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Thermodynamic Properties of Diphenylmethane[†]

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Measurements leading to the calculation of the standard thermodynamic properties for gaseous diphenylmethane (Chemical Abstracts registry number [101-81-5]) are reported. Experimental methods include adiabatic heat-capacity calorimetry, vibrating-tube densimetry, comparative ebulliometry, inclined-piston gauge manometry, and differential-scanning calorimetry (dsc). Measurement results for the enthalpy of combustion were reported previously. The critical temperature was measured with a differential scanning calorimeter. The critical pressure and critical density were estimated. Standard molar entropies, standard molar enthalpies, and standard molar Gibbs free energies of formation were derived at selected temperatures between 298.15 K and 700 K. All results are compared with experimental values reported in the literature.

1. Introduction

The background and justification for thermodynamic property measurements for diphenylmethane were discussed previously by us in a report of the experimental determination of the enthalpy of combustion for diphenylmethane and 2-methylbiphenyl.[1] This work is a product of research funded by the U.S. Department of Energy Office of Fossil Energy, Advanced Oil Recovery (AOR) program. Within a portion of this research program, the thermochemical and thermophysical properties are determined for key aromatics and hydroaromatics present in the spectrum of fossil-fuel materials. The results of the thermodynamic property measurements will be used to provide insights into the reaction networks and relative reactivities of polycyclic aromatics and hydroaromatics within the complex processes operating in hydroprocessing. The reported high-precision measurements also provide the basis for improved and extended estimation and correlation methods necessary to provide reliable property values for cyclic aromatics, which are key in the analysis of technological problems in a wide variety of fields, including pharmaceuticals, "science-based" environmental regulations, ecosystem restoration, gasoline formulation, control of greenhouse gases, plant and automotive emission standards, and fossil-fuel processing.

The thermodynamic properties of diphenylmethane reported here were measured by adiabatic heat-capacity calorimetry, comparative ebulliometry, inclined-piston gauge manometry, vibrating-tube densimetry, and differential scanning calorimetry (dsc). Through combination with the previously reported enthalpy of combustion, standard molar formation properties (Gibbs free energies, enthalpies, and entropies) in the ideal gaseous state were derived. All measured or derived thermodynamic property values are compared with those reported in the literature.

2. Experimental Section

The research group of Professor E. J. "Pete" Eisenbraun (retired) of Oklahoma State University synthesized and purified the calorimetric sample of diphenylmethane. Mole fraction impurity x of the sample of diphenylmethane ($x = 0.0002_1$) used in this research was determined by fractional melting as part of the adiabatic heat-capacity calorimetry studies reported here. This material was part of the same sample used in the determination of the enthalpy of formation using oxygen bomb calorimetry. The purity level was further corroborated in ebulliometric vapor-pressure studies reported here by the small differences observed between the boiling and condensation temperatures of the sample. All transfers of the purified sample were done under nitrogen or helium or by vacuum distillation.

The water used as a reference material in the ebulliometric vapor-pressure measurements was deionized and distilled from potassium permanganate. The decane also used as a reference material for the ebulliometric measurements was purified by urea complexation, two recrystallizations of the complex, decomposition of the complex with water, extraction with ether, drying with $MgSO_4$, and distillation at 337 K and 1 kPa pressure. GLC (gas−liquid chromatography) analysis of the decane sample failed to show any impurity peaks.

Molar values are reported in terms of $M = 168.234$ $g\cdot mol^{-1}$ for $C_{13}H_{12}$,[2] diphenylmethane, and the gas constant $R = 8.314472\ J\cdot K^{-1}\cdot mol^{-1}$ adopted in 1998 by CODATA.[3] The platinum resistance thermometers used in these

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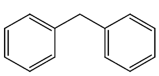
Table 1. Calorimeter and Sample Characteristics for Adiabatic Heat-Capacity Calorimetric Studies[a]



diphenylmethane

m/g	39.238
V_i(298.15 K)/cm^3	59.06
T_{cal}/K	299.0
p_{cal}/kPa	4.65
$r(T_{\max})$	2.9
$r_{\min}$	1.7
$10^2(\delta C/C)_{\max}$	0.038
x_{pre}	0.00021

[a] m is the sample mass; V_i is the internal volume of the calorimeter; T_{cal} is the temperature of the calorimeter when sealed; p_{cal} is the pressure of the helium and sample when sealed; $r(T_{\max})$ is the ratio of the heat capacity of the full calorimeter to that of the empty at the highest temperature $T_{\max} \approx 444$ K of these measurements; $r_{\min}$ is the minimum value of r observed in this study; $(\delta C/C)_{\max}$ is the vaporization correction at the highest temperature measured (i.e., $T_{\max} \approx 444$ K); and x_{pre} Is the mole-fraction impurity used for premelting corrections.

Table 2. Measured Values of Density ρ at Saturation Pressure[a]

T/K	ρ/kg·m^{-3}	$100(\rho - \rho_{\mathrm{cs}})/\rho$	$100(\rho - \rho_{\mathrm{poly}})/\rho$
308.14	996.7	0.4	0.0
323.14	985.3	0.3	0.0
348.13	965.6	0.2	0.0
373.12	945.8	0.1	−0.1
398.12	926.1	0.0	0.0
423.12	905.7	−0.1	0.0
448.11	885.4	−0.2	0.0
473.11	864.3	−0.2	0.1
498.11	842.6	−0.3	0.1
523.11	819.2	−0.4	−0.1

[a] Values of ρ_{cs} were calculated with the corresponding-states correlation (eq 4), and values of ρ_{poly} were calculated with the polynomial equation $\rho_{\mathrm{poly}}/\mathrm{kg{\cdot}m^{-3}} = 1195.4 - 0.54266(T/\mathrm{K}) - (3.3456 \times 10^{-4})(T/\mathrm{K})^2$.

measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST). All temperatures were measured in terms of IPTS-68[4] and were converted approximately to ITS-90 with published temperature increments.[5] The platinum resistance thermometer used in the adiabatic heat-capacity studies was calibrated below 13.81 K with the method of McCrackin and Chang.[6] Mass, time, electrical resistance, and potential difference were measured in terms of standards traceable to calibrations at NIST.

Adiabatic heat-capacity and enthalpy measurements were made with a calorimetric system that has been described previously.[7] The calorimeter characteristics and sealing conditions are given in Table 1. Energy measurement procedures were the same as those described for studies on quinoline.[7] Thermometer resistances were measured with self-balancing alternating-current resistance bridges (H. Tinsley & Co. Ltd.; models 5840C and 5840D), which were calibrated with standard resistors specifically designed for use with alternating current. Energies were measured with a repeatability of 0.01%, and temperatures were measured with a repeatability of 0.0001 K. The energy increments to the filled platinum calorimeter were corrected for enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the sample into the free space of the sealed vessel. The maximum correction to the measured energy for the helium exchange gas was 0.3% near $T = 5$ K for diphenylmethane. The sizes of the other two corrections are indicated in Table 1.

Densities along the liquid-phase saturation line ρ_{sat} for a range of temperatures were obtained in this research for diphenylmethane with a vibrating-tube densimeter. The instrument and its operation have been described.[8] Test measurements of the density of benzene between $T = 310$ K and $T = 523$ K have been reported.[9] Results agreed with the values published by Hales and Townsend[10] within $1 \times 10^{-3}\ \rho_{\mathrm{sat}}$. The repeatability of the measurements was approximately $5 \times 10^{-4}\rho_{\mathrm{sat}}$.

The essential features of the ebulliometric equipment and procedures have been described.[11,12] The ebulliometers were used to reflux the diphenylmethane with a standard of known vapor pressure under a common atmosphere of He(g). The boiling and condensation temperatures of the two substances were determined, and the vapor pressure of the diphenylmethane sample was derived from the condensation temperature of the standard. In the pressure region 25 kPa to 270 kPa, water was used as the standard, and the pressures were derived from the internationally accepted equation of state for ordinary water.[13] In the pressure region 2 kPa to 25 kPa, decane was used as the standard. Pressures were calculated for measurements with decane as the reference material with eq 1 of reference 14.

The standard uncertainty in the temperature measurements for the ebulliometric vapor-pressure studies was 0.002 K. Standard uncertainties in the pressures are adequately described by

$$\sigma(p) = (0.002\ \mathrm{K})\left\{\left(\frac{\mathrm{d}p_{\mathrm{ref}}}{\mathrm{d}T}\right)^2 + \left(\frac{\mathrm{d}p_x}{\mathrm{d}T}\right)^2\right\}^{1/2} \tag{1}$$

where p_{ref} is the vapor pressure of the reference substance and p_x is the vapor pressure of the sample under study. The repeatability of the temperature measurements was near 5×10^{-4} K. Values of $\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T$ for the reference substances were calculated from vapor pressures of the reference materials (decane and water).

Douslin and McCullough[15] and Douslin and Osborn[16] have described the equipment for the inclined-piston vapor-pressure measurements. Revisions to both the equipment and procedures have been reported.[7] Standard uncertainties in the pressures determined with the inclined-piston apparatus, on the basis of estimated uncertainties of measuring the mass, area, and angle of inclination of the piston, are adequately described by the expression

$$\sigma(p) = 1.5 \times 10^{-4}p + 0.2 \tag{2}$$

The pressure p in eq 2 is expressed in Pa. The standard uncertainties in the temperatures are 0.002 K. The contributions of the temperature uncertainties to $\sigma(p)$ are insignificant in the range of the measurements.

Experimental methods for the measurements by dsc were described previously.[17,18]

3. Results

Measured densities for diphenylmethane in the liquid phase at saturation pressure are listed in Table 2.

Vapor pressures for diphenylmethane are reported in Table 3. The pressures, the condensation temperatures, and the difference between condensation and boiling temperatures for the sample are reported. The small differences obtained between the boiling and condensation temperatures indicated correct operation of the equipment and the high purity of the sample.

Table 3. Summary of Vapor-Pressure Results[a]

method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
IP	329.988	0.0261	0.0000	0.0002	
IP	339.985	0.0523	0.0001	0.0002	
IP	349.976	0.0995	0.0001	0.0002	
IP	359.973	0.1814	0.0001	0.0002	
IP	369.982	0.3181	0.0001	0.0002	
IP	379.976	0.5378	0.0002	0.0003	
IP	389.969	0.8793	0.0001	0.0003	
IP	399.968	1.3953	−0.0003	0.0004	
decane	408.209	2.0002	0.0002	0.0003	0.039
IP	409.974	2.1548	−0.0004	0.0005	
IP	414.970	2.6515	−0.0002	0.0006	
decane	415.107	2.6663	−0.0003	0.0003	0.031
IP	419.972	3.2434	0.0000	0.0007	
decane	425.344	4.0003	−0.0001	0.0005	0.025
decane	432.994	5.3335	0.0000	0.0006	0.020
decane	444.380	7.9994	−0.0002	0.0009	0.014
decane	452.925	10.666	0.000	0.001	0.013
decane	459.840	13.332	0.001	0.001	0.013
decane	467.026	16.665	0.001	0.002	0.012
decane	472.998	19.932	0.000	0.002	0.012
water	480.859	25.020	0.002	0.003	0.011
decane	480.863	25.021	0.000	0.002	0.011
water	488.783	31.174	0.001	0.003	0.010
water	496.761	38.561	−0.002	0.004	0.010
water	504.791	47.371	−0.001	0.005	0.010
water	512.878	57.812	−0.003	0.005	0.011
water	521.020	70.114	−0.004	0.006	0.010
water	529.217	84.526	−0.002	0.007	0.011
water	537.469	101.315	−0.001	0.008	0.012
water	545.776	120.78	0.00	0.01	0.013
water	554.143	143.23	0.00	0.01	0.013
water	562.557	169.00	0.01	0.01	0.013
water	571.031	198.46	0.00	0.01	0.013
water	579.554	231.99	0.01	0.02	0.015
water	588.130	269.98	0.00	0.02	0.015

[a] IP denotes inclined piston; water or decane refers to the material used as the standard in the reference ebulliometer; T is the condensation temperature of the sample; the pressure p for ebulliometric measurements was calculated from the condensation temperature of the reference substance; δp is the difference in the value of pressure, calculated with eq 3 and the parameters listed in Table 9, from the observed value of pressure; σ is the propagated standard uncertainty calculated from eqs 1 and 2; and ΔT is the difference between the boiling and condensation temperatures ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the sample.

Table 4. Melting-Study Summaries[a]

F	$T(F)$/K
0.153	298.311
0.303	298.338
0.553	298.350
0.753	298.354

$T_{\mathrm{tp}} = 298.36_5$ K
$x = 0.00021$

[a] F is the fraction melted at observed temperature $T(F)$; T_{tp} is the triple-point temperature; and x is the mole-fraction impurity.

Table 5. Measurements of Molar Energy Increment $\Delta_{\mathrm{tot}}U_{\mathrm{m}}$ ($R = 8.314472\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)

N[a]	h[b]	T_{i} K	T_{f} K	T_{trs} K	$\Delta_{\mathrm{tot}}U_{\mathrm{m}}$[c] kJ·mol^{-1}	$\Delta_{\mathrm{trs}}H_{\mathrm{m}}$[d] kJ·mol^{-1}
Single-Phase Measurements in the Crystal Phase						
6	1	88.163	214.511		14.810	−0.001
6	1	214.505	293.209		15.222	−0.002
Crystal to Liquid-Phase Transition						
1	3	294.365	301.083	298.365	20.673	19.007
2	5	294.304	299.959		20.386	19.008
6	2	293.049	301.765		21.163	19.009
					average	19.008
Single-Phase Measurements in the Liquid Phase						
8	1	301.902	403.400		29.973	−0.002
8	1	403.436	441.550		12.640	0.000

[a] Adiabatic series number. [b] Number of heating increments. [c] $\Delta_{\mathrm{tot}}U_{\mathrm{m}}$ is the molar energy input from the initial temperature T_{i} to the final temperature T_{f}. [d] $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ is the net molar enthalpy of transition at the transition temperature T_{trs} or the excess enthalpy for single-phase measurements relative to the heat-capacity curve described in the text and defined in Table 11.

For enthalpy and heat capacity measurements with adiabatic calorimetry, crystallization of diphenylmethane was initiated by slow cooling (approximately 15 mK·s^{-1}) of the liquid sample. The sample supercooled between 5 K and 10 K before crystallization began. Complete crystallization was ensured by maintaining the sample under adiabatic conditions in the partially melted state (10% to 20% liquid) until ordering of the crystals was complete, as evidenced by the absence of spontaneous warming of the sample. In these experiments, the sample was maintained for approximately 10 h in the partially melted state and no spontaneous warming was observed, indicating that complete crystallization had been achieved rapidly. The sample was then cooled at an effective rate of 1.5 mK·s^{-1} to crystallize the remaining liquid. Finally, the sample was thermally cycled from approximately 100 K to within 3 K of the triple-point temperature ($T_{\mathrm{tp}} = 298.36_5$ K), where it was held for a minimum of 24 h to provide further tempering. All of the solid-phase measurements were performed upon crystals pretreated in a similar manner. As shown later, excellent repeatability was observed for three separate enthalpy-of-fusion determinations, which also is indicative of complete conversion to the crystalline state.

The triple-point temperature T_{tp} and the mole fraction purity x were determined by measurement of the equilibrium melting temperatures $T(F)$ as a function of fraction F of the sample in the liquid state.[19] Equilibrium melting temperatures were determined by measuring temperatures at intervals of approximately 240 s for 1 h to 1.5 h after an energy input and extrapolating to infinite time by assuming an exponential decay toward the equilibrium value. The observed temperatures at the end of the equilibration period were within 2 mK of the calculated equilibrium temperatures for F values listed in Table 4 and used in the determination of T_{tp}. No evidence for the presence of solid-soluble impurities was found. Published procedures[20] were used to derive the mole fraction purity x and T_{tp}. The results are summarized in Table 4.

Experimental molar enthalpy results are summarized in Table 5. The table includes molar enthalpies of fusion and results of measurements in single-phase regions, which serve as checks on the integration of the molar heat-capacity values. Corrections for premelting caused by impurities were made in these evaluations. Results with the same series number in Tables 5 and 6 were taken without interruption of adiabatic conditions.

Equilibrium was reached in less than 1 h for all measurements in the liquid phase and for measurements in the solid phase below 250 K. As the triple-point temperature ($T_{\mathrm{tp}} = 298.36_5$ K) was approached equilibration times increased gradually from 1 h near 250 K to 6 h near 295 K.

The experimental molar heat capacities under vapor saturation pressure $C_{\mathrm{sat,m}}$ determined by adiabatic calorimetry are listed in Table 6 and shown in Figure 1. Values in Table 6 were corrected for effects of sample vaporization into the gas space of the calorimeter, although the size of the correction is small, as indicated in Table 1. The values listed in Table 6 were not corrected for premelting, but an independent calculation can be made with the temperature increments provided. The temperature increments were small enough to obviate the need for corrections for nonlinear variation of $C_{\mathrm{sat,m}}$ with temperature. Combined uncertainties (95% level of confidence) for the heat-capacity

Table 6. Molar Heat Capacities $C_{\mathrm{sat,m}}$ at Vapor-Saturation Pressure Measured with Adiabatic Calorimetry ($R = 8.314472\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)

N^a	$\langle T\rangle$/K	$C_{\mathrm{sat,m}}/R^b$	ΔT/K	N^a	$\langle T\rangle$/K	$C_{\mathrm{sat,m}}/R^b$	ΔT/K
			Crystal				
5	5.364	0.056	0.955	6	76.620	8.703	7.184
5	6.296	0.091	0.908	4	78.191	8.827	6.965
5	7.218	0.140	0.931	3	81.129	9.042	6.756
5	8.187	0.206	0.997	6	84.193	9.256	7.943
5	9.195	0.291	1.006	4	85.518	9.352	7.688
5	10.212	0.398	1.029	3	88.471	9.563	7.911
5	11.330	0.528	1.206	3	96.788	10.136	8.681
5	12.599	0.690	1.332	3	105.906	10.765	9.495
5	13.993	0.896	1.460	3	115.546	11.421	9.744
5	15.532	1.135	1.622	3	125.311	12.092	9.737
5	17.238	1.424	1.794	3	135.115	12.779	9.848
5	19.131	1.755	1.985	3	145.055	13.489	10.007
5	21.210	2.124	2.168	3	155.051	14.233	9.983
5	23.510	2.544	2.430	3	165.031	14.995	9.975
5	26.075	3.003	2.698	3	175.009	15.760	9.977
5	28.932	3.499	3.013	3	185.003	16.614	10.011
5	32.110	4.025	3.340	3	195.046	17.453	10.072
5	35.662	4.569	3.763	3	205.137	18.339	10.109
5	39.617	5.121	4.148	3	215.252	19.264	10.119
5	44.018	5.684	4.655	3	225.344	20.224	10.075
5	48.941	6.247	5.192	3	235.385	21.219	10.010
4	50.871	6.464	3.677	3	245.372	22.251	9.970
6	52.950	6.668	4.525	1	246.513	22.369	10.331
5	54.430	6.824	5.786	3	255.317	23.320	9.930
4	55.007	6.869	4.582	1	257.334	23.545	11.315
6	57.890	7.166	5.327	1	268.603	24.828	11.248
4	59.908	7.341	5.208	1	279.290	26.118	10.172
6	63.588	7.656	6.058	2	289.278	27.609	10.085
4	65.428	7.825	5.826	1	289.372	27.650	10.076
6	69.821	8.185	6.403				
			Liquid				
2	303.376	32.482	6.839	7	356.661	35.758	17.000
1	305.339	32.592	8.529	7	373.628	36.844	16.887
6	305.589	32.611	7.650	7	390.489	37.870	16.798
1	313.821	33.106	8.453	7	407.290	38.944	16.771
7	325.590	33.824	10.000	7	424.083	39.987	16.793
7	339.575	34.686	17.118	7	438.407	40.870	11.849

[a] Adiabatic series number. [b] Average heat capacity for a temperature increment of ΔT with a mean temperature $\langle T\rangle$.

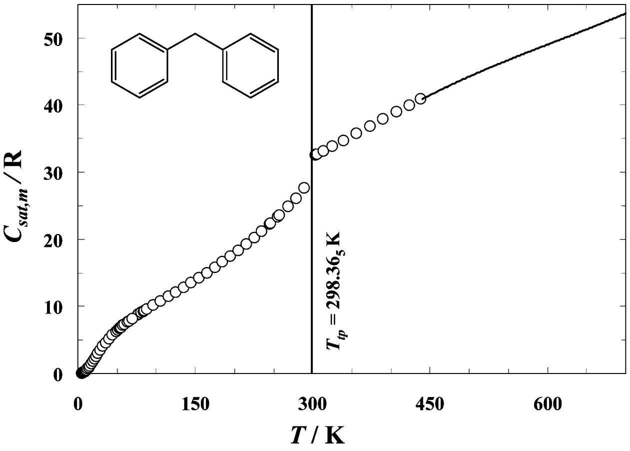


Figure 1. Molar heat capacities at saturation pressure $C_{\mathrm{sat,m}}$ for diphenylmethane measured in this research. The vertical line indicates the triple-point temperature. ○, Determined with adiabatic calorimetry; –, determined with differential scanning calorimetry.

measurements ranged from approximately 3% at 5 K, to 0.5% at 10 K, and improved gradually to better than 0.1% above 30 K. Extrapolation of the heat-capacity results to $T \to 0$ K was made with a plot of $C_{\mathrm{sat,m}}/T$ against T^2 for temperatures below 10 K.

Table 7 lists two-phase heat capacities for diphenylmethane measured by dsc for three cell fillings. Slow decomposition of the sample above approximately $T = 700$ K precluded reliable heat-capacity measurements in this region. However, sample decomposition was sufficiently slow to allow a rapid heating method[21,22] to be used to determine the temperature of conversion from the two-phase (liquid + gas) to the one-phase (fluid) region for a series of filling densities of the hermetically sealed dsc cells. The conversion temperature is indicated by a sudden decrease in heat capacity when the phase boundary is crossed during heating. The heating rate used was 0.33 K·s^{-1}. The filling densities and phase boundary temperatures are listed in Table 8 and are shown in Figure 2. The experimental critical temperature (T_c = 778 ± 2) K corresponds to the maximum in the temperature against filling-density curve.

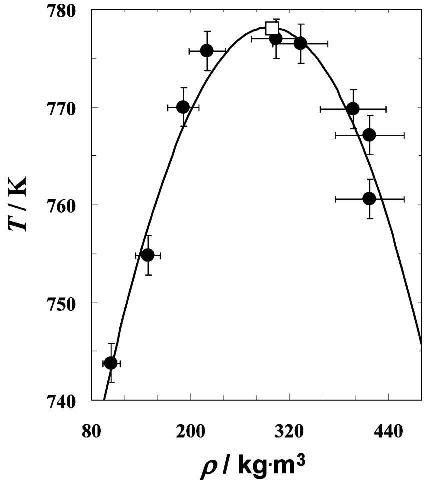


Figure 2. (Vapor + liquid) coexistence region for diphenylmethane. ρ denotes density. The curve represents a fit of a second-order polynomial to the experimental values. ●, Experimental values of this research (Table 8); □, experimental critical temperature T_c and estimated critical density ρ_c of this research.

Table 7. Measured Two-Phase (Liquid + Vapor) Heat Capacities/R^a

	T/K	$C_{x,\mathrm{m}}{}^{\mathrm{II}}/R$	$C_{x,\mathrm{m}}{}^{\mathrm{II}}/R$	$C_{x,\mathrm{m}}{}^{\mathrm{II}}/R$
m/g		0.011938	0.016483	0.021510
V_{cell}/cm^3		0.05336	0.05336	0.05336
	315.0	32.5	32.6	32.5
	335.0	33.6	33.8	33.6
	355.0	35.0	35.0	34.8
	375.0	36.0	36.2	36.0
	395.0	37.4	37.4	37.3
	415.0	38.4	38.4	38.6
	435.0	39.9	40.1	39.9
	455.0	41.8	41.5	41.2
	475.0	43.0	42.8	42.5
	495.0	44.3	44.0	43.7
	515.0	45.7	45.6	44.9
	535.0	47.3	46.6	46.0
	555.0	48.6	47.9	47.4
	575.0	49.9	49.1	48.3
	595.0	51.2	50.7	49.6
	615.0	53.2	51.8	50.6
	635.0	55.0	52.7	51.5
	655.0	56.0	53.9	52.7
	675.0	57.7	55.2	53.9
	695.0	60.3	56.3	54.5
	715.0	61.6	57.4	56.1

[a] m is the mass of sample, and V_{cell} is the volume of the dsc cell at T = 298.15 K after sealing ($R = 8.314472\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$).

Table 8. Measured Densities ρ and Temperatures T Used to Define the Two-Phase Coexistence Curve near $T = T_c$

T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
743.8	104.3	776.5	333.5
754.8	148.4	769.8	397.2
770.0	191.2	767.1	417.5
775.7	220.3	760.6	417.7
777.0	304.2		

Table 9. Parameters for the Wagner Vapor-Pressure Equation, Selected Critical Constants, and Acentric Factor

A	−9.023973	$T_c = 778$ K[a]
B	3.839191	$p_c = 3280$ kPa[b]
C	−4.942310	$\rho_c = 299.6$ kg·m^{-3}[b]
D	−3.424780	$\omega = 0.4445$

[a] The experimental critical temperature $T_c = (778 \pm 2)$ K determined in this research. [b] Critical parameter estimated in this research, as described in the text.

The Wagner equation,[23] as formulated by Ambrose,[24] was used to represent the vapor pressures:

$$\ln\left(\frac{p}{p_c}\right) = \left(\frac{1}{T_r}\right)\{A(1 - T_r) + B(1 - T_r)^{1.5} + C(1 - T_r)^{2.5} + D(1 - T_r)^5\} \quad (3)$$

where $T_r = T/T_c$. The fitting procedure has been described.[18] The critical temperature ($T_c = 778$ K) measured in this research was used in the fits. The critical pressure $p_c = 3280$ kPa was selected with Waring's criterion for $T_r = 0.85$.[25] Application of this criterion was discussed previously by Steele.[18] The critical density listed in Table 9 was chosen to optimize agreement between the measured densities listed in Table 2 and values calculated with the extended corresponding states equation of Riedel,[26] as formulated by Hales and Townsend[10]

$$\frac{\rho}{\rho_c} = 1.0 + 0.85(1.0 - T_r) + (1.6916 + 0.9846\omega)(1.0 - T_r)^{1/3} \quad (4)$$

Molar enthalpies of vaporization $\Delta_l^g V_m$ were derived from the Wagner equation fit by means of the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta_l^g H_m}{T\Delta_l^g V_m} \quad (5)$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. The Wagner equation fit was employed to derive dp/dT. Estimates of liquid-phase volumes were made with eq 4. Vapor-phase volumes were calculated with the virial equation of state truncated at the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl,[27] and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera.[28] The Bartlesville Thermodynamics Group has successfully applied this formulation for third virial coefficients in analyses of the thermodynamic properties of a range of compounds in recent years. A list of compounds studied successfully was included in a recent publication by the group.[14] In all cases the agreement between the entropies for the ideal gas-state derived using this formulation and those obtained from statistical thermodynamics via accurate spectroscopic measurements was better than 0.1% over a temperature range of greater than 250 K. Third virial coefficients are required for accurate calculation of the volume of gas for pressures greater than 0.1 MPa. Combined uncertainties (95% level of confidence) in the virial coefficients were assumed to be 10% in the calculation results reported here for diphenylmethane. Derived enthalpies of vaporization are reported in Table 10. For $p >$ 0.1 MPa, the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived molar enthalpies of vaporization.

Table 10. Enthalpies of Vaporization $\Delta_l^g H_m$ Obtained from the Wagner and Clapeyron Equations

T/K	$\Delta_l^g H_m$/ kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/ kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/ kJ·mol^{-1}
298.15[a]	67.64 ± 0.16	440.00	56.47 ± 0.10	600.00[a]	43.66 ± 0.48
300.00[a]	67.48 ± 0.16	460.00	55.00 ± 0.11	620.00[a]	41.73 ± 0.58
320.00[a]	65.78 ± 0.14	480.00	53.53 ± 0.12	640.00[a]	39.68 ± 0.70
340.00	64.13 ± 0.13	500.00	52.02 ± 0.15	660.00[a]	37.48 ± 0.82
360.00	62.52 ± 0.12	520.00	50.49 ± 0.19	680.00[a]	35.10 ± 0.96
380.00	60.95 ± 0.12	540.00	48.89 ± 0.25	700.00[a]	32.49 ± 1.11
400.00	59.43 ± 0.11	560.00	47.23 ± 0.32		
420.00	57.94 ± 0.10	580.00	45.49 ± 0.39		

[a] Values at this temperature were calculated with extrapolated vapor pressures determined from the fitted parameters of the Wagner equation.

Table 11. Molar Thermodynamic Functions at Vapor-Saturation Pressure (R = 8.314472 J·K^{-1}·mol^{-1})[a]

$\frac{T}{\text{K}}$	$\frac{C_{\text{sat,m}}}{R}$	$\frac{\Delta_0^T S_m}{R}$	$\frac{\Delta_0^T H_m}{RT}$	$\frac{T}{\text{K}}$	$\frac{C_{\text{sat,m}}}{R}$	$\frac{\Delta_0^T S_m}{R}$	$\frac{\Delta_0^T H_m}{RT}$
			Crystal				
5.00[b]	0.046	0.015	0.012	120.00	11.726	12.238	6.573
10.00	0.375	0.124	0.093	140.00	13.125	14.149	7.408
20.00	1.909	0.813	0.587	160.00	14.609	15.998	8.215
30.00	3.679	1.926	1.327	180.00	16.183	17.807	9.011
40.00	5.172	3.197	2.109	200.00	17.882	19.600	9.813
50.00	6.365	4.484	2.845	220.00	19.708	21.389	10.628
60.00	7.350	5.734	3.516	240.00	21.685	23.187	11.466
70.00	8.198	6.932	4.126	260.00	23.828	25.007	12.334
80.00	8.957	8.077	4.683	280.00	26.152	26.856	13.237
90.00	9.668	9.174	5.197	298.15[b]	28.416	28.569	14.091
100.00	10.358	10.228	5.679	298.36$_5$[b]	28.444	28.589	14.101
			Liquid				
298.15[b]	32.156	36.228	21.756	500.00[c]	44.21	55.78	28.45
298.36$_5$[b]	32.170	36.251	21.763	520.00[c]	45.26	57.54	29.08
300.00[b]	32.271	36.427	21.820	540.00[c]	46.26	59.26	29.70
320.00	33.487	38.549	22.512	560.00[c]	47.23	60.96	30.31
340.00	34.713	40.616	23.193	580.00[c]	48.17	62.64	30.91
360.00	35.974	42.635	23.868	600.00[c]	49.06	64.28	31.50
380.00	37.232	44.614	24.539	620.00[c]	49.93	65.91	32.08
400.00	38.477	46.555	25.204	640.00[c]	50.79	67.51	32.65
420.00	39.737	48.463	25.866	660.00[c]	51.67	69.08	33.21
440.00	40.953	50.340	26.525	680.00[c]	52.61	70.64	33.77
460.00	42.035	52.185	27.176	700.00[c]	53.75	72.18	34.32
480.00[c]	43.138	53.997	27.818				

[a] Values are reported with one digit more than is justified by the experimental uncertainty. This is to avoid round-off errors in calculations based on these results. [b] Values at this temperature were calculated with graphically extrapolated heat capacities. [c] Values at this temperature are based on the fits of the dsc and vapor-pressure measurements described in the text. All other values are based on the adiabatic calorimetric results.

Calculation of $C_{\text{sat,m}}$ values from the values listed in Table 7 has been described.[18,29] Reliable vapor pressures and densities for the liquid phase are required for the calculation of $C_{\text{sat,m}}$ values. The Wagner equation (eq 3) was used with the parameters listed in Table 9 for the vapor pressures, and densities were calculated with eq 4, also with the parameters in Table 9. A polynomial was fit to the liquid phase heat capacities derived from the dsc results. Values of $C_{\text{sat,m}}$ determined with adiabatic calorimetry in this research for the temperature range $300 < (T/\text{K}) < 445$ were included and weighted by a factor of 100 greater than the dsc values. These were included to ensure a smooth junction between the values determined with the two methods.

Condensed-phase molar entropies and molar enthalpies relative to that of the crystals at $T \rightarrow 0$ K for the solid and liquid phases under vapor saturation pressure are listed in Table 11. These were derived by integration of the smoothed molar heat capacities corrected for premelting, together with the molar entropy and molar enthalpy of

Table 12. Standard Molar Thermodynamic Properties in the Gaseous State at $p = p^\circ = 101.325$ kPa for Diphenylmethane ($R = 8.314472$ J·K^{-1}·mol^{-1})[a]

T/K	$\Delta_0^T H_m^\circ/RT$	$\Delta_{imp}H_m^{\circ\,a}/RT$	$\Delta_0^T S_m^\circ/R$	$\Delta_{imp}S_m^{\circ\,b}/R$	$\Delta_f H_m^\circ/RT$	$\Delta_f S_m^\circ/R$	$\Delta_f G_m^\circ/RT$
298.15[c]	49.04 ± 0.07	0.00	52.67 ± 0.07	0.00	66.45 ± 0.29	−50.53 ± 0.07	116.98 ± 0.28
300.00[c]	48.87 ± 0.07	0.00	52.80 ± 0.07	0.00	65.97 ± 0.29	−50.61 ± 0.07	116.58 ± 0.28
320.00[c]	47.24 ± 0.06	0.00	54.27 ± 0.07	0.00	61.09 ± 0.27	−51.39 ± 0.07	112.48 ± 0.27
340.00	45.88 ± 0.05	0.00	55.73 ± 0.06	0.00	56.80 ± 0.25	−52.10 ± 0.06	108.90 ± 0.25
360.00	44.76 ± 0.05	0.00	57.20 ± 0.06	0.00	53.02 ± 0.24	−52.75 ± 0.06	105.77 ± 0.24
380.00	43.84 ± 0.04	0.01	58.67 ± 0.06	0.00	49.66 ± 0.22	−53.33 ± 0.06	102.99 ± 0.23
400.00	43.08 ± 0.04	0.01	60.15 ± 0.06	0.01	46.67 ± 0.21	−53.86 ± 0.06	100.52 ± 0.22
420.00	42.48 ± 0.04	0.02	61.63 ± 0.06	0.01	43.98 ± 0.20	−54.33 ± 0.06	98.31 ± 0.21
440.00	41.99 ± 0.04	0.03	63.11 ± 0.06	0.02	41.56 ± 0.19	−54.76 ± 0.06	96.32 ± 0.20
460.00	41.60 ± 0.04	0.04	64.58 ± 0.06	0.03	39.37 ± 0.19	−55.15 ± 0.06	94.52 ± 0.19
480.00	41.30 ± 0.04	0.07	66.04 ± 0.06	0.05	37.38 ± 0.18	−55.51 ± 0.06	92.89 ± 0.18
500.00	41.06 ± 0.05	0.10	67.48 ± 0.07	0.07	35.56 ± 0.17	−55.84 ± 0.07	91.40 ± 0.18
520.00	40.89 ± 0.06	0.13	68.92 ± 0.07	0.10	33.89 ± 0.17	−56.15 ± 0.07	90.04 ± 0.17
540.00	40.77 ± 0.07	0.18	70.34 ± 0.09	0.13	32.36 ± 0.17	−56.43 ± 0.09	88.79 ± 0.17
560.00	40.69 ± 0.09	0.24	71.74 ± 0.10	0.18	30.94 ± 0.17	−56.69 ± 0.10	87.63 ± 0.18
580.00	40.64 ± 0.11	0.31	73.13 ± 0.12	0.23	29.63 ± 0.18	-56.94 ± 0.12	86.57 ± 0.18
600.00[c]	40.63 ± 0.13	0.39	74.50 ± 0.14	0.29	28.41 ± 0.19	−57.16 ± 0.14	85.58 ± 0.19
620.00[c]	40.65 ± 0.15	0.48	75.86 ± 0.17	0.36	27.28 ± 0.20	−57.37 ± 0.17	84.66 ± 0.20
640.00[c]	40.69 ± 0.18	0.59	77.20 ± 0.19	0.44	26.23 ± 0.22	−57.57 ± 0.19	83.80 ± 0.22
660.00[c]	40.75 ± 0.20	0.71	78.52 ± 0.22	0.53	25.24 ± 0.24	−57.76 ± 0.21	83.00 ± 0.23
680.00[c]	40.82 ± 0.23	0.84	79.82 ± 0.24	0.63	24.31 ± 0.26	−57.93 ± 0.24	82.25 ± 0.25

[a] Gas-imperfection correction included in the standard molar enthalpy for the gas. The standard molar enthalpy of the gas is calculated relative to that of the crystals at $T \rightarrow 0$. [b] Gas-imperfection correction included in the standard molar entropy of the gas. [c] Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted parameters of the Wagner equation.

fusion. The molar heat capacities were smoothed with cubic-spline functions by least-squares fits to six points at a time and by requiring continuity in value, slope, and curvature at the junction of successive cubic functions. Because of limitations in the spline-function procedure, some acceptable values from Table 3 were not included in the fit, whereas in other regions graphical values were introduced to ensure that the second derivative of the heat capacity with respect to temperature was a smooth function of temperature. Premelting corrections were made using standard methods[20] for solid-insoluble impurities and the mole-fraction impurity value shown in Table 1.

Standard molar enthalpies and standard molar entropies for diphenylmethane ($C_{13}H_{12}$) at selected temperatures for the ideal gas at $p = 101.325$ kPa were calculated with values in Tables 10 and 11 and are listed in columns 2 and 4 of Table 12. The derived standard molar enthalpies and standard molar entropies for diphenylmethane in the ideal gaseous state were combined with the standard molar enthalpies of formation for the liquid {(97.1 ± 1.4) kJ·mol^{-1}} published previously[1] to calculate the standard molar enthalpies, standard molar entropies, and standard molar Gibbs free energies of formation listed in columns 6, 7, and 8, respectively, of Table 12. Standard molar enthalpies and standard molar entropies for H_2(equilibrium, g) and C(graphite) were calculated with parameters from JANAF tables.[30] Uncertainties in Table 12 are combined standard uncertainties and do not include uncertainties in the properties of the elements.

Sublimation pressures for diphenylmethane were calculated with the Wagner equation and parameters listed in Table 9 together with the enthalpies and entropies for the liquid and crystalline phases (Table 11). The method is the same as that described previously for biphenyl.[31] Sublimation pressures between the temperatures $T = 270$ K and T_{tp} (298.36$_5$ K) are represented with the following equation

$$\ln\left(\frac{p}{p^\circ}\right) = 27.159 - 3892.5(T/\mathrm{K})^{-1} - 1.6357 \times 10^6(T/\mathrm{K})^{-2} + 1.3183 \times 10^8(T/\mathrm{K})^{-3} \quad (6)$$

where $p^\circ = 1$ Pa.

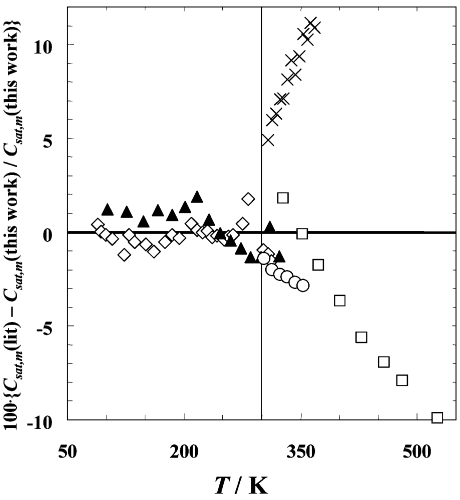


Figure 3. Deviation plot for condensed-phase heat capacities reported in the literature from those of this research. The vertical line indicates the triple-point temperature T_{tp} for diphenylmethane. ◇, Huffman et al.;[34] ▲, Smith and Andrews;[35] ○, Duff and Everett;[38] □, Kurbatov;[37] ×, Blacet et al.[36]

4. Discussion

The critical properties for diphenylmethane were reviewed most recently by Tsonopoulos and Ambrose,[32] who recommended T_c/K = (760 ± 8) based primarily on a preliminary value from this laboratory. The new value reported here, T_c/K = (778 ± 2), should be substituted for the preliminary value cited by Tsonopoulos and Ambrose. The only other modern measurement of the critical temperature for diphenylmethane T_c/K = (767 ± 1) was reported in the Ph.D. thesis of Smith[33] in 1985. It is difficult to assess the reliability of the uncertainty reported by Smith because this work represents an early result using an apparatus with a low residence time.

A deviation plot of literature values for heat capacities of the condensed phases for diphenylmethane is given in Figure 3. Huffman et al.[34] and Smith and Andrews[35] measured heat capacities between approximately $T = 90$ K and $T = 320$ K. Deviations from the present research

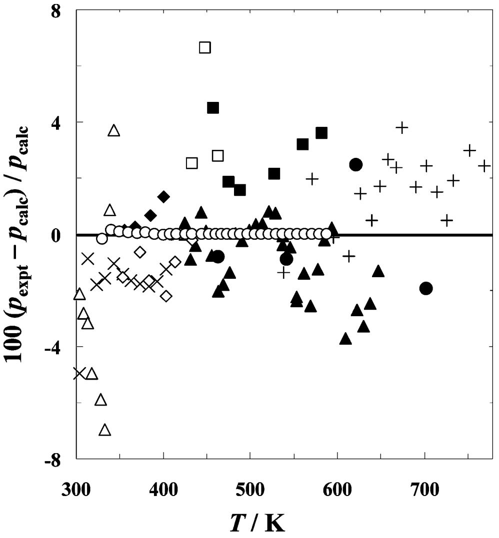


Figure 4. Deviation plot for vapor pressures reported in the literature from values calculated with eq 3 and the parameters listed in Table 9. ○, This research; +, Glaser and Rüland;[39] ♦, API Report;[45] ▲, Wieczorek and Kobayashi;[40] □, Klara et al.;[42] ×, Sasse et al.;[44] □, Hwang et al.;[41] △, Verevkin;[46] ◇, Sohda et al.;[47] ●, Simnick et al.[43]

are typically between (1 and 2)% (Figure 3), and are near the uncertainty expected for measurements of that era. Blacet et al.[36] reported measurements of heat capacities for the liquid phase obtained with an early scanning calorimeter with a sample capacity of 0.15 dm^3. These measurements and those by Kurbatov[37] show large deviations with increasing temperature from those of the present research. Duff and Everett[38] determined heat capacities for the liquid phase with an indirect method that involved combined measurements of $(\partial T/\partial p)_s$ with the thermal expansion coefficient. These values are (2 to 3)% lower than those reported here.

Deviations of literature vapor pressures from those of this research are shown in Figure 4. High-temperature measurements by Glaser and Rüland[39] and Wieczorek and Kobayashi[40] show relatively low precision, but the values are in accord with those reported here, once uncertainties for the literature values are considered. Similarly, values reported as part of vapor−liquid equilibrium studies for various mixtures[41−43] are within several percent of the present values. At low pressures, the closed cell measurements by Sasse et al.[44] and API Project 42[45] and the gas-saturation results by Verevkin[46] and Sohda et al.[47] are also in accord with the present research. Uncertainties for the results of the present research (Table 3) are smaller by more than 1 order of magnitude than the literature values in all cases.

Deviations of literature sublimation pressures from those calculated in this research (eq 6) are shown in Figure 5. All literature values show large deviations[44,48,49] from those calculated here except for those measured recently by Verevkin[46] with a gas-saturation (transpiration) method. Agreement with the results of Verevkin is good in terms of both absolute value and slope, which results in excellent agreement between the enthalpy of vaporization calculated by Verevkin, $\Delta_l^g H_m$ (298.15 K) = (67.9 ± 0.5) kJ·mol^{-1}, and that of this research, (67.64 ± 0.16) kJ·mol^{-1}. The direct measurement by Morawetz,[50] $\Delta_l^g H_m$(298.15 K) = (67.49 ± 0.29) kJ·mol^{-1}, is also in excellent agreement with the present work.

Although the sublimation pressures reported by Aihara[49] show large deviations from those of the present research, it should be noted that those values were determined relative to sublimation pressures for benzophenone published more than 50 years ago. The work of Aihara should be reassessed, after a modern critical evaluation of the sublimation pressures for benzophenone has been completed.

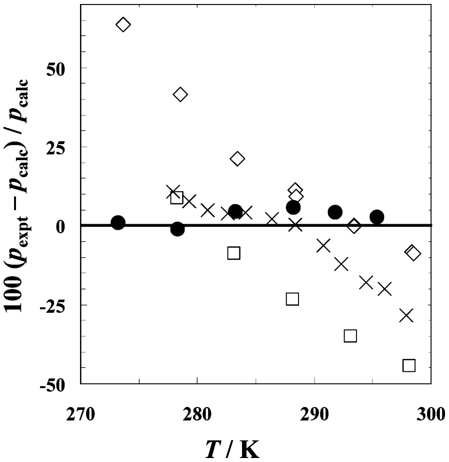


Figure 5. Deviation plot for sublimation pressures reported in the literature from values derived in this research (eq 6). ●, Verevkin;[46] ◇, Sasse et al.;[44] ×, Aihara;[49] □, Bright.[48]

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