
298			93.35 ± 0.66	calorimetric	34*
305	95.0 ± 1.3	0.32	95.32	TE, ME	55*
306	92.9 ± 0.8	0.37	93.3	ME	56*
308	90.0	0.47	90.4	ME	57
298			92.0 ± 0.8	calorimetric	58
309	92.4 ± 2.2	0.53	92.9	saturation	41
304	95.0 ± 0.2	0.28	95.3	ME	59*
	96.1			ME	47
298			84.4 ± 1.1	calorimetric	60
298	77.0 ± 2.5	0.00	77.0	ME	45
306	96.1	0.37	96.5	NA	49
	91.2			NA	48
303	78.2 ± 1.3	0.23	78.4	TE	46
302	95.0 ± 0.3	0.18	95.2	TE	16*
298	91.2 ± 1.6	0.00	91.2	ME	61
308	95.4 ± 0.4	0.48	95.9	ME	40*
315	95.1 ± 0.2	0.83	95.9	static	this work*
			95.0 ± 1.9**	mean	

[a] An asterisk (*) indicates that data are included in the calculation of the mean. TE, torsion effusion; ME, mass effusion; TCM, thermal conductivity manometer; NA, method is not available. Two asterisks (**) indicate that uncertainty is twice the estimated standard deviation of the mean (coverage factor $k = 2$).

The equation given by Chickos et al.[43] uses $C_{p,\text{m}}^0(\text{cr})$ estimated by group additivity method[44] and for benzophenone provides a constant value $\Delta_{\text{cr}}^{\text{g}} C_{p,\text{m}}^0 = -33.8$ J·K^{-1}·mol^{-1} while $\Delta_{\text{cr}}^{\text{g}} C_{p,\text{m}}^0$ calculated from eq 6 varies from -46.6 J·K^{-1}·mol^{-1} ($T = 298.15$ K) to -52.2 J·K^{-1}·mol^{-1} (triple-point temperature).

The selected values of $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^0(298.15$ K) of benzophenone used in the calculation of the mean are marked by asterisk in Table 6. Values derived including (inappropriately) some measurements on undercooled liquid[45,46] and values from sources that do not report temperature range of the measurement (i.e., mean temperature of measurement is not available),[47,48] and/or where method of the measurement is not available[48,49] were rejected. Then data showing mutual agreement and originating from research groups that provided reliable results on the enthalpy of sublimation for other compounds (including for naphthalene), were selected. Data by Verevkin[41] were rejected due to high scatter of reported vapor pressure data. The arithmetic mean of the values selected from Table 6 (which includes our value), $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^0(298.15$ K$) = (95.1 \pm 1.9)$ kJ·mol^{-1}, where the uncertainty is twice the estimated standard deviation of the mean, is therefore recommended in this work.

The enthalpy of vaporization at the triple point was determined in this work as $\Delta_{\text{l}}^{\text{g}} H_{\text{m}}^0(T_{\text{tp}}) = (76.3 \pm 0.1)$ kJ·mol^{-1}. De Kruif reported $\Delta_{\text{l}}^{\text{g}} H_{\text{m}}^0(T_{\text{tp}}) = (76.7 \pm 0.4)$ kJ·mol^{-1}. Combining the mean value $\Delta_{\text{l}}^{\text{g}} H_{\text{m}}^0(T_{\text{tp}}) = (76.5 \pm 0.5)$ kJ·mol^{-1} with the enthalpy of fusion $\Delta_{\text{l}}^{\text{cr}} H_{\text{m}}^0 = (18.606 \pm 0.018)$ kJ·mol^{-1}, measured by adiabatic calorimetry,[17] yield the value $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^0(298.15$ K$) = (96.2 \pm 0.5)$ kJ·mol^{-1}, which is in good agreement with our recommended value.

The triple-point values calculated in this work from intersection of the vapor pressure equations for the crystalline and liquid phases, $T_{\text{tp}} = (321.1 \pm 0.7)$ K and $p_{\text{tp}} = (1.4 \pm 0.1)$ Pa, are in good accordance with the values $T_{\text{tp}} = (321.03 \pm 0.05)$ K and $p_{\text{tp}} = 1.34$ Pa determined by de Kruif et al.[14] and also with the triple point temperatures $T_{\text{tp}} = 321.19$ K and $T_{\text{tp}} = (321.28 \pm 0.01)$ K determined by Chirico et al.[17] and Hanaya et al.,[50] respectively, using adiabatic calorimeters. The value for the enthalpy of fusion at the triple point calculated in this
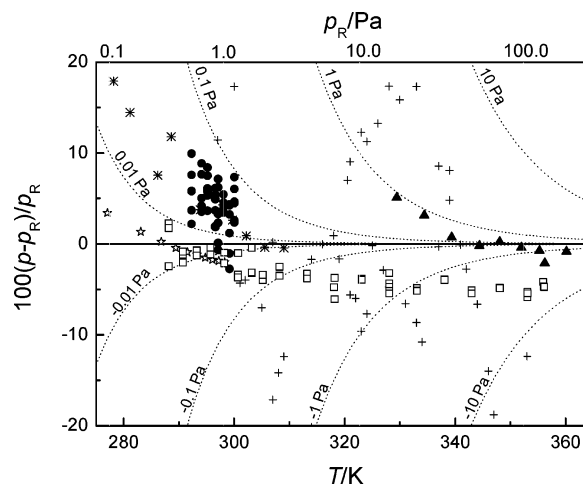

Figure 10. Comparison of vapor pressure of ferrocene obtained in this work with literature data: □, this work; ▲, Jacobs et al.[22] (static method); ☆, Jacobs et al.[22] (torsion and mass effusion); ●, Ribeiro da Silva and Monte[2] (mass effusion); *, Torres-Gomes et al.[51] (mass effusion); +, Pelino et al.[52] (torsion effusion). p_{R} is calculated using vapor pressure equation reported by Jacobs et al.;[22] ···, absolute errors (0.01 Pa, 0.1 Pa, 1 Pa, 10 Pa).

work, $\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^0 = (18.4 \pm 0.2)$ kJ·mol^{-1}, is in excellent agreement with calorimetrically determined values $\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^0 = (18.194 \pm 0.050)$ kJ·mol^{-1},[14] $\Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^0 = (18.606 \pm 0.018)$ kJ·mol^{-1},[17] and $\Delta_{\text{fus}} H_{\text{m}} = (18.47 \pm 0.02)$ kJ·mol^{-1}.[50]

The value $\Delta_{\text{l}}^{\text{g}} C_{p,\text{m}}^0 = -(107.2 \pm 2.9)$ J·K^{-1}·mol^{-1} derived from our vapor pressure data for the liquid phase is in good agreement (see Figure 11) with that obtained from the difference between $C_{p,\text{m}}^0(\text{g})$ estimated by Benson's group contribution method[42] and $C_{p,\text{m}}^0(\text{l})$ measured by Chirico et al.[17]

Ferrocene. As concluded by van Genderen and Oonk,[9] ferrocene has the potential of being a suitable compound for testing or calibrating vapor pressure instruments. Collection of new data sets on vapor pressure covering a wide temperature range is highly required for ferrocene. The data published by Jacobs et al.[22] were used as a reference in the deviation plot
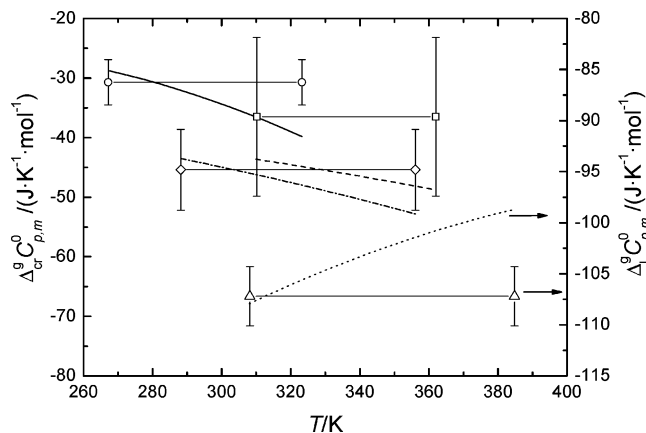
Figure 11. Comparison of differences $\Delta_{cr}^{g}C_{p,m}^{0} = C_{p,m}^{0}(g) - C_{p,m}^{0}(cr)$ (naphthalene, benzoic acid, and ferrocene) and $\Delta_{l}^{g}C_{p,m}^{0} = C_{p,m}^{0}(g) - C_{p,m}^{0}(l)$ (benzophenone, right y axis) obtained from vapor pressure data determined in this work with those calculated from published or estimated $C_{p,m}^{0}(g)$ and $C_{p,m}^{0}(cr)$ or $C_{p,m}^{0}(l)$ determined calorimetrically. $\bigcirc-\bigcirc$, naphthalene from vapor pressure data; $-$, naphthalene using $C_{p,m}^{0}(g)$ taken from Frenkel et al.[27] and $C_{p,m}^{0}(cr)$ from Chirico et al.;[26] $\square-\square$, benzoic acid from vapor pressure data; $--$, benzoic acid using $C_{p,m}^{0}(g)$ taken from Stull et al.[39] and $C_{p,m}^{0}(cr)$ recommended by Sabbah et al.;[7] $\triangle-\triangle$, benzophenone from vapor pressure data; $\cdots$, benzophenone using $C_{p,m}^{0}(g)$ estimated by Benson's group contribution method[42] and $C_{p,m}^{0}(l)$ taken from Chirico et al.;[17] $\diamond-\diamond$, ferrocene from vapor pressure data; $-\cdot-$, ferrocene using $C_{p,m}^{0}(g)$ taken from Turnbull[53] and $C_{p,m}^{0}(cr)$ from Tomassetti et al.[54] Error bars correspond to uncertainties of $\Delta_{cr}^{g}C_{p,m}^{0}$ or $\Delta_{l}^{g}C_{p,m}^{0}$ reported in Table 5.

shown in Figure 10. Our data at lower temperatures are in very good accordance with those obtained by combined torsion and mass-loss effusion methods by Jacobs et al.[22] The agreement between our data and those reported by Ribeiro da Silva and Monte[2] and by Torres-Gomez et al.[51] is reasonable. Data given by Pelino et al.[52] show very high scatter, although the mean value is in accordance with our data. At temperatures higher than 305 K our data start to be systematically lower than data reported by Jacobs et al.[22] (deviating by -2.52 % up to -6.10 %). Comparison between other vapor pressure data published prior to year 1983 can be found in ref 22.

The value $\Delta_{cr}^{g}H_{m}^{0}(298.15 \text{ K}) = (74.5 \pm 0.1) \text{ kJ·mol}^{-1}$, determined in this research, is in good agreement with that recommended by ICTAC,[7] $\Delta_{cr}^{g}H_{m}^{0}(298.15 \text{ K}) = (73.42 \pm 1.08) \text{ kJ·mol}^{-1}$.

The agreement between the value $\Delta_{cr}^{g}C_{p,m}^{0} = -(45.4 \pm 6.8) \text{ J·K}^{-1}\text{·mol}^{-1}$, derived from our vapor pressure, and that calculated from $C_{p,m}^{0}(g)$ and $C_{p,m}^{0}(s)$ reported by Turnbull[53] and Tomassetti et al.,[54] respectively, is satisfactory (see Figure 11).

Conclusions

Considering the results obtained and the above comments, we conclude that the new static apparatus seems to be suitable for the accurate determination of vapor pressures of both crystalline and liquid compounds in the temperature range (243 to 413) K and in the pressure range (0.4 to 133) Pa.

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