

The thermodynamic properties of dibenzofuran ^{a, b, c}

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Measurements leading to the calculation of the ideal-gas thermodynamic properties for dibenzofuran are reported. Experimental methods included combustion calorimetry, adiabatic heat-capacity calorimetry, comparative ebulliometry, inclined-piston manometry, and differential scanning calorimetry. Entropies, enthalpies, and Gibbs energies of formation were derived for the ideal gas for selected temperatures between 298.15 K and 720 K. The critical temperature and critical density were determined with a differential scanning calorimeter, and the critical pressure was derived. These are the first reported experimental critical properties for dibenzofuran. Measured combustion enthalpies, vapor pressures, critical properties, and ideal-gas entropies are compared with literature values.

1. Introduction

Products of the liquefaction of coal differ from petroleum in their much higher oxygen contents.⁽¹⁾ Development of methods to remove the oxygen is necessary to

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reduce production of residua in the generation of coal-derived liquids and to ensure a thermally stable finished fuel. Under hydroprocessing conditions, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO), are expected to occur simultaneously. The presence of oxygen compounds can impact negatively on HDS and HDN processes by competitive adsorption on catalytic sites, and catalyst "poisoning" by water, the HDO product.⁽²⁾

In this paper, thermodynamic properties leading to the calculation of the Gibbs energy of formation for the ideal-gas state are reported for dibenzofuran. Properties of the initial products of each of the two postulated HDO reaction paths,^(3,4) 1,2,3,4-tetrahydrodibenzofuran and 2-hydroxybiphenyl, have been determined in this laboratory, and will be published separately. These properties are needed for complete reaction-study interpretation, reaction modeling, and catalyst comparisons.

Experimental investigations reported here include combustion calorimetry, inclined-piston manometry, comparative ebulliometry, adiabatic heat-capacity calorimetry, and differential scanning calorimetry. Detailed comparisons with available literature values are provided for all properties.

Vapor-pressure measurements by comparative ebulliometry were funded entirely by Exxon Research and Engineering Company. All other work was funded by the U.S. Department of Energy (DOE) Office of Fossil Energy, Advanced Research (AR) section of the Coal Liquefaction program, in which thermodynamic and thermophysical properties are determined for "key" organic compounds important to the processing of alternative fuels sources (shale oil, tar sands, heavy petroleum, and particularly liquids derived from coal).

2. Experimental

The sample of dibenzofuran was prepared by Professor E. J. Eisenbraun and his research group at Oklahoma State University. A commercial sample of 2,2'-dihydroxybiphenyl was purified by recrystallization from (diethylether + cyclohexane). The melting range of the purified material was 357 K to 358 K. The 2,2'-dihydroxybiphenyl was heated at 583 K, with magnetic stirring, under nitrogen for 44 h in the presence of ZnCl_2 . The reaction mixture was cooled, water and diethylether were added, and the separated diethylether layer was washed with $\text{KOH}(\text{aq})$ (10 mass per cent) and with water. The diethylether layer was then dried (MgSO_4), filtered, and concentrated to give crude dibenzofuran. The yield was approximately 40 moles per cent. For purification, the picrate was formed by treatment with picric acid (240 g of 85 mass per cent picric acid) in methanol (1.2 dm^3) at steam-bath temperature. After three crystallizations from methanol, the picrate was cleaved by extraction through basic alumina using *n*-hexane in a Soxhlet apparatus to give a purified sample of dibenzofuran.

Molar values are reported in terms of $M = 168.1949 \text{ g} \cdot \text{mol}^{-1}$, which is based on the relative atomic masses of 1981,⁽⁵⁾ and the gas constant, $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, adopted by CODATA.⁽⁶⁾

The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the

National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS). All temperatures reported are in terms of the IPTS-68.⁽⁷⁾ The platinum resistance thermometer used in the adiabatic heat-capacity studies was calibrated below 13.81 K with the method of McCrackin and Chang.⁽⁸⁾ Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

The apparatus and experimental procedures used in the combustion calorimetry of organic compounds at the National Institute for Petroleum and Energy Research (NIPER) have been described.⁽⁹⁻¹²⁾ A rotating-bomb calorimeter (laboratory designation BMR II)⁽¹³⁾ and platinum-lined bomb (laboratory designations Pt-3b)⁽¹⁴⁾ with an internal volume of 0.393_4 dm^3 were used without bomb rotation. Temperatures were measured by quartz-crystal thermometry.⁽¹⁵⁻¹⁷⁾ For each experiment, 0.001 dm^3 of water was added to the bomb, and the bomb was flushed and charged to 3.04 MPa with pure oxygen. The sample and auxiliary masses were chosen to give the same temperature rise (within 0.1 per cent) in the dibenzofuran combustions and the corresponding calibrations. All experiments were completed within 0.01 K of 298.15 K.

The calorimeter was calibrated with NBS benzoic acid (sample 39i); its specific energy of combustion is $-(26434.0 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$ under certificate conditions. Conversion to standard states⁽¹⁸⁾ gives $-(26413.7 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$ for $\Delta_c U_m^\circ/M$, the specific energy of the idealized combustion reaction. Calibration experiments were interspersed with each series of measurements. Nitrogen oxides did not form in any of the experiments because high-purity oxygen was used in the preliminary bomb flushing and in charging the bomb. The energy equivalent of the calorimeter obtained in the calibration series $e(\text{calor})$ was $(16784.3 \pm 0.4) \text{ J} \cdot \text{K}^{-1}$.

For the cotton fuse, empirical formula $\text{CH}_{1.774}\text{O}_{0.887}$, $\Delta_c U_m^\circ/M$ was $-16945 \text{ J} \cdot \text{g}^{-1}$. Auxiliary information necessary for reducing apparent mass to mass, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states,⁽¹⁸⁾ included a density of $1089 \text{ kg} \cdot \text{m}^{-3}$ and estimated value of $1.3 \times 10^{-7} \text{ m}^3 \cdot \text{K}^{-1}$ for $(\partial V_m/\partial T)_p$ for dibenzofuran. The value of the molar heat capacity at 298.15 K for dibenzofuran used in the corrections to standard states is given as part of the heat-capacity study results later in this paper.

Carbon dioxide was recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as absorbent.⁽¹¹⁾ The combustion products were checked for unburned carbon and other products of incomplete combustion, but none was detected. Carbon dioxide recoveries for the calibrations and dibenzofuran combustions were (100.009 ± 0.010) per cent (mean and standard deviation of the mean) and (99.993 ± 0.008) per cent, respectively.

The essential features of the ebulliometric equipment and procedures for vapor-pressure measurements are described in the literature.⁽¹⁹⁻²¹⁾ The ebulliometers were used to reflux the substance under study with a standard of known vapor pressure under a common helium atmosphere. The boiling and condensation temperatures of the two substances were determined, and the vapor pressure was derived using the condensation temperature of the standard.⁽²¹⁾

The uncertainties in the temperature measurements for the ebulliometric vapor-

pressure studies were 0.001 K. Uncertainties in the vapor pressures of the sample were described adequately by the expression:

$$\sigma(p) = (0.001 \text{ K}) \{ (dp_{\text{std}}/dT)^2 + (dp_x/dT)^2 \}^{1/2}, \quad (1)$$

where p_{std} is the vapor pressure of the reference substance, and p_x is the vapor pressure of the sample under study. Values of dp_{ref}/dT for the reference substances were calculated from fits of the Antoine equation⁽²²⁾ to vapor pressures of the reference materials (benzene and water) reported in reference 21.

The equipment for vapor-pressure measurements with an inclined-piston gauge has been described by Douslin and McCullough⁽²³⁾ and Douslin and Osborn.⁽²⁴⁾ Recent revisions to the equipment and procedures were reported by Steele *et al.*⁽¹²⁾ Uncertainties in the pressures determined with the inclined-piston apparatus, on the basis of estimated precision of measuring the mass, area, and angle of inclination of the piston, were adequately described by the expression:

$$\sigma(p/\text{Pa}) = 1.5 \times 10^{-4}(p/\text{Pa}) + 0.200. \quad (2)$$

The uncertainties in the temperatures were 0.001 K.

Adiabatic heat-capacity and enthalpy measurements were made with a calorimetric system that has been described previously.⁽¹²⁾ The calorimeter characteristics and sealing conditions are given in table 1. The temperature-measurement system employed direct-current methods described previously.⁽²⁵⁻²⁷⁾ Energy-measurement procedures were the same as those described for studies on quinoline.⁽¹²⁾ Energies were measured to a precision of 0.01 per cent, and temperatures were measured to a precision of 1×10^{-4} K. The energy increments to the filled calorimeter were corrected for enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the sample. The maximum correction to the measured energy for the helium exchange gas was approximately 0.5 per cent near 5 K. The sizes of the other two corrections are indicated in table 1.

Differential-scanning calorimetric measurements were made with a Perkin-Elmer DSC II. Experimental methods were described previously.⁽²⁸⁾

TABLE 1. Calorimeter and sample characteristics; 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 is the ratio of the heat capacity of the full calorimeter to that of the empty, T_{max} is the highest temperature of the measurements, $(\delta C/C)_{\text{max}}$ is the fractional vaporization correction at T_{max} , and x_{pre} is the mole-fraction impurity used for pre-melting corrections

Dibenzofuran	
m/g	53.164
$V_i(298.15 \text{ K})/\text{cm}^3$	61.78
T_{cal}/K	299.7
$p_{\text{cal}}/\text{kPa}$	10.5
$r(T_{\text{max}})$	3.4
r_{min}	1.7
$10^2(\delta C/C)_{\text{max}}$	0.033
x_{pre}	0.0001

TABLE 2. Typical combustion experiment for dibenzofuran at 298.15 K. ($p^{\circ} = 101.325 \text{ kPa}$)^a

$m'(\text{compound})/\text{g}$	0.967275
$m''(\text{fuse})/\text{g}$	0.001170
$n_i(\text{H}_2\text{O})/\text{mol}$	0.05535
$m(\text{Pt})/\text{g}$	20.814
$\Delta T/\text{K} = (t_i - t_f + \Delta t_{\text{corr}})/\text{K}$	1.99880
$a(\text{calor})(\Delta T)/\text{J}$	-33548.4 ₅
$a(\text{cont})(\Delta T)/\text{J}^b$	-37.3
$\Delta U_{\text{ign}}/\text{J}$	0.7 ₅
$\Delta U(\text{corr. to std. states})/\text{J}^c$	21.8
$-m''(\Delta_c U_m^{\circ}/M)(\text{fuse})/\text{J}$	19.8
$m'(\Delta_c U_m^{\circ}/M)(\text{compound})/\text{J}$	-33543.4
$(\Delta_c U_m^{\circ}/M)(\text{compound})/(\text{J} \cdot \text{g}^{-1})$	-34678.2

^a The symbols and abbreviations of this table are those of reference 18 except as noted.

^b $\varepsilon_i(\text{cont})(t_i - t_r) + \varepsilon_r(\text{cont})(t_r - t_f + \Delta t_{\text{corr}})$, where t_r is 298.15 K.

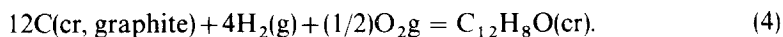
^c Items 81 to 85, 87 to 90, 93, and 94 of the computational form of reference 18.

3. Results

A typical combustion experiment for dibenzofuran is summarized in table 2. It is impractical to list summaries for each combustion, but values of $\Delta_c U_m^{\circ}/M$ for all the experiments are reported in table 3. All values of $\Delta_c U_m^{\circ}/M$ in table 3 refer to the reaction:



Table 3 also gives derived values of the standard molar energy of combustion $\Delta_c U_m^{\circ}$, the standard molar enthalpy of combustion $\Delta_c H_m^{\circ}$, and the standard molar enthalpy of formation $\Delta_f H_m^{\circ}$ for dibenzofuran. Values of $\Delta_c U_m^{\circ}$ and $\Delta_c H_m^{\circ}$ refer to reaction (3). The values of $\Delta_f H_m^{\circ}$ refer to the reaction:



Uncertainties given in table 3 are the "uncertainty interval".⁽²⁹⁾ The standard molar enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ were taken to be $-(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$ and $-(285.830 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$, respectively, as assigned by CODATA.⁽³⁰⁾

TABLE 3. Summary of experimental energies of combustion and molar thermochemical functions for dibenzofuran at $T = 298.15 \text{ K}$ and $p^{\circ} = 101.325 \text{ kPa}$

$\{(\Delta_c U_m^{\circ}/M)(\text{compound})\}/(\text{J} \cdot \text{g}^{-1})$					
-34678.2	-34676.6	-34674.2	-34677.7	-34679.4	-34679.0
$\langle \{(\Delta_c U_m^{\circ}/M)(\text{compound})\}/(\text{J} \cdot \text{g}^{-1}) \rangle$					-34677.5 ± 0.8
$(\Delta_c U_m^{\circ})(\text{compound})/(\text{kJ} \cdot \text{mol}^{-1})$					-5832.58 ± 0.38
$(\Delta_c H_m^{\circ})(\text{compound})/(\text{kJ} \cdot \text{mol}^{-1})$					-5836.30 ± 0.38
$(\Delta_f H_m^{\circ})(\text{compound})/(\text{kJ} \cdot \text{mol}^{-1})$					-29.14 ± 0.60

Measured vapor pressures are listed in table 4. Following previous practice,⁽²⁰⁾ the ebulliometric results were adjusted to common pressures. The common pressures, the condensation temperatures, and the difference between the boiling and condensation temperatures for the sample are reported in table 4.

Previous studies⁽³¹⁾ have shown that the Cox equation⁽³²⁾ can adequately represent measured vapor pressures from the triple-point pressure to 0.3 MPa, and can be used for extrapolation with good precision over a 50 K range. The Cox equation in the form:

$$\ln(p/p_{\text{ref}}) = \{1 - (T_{\text{ref}}/T)\} \exp\{A + B(T/K) + C(T/K)^2\}, \quad (5)$$

TABLE 4. Summary of vapor-pressure results for dibenzofuran: IP refers to measurements performed with the inclined-piston gauge; water or benzene refers to which material was used as the standard in the reference ebulliometer; T is the temperature of the experimental inclined-piston pressure gauge measurements or, for ebulliometric measurements, of 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 of the calculated value of pressure from the observed value of pressure; σ_i is the propagated error calculated from equations (1) and (2); ΔT is the difference between the boiling and condensation temperatures ($T_{\text{boil}} - T_{\text{cond}}$) for the sample in the ebulliometer

Method	T/K	p/kPa	$\Delta p/\text{kPa}$	σ_i/kPa	$\Delta T/K$
IP	358.150	0.0903	-0.0002	0.0002	
IP	363.147	0.1209	-0.0002	0.0002	
IP	368.150	0.1607	0.0002	0.0002	
IP	373.148	0.2106	-0.0002	0.0002	
IP	378.149	0.2747	0.0002	0.0002	
IP	383.149	0.3548	0.0003	0.0003	
IP	388.149	0.4545	0.0001	0.0003	
IP	393.152	0.5785	0.0003	0.0003	
IP	403.152	0.9166	0.0005	0.0003	
IP	413.155	1.4130	-0.0006	0.0004	
IP	418.151	1.7383	-0.0012	0.0005	
IP	423.155	2.1282	-0.0002	0.0005	
IP	428.153	2.5891	-0.0002	0.0006	
IP	433.152	3.1328	-0.0002	0.0007	
benzene	465.606	9.5897	-0.0011	0.0006	0.015
benzene	469.677	10.8926	0.0000	0.0006	0.012
benzene	473.764	12.3446	0.0003	0.0007	0.011
benzene	477.865	13.960	0.001	0.001	0.011
benzene	481.975	15.752	0.001	0.001	0.008
benzene	486.101	17.737	0.002	0.001	0.006
benzene	490.242	19.933	0.002	0.001	0.002
water	498.566	25.023	-0.002	0.001	0.001
water	506.939	31.178	-0.002	0.002	-0.001
water	515.364	38.565	-0.001	0.002	-0.003
water	523.844	47.375	-0.002	0.002	-0.003
water	532.380	57.818	-0.003	0.003	-0.004
water	540.969	70.121	-0.003	0.003	-0.005
water	549.611	84.533	-0.001	0.004	-0.005
water	558.308	101.325	-0.000	0.004	-0.005
water	567.057	120.793	0.006	0.005	-0.004
water	575.859	143.246	0.015	0.006	-0.003
water	584.722	169.019	-0.008	0.006	-0.004
water	593.628	198.49	0.00	0.01	-0.003
water	602.589	232.02	-0.01	0.01	-0.003

TABLE 5. Cox equation coefficients for dibenzofuran

T_{ref}/K	558.308
$p_{\text{ref}}/\text{kPa}$	101.325
A	2.85899
$10^3 B$	-1.19845
$10^6 C$	0.78688
T/K^a	358 to 603

^aTemperature range of the vapor pressures used in the fit.

was fitted to the experimental vapor pressures; p_{ref} was chosen to be 101.325 kPa so that T_{ref} was the normal boiling temperature. The fitting procedure has been described.^(12, 21, 33) Parameters derived from the fit are given in table 5. Details of the Cox equation fit are given in table 4.

Enthalpies of vaporization $\Delta_f^\# H_m$ were derived from the Cox equation fits by means of the Clapeyron equation:

$$dp/dT = \Delta_f^\# H_m / (T \cdot \Delta_f^\# V_m), \tag{6}$$

where $\Delta_f^\# V_m$ is the increase in molar volume from the liquid to the real vapor. Estimates of second virial coefficients were made with the extended corresponding-states equation of Pitzer and Curl.⁽³⁴⁾ Densities were estimated using the correlation of Riedel.⁽³⁵⁾ Uncertainties in the second virial coefficients and liquid-phase densities were estimated to be 10 per cent and 3 per cent of the calculated values, respectively. Derived enthalpies of vaporization and entropies of compression are reported in table 6.

TABLE 6. Molar enthalpies of vaporization and entropies of compression for dibenzofuran obtained from the Cox and Clapeyron equations^a

T/K	$\Delta_f^\# H_m / (R \cdot \text{K})$	$\Delta S_{\text{comp}, m} / R$	T/K	$\Delta_f^\# H_m / (R \cdot \text{K})$	$\Delta S_{\text{comp}, m} / R$
298.15 ^b	8047 ± 18	-11.419 ± 0.002	520.00	6386 ± 15	-0.852 ± 0.000
300.00 ^b	8032 ± 18	-11.253 ± 0.002	540.00	6231 ± 20	-0.389 ± 0.000
320.00 ^b	7876 ± 11	-9.596 ± 0.001	560.00	6072 ± 27	0.034 ± 0.000
340.00 ^b	7722 ± 7	-8.162 ± 0.001	580.00	5908 ± 35	0.424 ± 0.000
360.00	7569 ± 4	-6.912 ± 0.000	600.00	5740 ± 43	0.784 ± 0.000
380.00	7419 ± 3	-5.816 ± 0.000	620.00 ^b	5566 ± 53	1.117 ± 0.000
400.00	7271 ± 2	-4.848 ± 0.000	640.00 ^b	5387 ± 65	1.427 ± 0.000
420.00	7124 ± 2	-3.990 ± 0.000	660.00 ^b	5202 ± 77	1.717 ± 0.000
440.00	6978 ± 3	-3.224 ± 0.000	680.00 ^b	5009 ± 91	1.988 ± 0.000
460.00	6833 ± 5	-2.537 ± 0.000	700.00 ^b	4808 ± 106	2.244 ± 0.000
480.00	6686 ± 7	-1.919 ± 0.000	720.00 ^b	4594 ± 122	2.485 ± 0.001
500.00	6537 ± 11	-1.360 ± 0.000			

^a $\Delta S_{\text{comp}}/R = \ln(p/p^\circ)$ where $p^\circ = 101.325 \text{ kPa}$ and $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

^b Values at this temperature were calculated with extrapolated vapor pressures determined from the fitted Cox coefficients.

TABLE 7. Melting-study summary for dibenzofuran: F is the fraction melted at observed temperature $T(F)$; T_p is the triple-point temperature; x is the mole-fraction impurity

F	$T(F)/K$
0.175	355.1680
0.275	355.2200
0.426	355.2515
0.626	355.2750
T_p/K	355.31
x	0.00045

For the adiabatic heat-capacity and enthalpy studies, crystallization of the sample was initiated by slowly cooling the liquid sample ($3 \text{ mK} \cdot \text{s}^{-1}$). The dibenzofuran supercooled approximately 2 K prior to nucleation. The crystals were annealed by maintaining the sample under adiabatic conditions in the partially melted state (10 per cent to 20 per cent liquid) for approximately 24 h. No spontaneous warming of the sample was observed in this period. The sample was cooled at an effective rate of $0.3 \text{ mK} \cdot \text{s}^{-1}$ to crystallize the remaining liquid. Finally, the sample was thermally cycled between $< 100 \text{ K}$ and within 2 K of its triple-point temperature, where it was held for a minimum of 24 h to provide further tempering. All of the solid-phase measurements were performed upon crystals pre-treated in this manner.

The triple-point temperature T_p and sample purity were determined from the measurement of the equilibrium melting temperature $T(F)$ as a function of fraction F of the sample in the liquid state.⁽³⁶⁾ Equilibrium melting temperatures were determined by measuring temperatures at approximately 300 s intervals for 0.75 h to 1 h after an energy input and extrapolating to infinite time by assuming an exponential decay toward the equilibrium value. The observed temperatures at 0.75 h to 1 h after an energy input were invariably within 3 mK of the calculated equilibrium temperatures for F values listed in table 7. An attempt was made to determine an equilibrium temperature for $F = 0.83$, but equilibration was too slow to obtain a reliable value. The results are summarized in table 7.

Experimental molar enthalpy results are summarized in table 8. The table includes both phase-transition enthalpies and single-phase measurements, which serve as checks on the integration of the heat-capacity results. Corrections for pre-melting caused by impurities were made in these evaluations. Results with the same series number in tables 8 and 9 were taken continuously without interruption of adiabatic conditions.

Excellent reproducibility (within ± 0.01 per cent) was obtained in the enthalpy-of-fusion results. This shows that phase cr(I) was formed reproducibly by means of the tempering methods described above. The sample showed a single solid-phase transition near 292 K with little associated enthalpy. Prior to measurements of the transition enthalpy, the sample was annealed for 6 d, 4 d and 2 d for series 4, 8, and 10, respectively. No correlation between annealing time and transition enthalpy was observed, as shown in table 8. No equilibrium measurements were made across the transition for crystals annealed for less than 2 d near 290 K.

TABLE 8. Experimental molar enthalpy measurements for dibenzofuran ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

N^a	h^b	T_i K	T_f K	T_{trs} K	$\frac{\Delta_{\text{tot}}H_m^c}{R \cdot K}$	$\frac{\Delta_{\text{trs}}H_m^d}{R \cdot K}$
Single-phase measurements in cr(II)						
2	1	53.317	101.088		328.63	-0.09
2	1	101.101	161.103		617.30	-0.18
2	1	161.106	221.088		867.20	-0.13
4	1	221.246	281.491		1154.03	-0.73
10	1	82.441	144.583		569.79	-0.33
10	1	144.545	203.780		782.81	-0.35
10	1	203.736	274.023		1276.45	-0.30
cr(II) to cr(I)						
4	1	281.433	323.572	292.5	1019.94	0.29
8	1	277.319	310.233		766.25	-0.95
10	1	280.162	310.073		702.96	0.66
					Average:	0.00
Single-phase measurements in cr(I)						
10	1	310.086	347.281		988.71	0.39
11	1	310.944	348.101		989.23	-0.78
cr(I) to liquid						
1	2	347.452	358.123	355.31	2634.45	2320.72
10	2	347.291	357.983		2633.87	2320.09
11	6	348.556	360.181		2668.92	2320.64
					Average:	2320.48
Single-phase measurements in liquid						
13	1	363.759	438.275		2553.52	0.31
13	1	438.273	491.096		1988.81	-0.29

^a Adiabatic series number.

^b Number of heating increments.

^c $\Delta_{\text{tot}}H_m$ is the molar energy input from the initial temperature T_i to the final temperature T_f .

^d $\Delta_{\text{trs}}H_m$ is the net molar enthalpy of transition at the transition temperature T_{trs} for phase changes, and is the difference from enthalpies calculated from smoothed heat capacities corrected for pre-melting for single-phase measurements.

The experimental molar heat capacities under vapor saturation pressure $C_{\text{sat},m}$ determined by adiabatic calorimetry are listed in table 9. Values in table 9 were corrected for effects of sample vaporization into the gas space of the calorimeter. The temperature increments were small enough to obviate the need for corrections for non-linear variation of $C_{\text{sat},m}$ with temperature. The precision of the heat-capacity measurements ranged from approximately 5 per cent at 5 K, to 2 per cent at 11 K, 0.2 per cent near 20 K, and improved gradually to less than 0.1 per cent above 100 K, except in the solid-phase region near the triple-point temperature where equilibration times were long. The heat capacities in table 9 have not been corrected for pre-melting, but an independent calculation can be made from the temperature increments provided.

TABLE 9. Experimental molar heat capacities at vapor-saturation pressure for dibenzofuran ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

N^a	$\langle T \rangle$ K	ΔT K	$C_{\text{sat,m}}^b$ R	N^a	$\langle T \rangle$ K	ΔT K	$C_{\text{sat,m}}^b$ R
cr(II)							
4	4.928	0.9275	0.053	1	116.290	9.9653	9.332
4	6.011	0.7018	0.096	1	126.293	10.0370	9.961
4	6.924	0.5914	0.149	1	136.330	10.0354	10.608
4	7.781	0.7028	0.202	1	146.379	10.0610	11.267
4	8.735	0.8908	0.286	1	156.379	9.9374	11.947
4	9.782	1.1360	0.392	1	166.326	9.9626	12.636
4	10.971	1.2231	0.526	1	176.296	9.9792	13.349
4	12.272	1.3920	0.688	1	186.298	10.0296	14.090
4	13.724	1.5333	0.877	1	196.312	10.0059	14.821
4	15.331	1.7012	1.099	1	206.325	10.0262	15.590
4	17.088	1.8253	1.340	1	216.347	10.0270	16.366
4	18.992	1.9868	1.601	2	225.944	9.7732	17.121
4	21.073	2.1749	1.881	1	226.366	10.0206	17.154
4	23.364	2.4051	2.184	2	235.774	10.0018	17.894
4	25.941	2.7463	2.509	1	236.271	9.9925	17.939
4	28.839	3.0490	2.856	2	245.913	10.3381	18.712
4	32.078	3.4195	3.228	1	246.334	10.1492	18.747
4	35.772	3.9692	3.624	2	256.181	10.3191	19.547
4	39.713	3.9141	4.020	1	256.404	10.0077	19.571
4	43.930	4.5190	4.411	1	266.411	10.0149	20.390
4	48.675	4.9715	4.831	2	266.544	10.5364	20.381
4	54.047	5.7720	5.285	8	271.894	10.8743	20.827
1	55.025	5.8048	5.352	11	275.640	9.0998	21.105
1	60.566	5.2617	5.771	1	276.421	10.0038	21.209
1	66.336	6.2640	6.192	3	276.647	10.7575	21.214
1	72.961	6.9760	6.640	10	276.693	6.9992	21.220
1	80.261	7.6162	7.111	2	277.122	10.7483	21.258
1	88.105	8.0535	7.602	3	287.246	10.5727	22.693
1	96.774	9.2103	8.133	2	287.857	10.8637	22.473
1	106.344	9.9233	8.718				
cr(I)							
6	306.694	9.2154	24.679	5	330.299	9.8011	26.733
5	311.238	8.3305	25.057	9	334.704	9.7188	27.104
6	316.271	9.2976	25.509	5	339.975	9.6086	27.617
9	325.666	9.2632	26.349	9	344.171	9.9316	28.034
liquid							
10	361.981	7.9999	32.110	12	433.814	13.5499	36.050
1	362.144	7.9991	32.124	12	447.241	13.3927	36.759
11	365.047	9.6537	32.281	12	460.511	13.2445	37.457
12	368.649	11.5425	32.475	12	473.628	13.1064	38.118
1	370.605	8.8387	32.594	12	486.614	12.9779	38.760
12	381.047	13.2957	33.162	12	499.044	11.9877	39.439
12	394.228	13.1215	33.895	12	510.990	11.8762	40.055
12	407.235	12.9547	34.622	12	520.281	6.7418	40.503
12	420.473	13.7142	35.329				

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

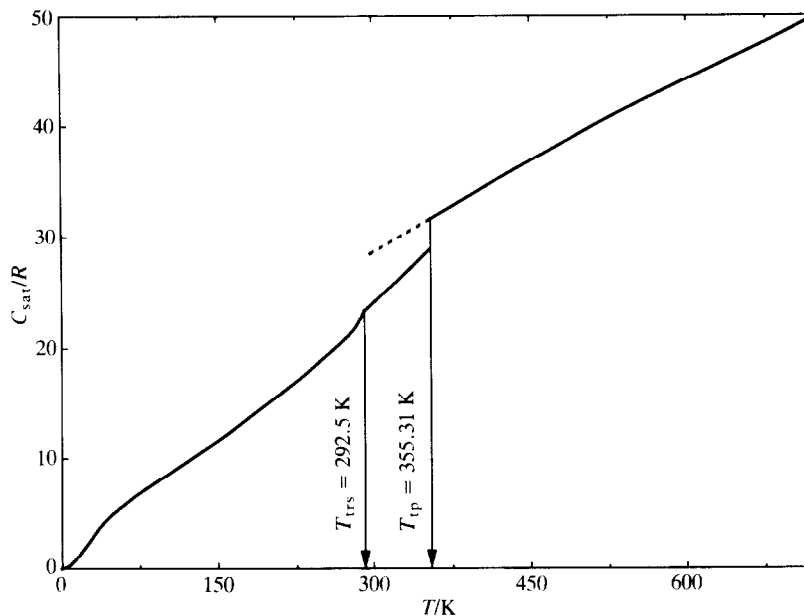


FIGURE 1. Curve of heat capacity against temperature for dibenzofuran. The vertical lines indicate phase transition temperatures; ---, heat capacities obtained by extrapolation of the liquid heat-capacity curve.

For heat-capacity measurements in the liquid phase, equilibrium was reached in less than 1 h. Equilibration times for the crystal phase were all less than 1 h for temperatures below 260 K. Above 260 K, equilibration times increased to 2 h near 270 K, 5 h near 280 K, and to greater than 48 h near 290 K. In phase cr(I), the equilibration time increased from approximately 10 h near 300 K to 20 h near 350 K ($T_{\text{tp}} = 355.31$ K). Heat-capacity measurements with small temperature increments were not made in the transition region because of the long equilibration times involved.

The curve of heat capacity against temperature is shown in figure 1. Values in the transition region, roughly 280 K to 300 K, were estimated by graphical extrapolation. The extrapolated values are included in table 10. T_{trs} was chosen to make the integral of the heat-capacity curve consistent with the measured cr(II) to cr(I) enthalpies listed in table 8.

Extrapolation of the heat-capacity results to $T \rightarrow 0$ was made by means of a least-squares fit of the Debye heat-capacity equation to results below 11 K. The derived Debye characteristic temperature was $\Theta = 86.7$ K with 3.70 degrees of freedom.

The theoretical background for the determination of heat capacities at vapor-saturation pressure $C_{\text{sat}, m}$ with results obtained with a d.s.c. has been described.⁽²⁸⁾ If two phases are present and the liquid is a pure substance, then the vapor pressure p and the chemical potential μ are independent of the amount of substance n and the cell volume V_x , and are equal to p_{sat} and μ_{sat} . The two-phase heat capacities at cell

TABLE 10. Molar thermodynamic functions at vapor-saturation pressure for dibenzofuran ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

$\frac{T}{\text{K}}$	$\frac{C_{\text{sat,m}}}{R}$	$\frac{\Delta_0^T S_m}{R}$	$\frac{\Delta_0^T H_m}{RT}$	$\frac{T}{\text{K}}$	$\frac{C_{\text{sat,m}}}{R}$	$\frac{\Delta_0^T S_m}{R}$	$\frac{\Delta_0^T H_m}{RT}$
cr(II)							
5.000	0.055	0.018	0.014	130.000	10.198	10.735	5.616
6.000	0.095	0.032	0.024	140.000	10.846	11.514	5.966
7.000	0.151	0.050	0.038	150.000	11.511	12.285	6.314
8.000	0.223	0.075	0.056	160.000	12.196	13.050	6.660
9.000	0.312	0.106	0.080	170.000	12.896	13.810	7.006
10.000	0.415	0.144	0.108	180.000	13.623	14.568	7.353
12.000	0.653	0.241	0.178	190.000	14.359	15.324	7.703
14.000	0.915	0.361	0.265	200.000	15.102	16.079	8.054
16.000	1.191	0.501	0.363	210.000	15.873	16.835	8.408
18.000	1.466	0.657	0.471	220.000	16.652	17.591	8.765
20.000	1.737	0.826	0.584	230.000	17.439	18.349	9.125
25.000	2.392	1.285	0.881	240.000	18.233	19.107	9.488
30.000	2.992	1.774	1.183	250.000	19.043	19.868	9.854
35.000	3.543	2.278	1.482	260.000	19.863	20.631	10.223
40.000	4.047	2.784	1.771	270.000	20.674	21.396	10.595
45.000	4.508	3.288	2.050	280.000	21.565	22.163	10.970
50.000	4.946	3.786	2.318	282.000	21.808	22.317	11.046
60.000	5.732	4.759	2.823	284.000	22.074	22.472	11.122
70.000	6.443	5.697	3.290	286.000	22.362	22.628	11.200
80.000	7.095	6.600	3.726	288.000 ^a	22.670	22.785	11.279
90.000	7.719	7.472	4.135	290.000 ^a	22.998	22.943	11.358
100.000	8.330	8.317	4.524	292.000 ^a	23.350	23.102	11.439
110.000	8.943	9.140	4.898	292.500 ^a	23.444	23.142	11.460
120.000	9.564	9.944	5.261				
cr(I)							
292.500 ^a	23.444	23.142	11.460	330.000	26.686	26.162	13.006
298.150 ^a	23.935	23.595	11.691	340.000	27.548	26.971	13.421
300.000 ^a	24.095	23.744	11.767	350.000 ^a	28.410	27.782	13.837
310.000	24.959	24.548	12.179	355.310 ^a	28.870	28.214	14.058
320.000	25.823	25.354	12.592				
liquid							
298.150 ^a	28.573	29.463	18.755	460.000	37.429	43.652	23.782
300.000 ^a	28.676	29.640	18.815	480.000	38.430	45.267	24.371
310.000 ^a	29.230	30.590	19.142	500.000	39.488	46.857	24.955
320.000 ^a	29.784	31.526	19.466	520.000	40.491	48.425	25.533
330.000 ^a	30.338	32.451	19.787	540.000	41.411	49.971	26.104
340.000 ^a	30.892	33.365	20.106	560.000	42.303	51.493	26.667
350.000 ^a	31.447	34.269	20.422	580.000	43.201	52.993	27.222
355.310 ^a	31.743	34.745	20.589	600.000	44.103	54.473	27.769
360.000 ^a	32.005	35.162	20.736	620.000	44.992	55.934	28.311
370.000	32.560	36.047	21.048	640.000	45.809	57.375	28.845
380.000	33.106	36.923	21.358	660.000	46.698	58.798	29.372
390.000	33.659	37.790	21.666	680.000	47.595	60.206	29.895
400.000	34.219	38.649	21.973	700.000	48.500	61.598	30.413
420.000	35.306	40.345	22.583	720.000	49.601	62.979	30.930
440.000	36.378	42.012	23.185				

^a Values at this temperature were calculated with graphically extrapolated heat capacities.

volume V_x , $C_{x,m}^{\text{II}}$, can be expressed in terms of the temperature derivatives of these quantities:

$$nC_{x,m}^{\text{II}}/T = -n(\partial^2\mu/\partial T^2)_{\text{sat}} + V_x(\partial^2 p/\partial T^2)_{\text{sat}} + \{(\partial V_x/\partial T)_x(\partial p/\partial T)_{\text{sat}}\}. \quad (7)$$

The third term on the right-hand side of equation (7) includes the thermal expansion of the cell. In this research the thermal expansion of the cells was expressed as:

$$V_x(T)/V_x(298.15 \text{ K}) = 1 + ay + by^2, \quad (8)$$

where, $y = (T - 298.15 \text{ K})$, $a = 3.216 \times 10^{-5} \text{ K}^{-1}$, and $b = 5.4 \times 10^{-8} \text{ K}^{-2}$.

$(\partial p/\partial T)_{\text{sat}}$ can be calculated based on the vapor pressures measured in this research. Therefore, with a minimum of two different filling levels of the cell, $(\partial^2 p/\partial T^2)_{\text{sat}}$ and $(\partial^2 \mu/\partial T^2)_{\text{sat}}$ can be determined. In this research three fillings were used. To obtain the saturation heat capacity $C_{\text{sat},m}$ at vapor pressures greater than 0.1 MPa, the limit where the cell is full of liquid is required, $(n/V_x) = \{1/V_m(\text{l})\}$, where $V_m(\text{l})$ is the molar volume of the liquid:

$$\lim_{(n/V_x) \rightarrow \{1/V_m(\text{l})\}} (nC_{V,m}^{\text{II}}/T) = V_m(\text{l})(\partial^2 p/\partial T^2)_{\text{sat}} - n(\partial^2 \mu/\partial T^2)_{\text{sat}}. \quad (9)$$

$C_{\text{sat},m}$ is obtained using the expression:

$$\lim_{(n/V_x) \rightarrow \{1/V_m(\text{l})\}} (nC_{V,m}^{\text{II}}) = n[C_{\text{sat},m} - \{T(\partial p/\partial T)_{\text{sat}}(\partial V_m(\text{l})/\partial T)\}]. \quad (10)$$

Thus, reliable liquid density values are also required to determine $C_{\text{sat},m}$.

TABLE 11. Experimental $C_{x,m}^{\text{II}}/R$ values for mass m of dibenzofuran ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

m/g $V_x(298.15 \text{ K})/\text{cm}^3$ T/K	0.011682 0.0539 $C_{x,m}^{\text{II}}/R$	0.015147 0.0557 $C_{x,m}^{\text{II}}/R$	0.024747 0.0539 $C_{x,m}^{\text{II}}/R$
375.0	32.8	32.8	32.7
395.0	33.9	33.8	33.6
415.0	35.2	35.1	34.8
435.0	36.0	36.2	36.1
455.0	37.1	37.5	37.1
475.0	38.4	38.5	38.2
495.0	39.7	39.6	39.0
515.0	41.2	40.5	40.1
535.0	42.3	42.0	41.4
555.0	43.5	42.9	42.5
575.0	45.0	44.2	43.6
595.0	46.1	45.4	44.2
615.0	47.8	46.5	45.5
635.0	49.1	47.4	46.3
655.0	51.1	48.9	47.5
675.0	52.3	50.2	48.0
695.0	53.7	51.1	49.2
715.0	55.5	52.8	50.0
735.0	57.2	54.4	51.2
755.0	58.7	55.1	52.3
775.0	61.0	55.7	52.7
795.0	63.5	59.2	56.2

TABLE 12. Densities and temperatures for the conversion from two phases to a single phase for dibenzofuran

$\rho(\text{kg}\cdot\text{m}^{-3})$	T/K
140.7	807.0
203.0	817.7
273.9	822.9
345.6	823.3
438.6	821.4
441.6	821.8
505.4	815.9

Table 11 lists the experimental two-phase heat capacities $C_{x,m}^{\text{II}}$ for dibenzofuran obtained for three cell fillings. The temperature at which conversion to a single phase occurred was measured for four additional cell fillings. Table 12 reports the density, obtained from the mass of sample and the cell volume calculated from equation (8), and the measured temperatures at which conversion to a single phase was observed for all seven fillings. A critical temperature of (824 ± 2) K and a corresponding critical density of (340 ± 10) $\text{kg}\cdot\text{m}^{-3}$ were derived graphically for dibenzofuran from these results, as seen in figure 2.

The critical pressure was not measured directly, but was estimated by means of simultaneous non-linear least-squares fits from the vapor pressures listed in table 4 and the $C_{x,m}^{\text{II}}$ values given in table 11. $C_{\text{sat},m}$ values were derived from results of the fit and equation (10). Experimental $C_{x,m}^{\text{II}}$ were converted to $C_{v,m}^{\text{II}}$ values by means of

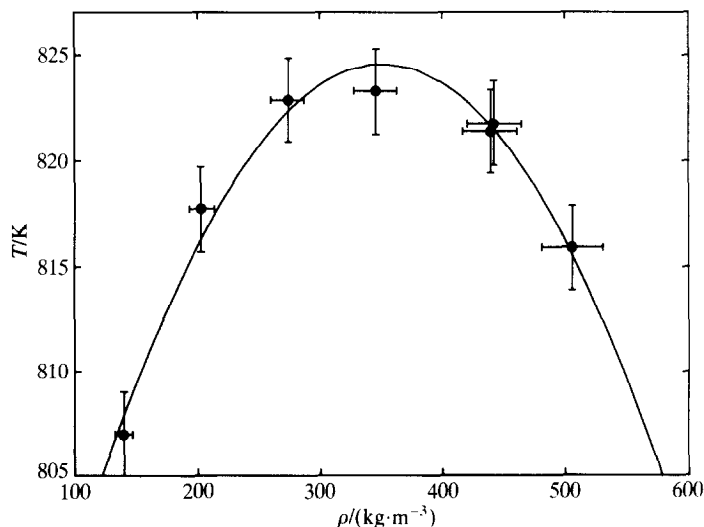


FIGURE 2. (Vapor + liquid) coexistence region for dibenzofuran. The error bars represent 5 per cent uncertainty in the calculated density ρ and ± 2 K uncertainty in the saturation temperature.

TABLE 13. Parameters for equations (11) and (12) for dibenzofuran

A	2.48656	b_0	-0.47907
B	-1.25256	b_1	-0.44632
C	0.82947		
$T_c = 824$ K	$p_c = 3636$ kPa		$\rho_c = 340$ kg · m ⁻³

equation (8) for the cell expansion and the vapor-pressure fit described below for $(dp/dT)_{\text{sat}}$. The values of $C_{V,m}^{\text{II}}$ were used to derive functions for $(d^2p/dT^2)_{\text{sat}}$ and $(d^2\mu/dT^2)_{\text{sat}}$. The Cox equation^(3,2) was used to represent the vapor pressures in the form:

$$\ln(p/p_c) = (1 - 1/T_r)\exp(A + BT_r + CT_r^2), \quad (11)$$

with $T_r = T/T_c$, where T_c and p_c are the critical temperature and critical pressure. The critical pressure was included as a variable in the non-linear least-squares analysis. The functional form chosen for variation of the second derivative of the chemical potential with temperature was:

$$(\partial^2\mu/\partial T^2)_{\text{sat}}/(\text{J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}) = \sum_{i=0}^n b_i(1 - T/T_c)^i. \quad (12)$$

(The precision of the heat-capacity measurements did not justify determination of b_i for $i > 1$.) In these fits the sum of the weighted squares in the following function was minimized:

$$\Delta = C_{V,m}^{\text{II}}/R - \{V_m(l)T/nR\}(\partial^2p/\partial T^2)_{\text{sat}} + (T/R)(\partial^2\mu/\partial T^2)_{\text{sat}}. \quad (13)$$

For the vapor-pressure fits, the functional forms of the weighting factors used have been reported.^(12, 21) Within the heat-capacity results the weighting factors were proportional to the square of the mass of sample used in the measurements.

Table 13 lists the coefficients determined in the non-linear least-squares fit. A weighting factor of 20 was used to increase the relative weights of the vapor-pressure measurements in the fit. The weighting factor reflects the higher precision of the vapor-pressure values relative to the experimental heat capacities.

Values of $C_{\text{sat},m}$ were derived from $C_{V,m}^{\text{II}}(\rho = \rho_{\text{sat}})$ with the densities obtained from the corresponding-states equation in the form:^(3,5)

$$(\rho/\rho_c) = 1.0 + 0.85(1.0 - T/T_c) + (1.6916 + 0.9846\omega)(1.0 - T/T_c)^{1/3}, \quad (14)$$

with $\rho_c = 340$ kg · m⁻³, $T_c = 824$ K, and the acentric factor $\omega = 0.397$. The acentric factor is defined as $\{-\lg(p/p_c) - 1.0\}$, where p is the vapor pressure at $T_r = 0.7$ and p_c is the critical pressure. For dibenzofuran, values of 145.81 kPa and 3636 kPa were used for p and p_c , respectively. The Cox equation coefficients given in table 5 were used to calculate p . The results for $C_{V,m}^{\text{II}}(\rho = \rho_{\text{sat}})/R$ and $C_{\text{sat},m}/R$ are reported in table 14. The estimated uncertainty in these values is 1 per cent.

Condensed-phase entropies and enthalpies relative to those of the crystals at $T \rightarrow 0$ for the solid and liquid phases under vapor-saturation pressure are listed in

TABLE 14. Values of $C_{V,m}^{\text{II}}(\rho = \rho_{\text{sat}})/R$ and $C_{\text{sat},m}/R$ for dibenzofuran

T/K	$C_{V,m}^{\text{II}}(\rho = \rho_{\text{sat}})/R$	$C_{\text{sat},m}/R$	T/K	$C_{V,m}^{\text{II}}(\rho = \rho_{\text{sat}})/R$	$C_{\text{sat},m}/R$
400.0	34.1	34.1	580.0	43.2	43.2
420.0	35.3	35.3	600.0	44.0	44.1
440.0	36.4	36.4	620.0	44.9	45.0
460.0	37.5	37.5	640.0	45.7	45.8
480.0	38.5	38.5	660.0	46.5	46.7
500.0	39.5	39.5	680.0	47.3	47.6
520.0	40.5	40.5	700.0	48.1	48.5
540.0	41.4	41.4	720.0	49.0	49.6
560.0	42.3	42.3			

table 10. These were derived by integration of the smoothed heat capacities corrected for pre-melting, together with the entropies and enthalpies of fusion. The 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. Due to limitations in the spline-function procedure, some acceptable values from tables 9 and 14 were not included in the fit, while 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. Pre-melting corrections were made by means of standard methods for a solid-insoluble impurity and the mole-fraction impurity value shown in table 1.

Enthalpies and entropies at selected temperatures for the ideal gas were calculated with values in tables 10 and 6, and are listed in columns 2 and 4 of table 15. Values above 720 K are not reported because gas-imperfection corrections are large and cannot be determined with sufficient accuracy. The derived ideal-gas enthalpies and entropies were combined with the enthalpy of combustion for the crystals given in table 3 to calculate the enthalpies, entropies, and Gibbs energies of formation listed in columns 6, 7, and 8, respectively, of table 15. Enthalpies and entropies for oxygen, equilibrium hydrogen, and graphite were determined from the JANAF tables.⁽³⁷⁾ All uncertainties in table 15 represent one standard deviation, and do not include uncertainties in the properties of the elements.

The "third-law" method was employed to calculate sublimation vapor pressures for dibenzofuran from 298.15 K to the triple-point temperature. The "third-law" values were calculated from the tabulated thermodynamic functions of the ideal gas (table 15) and the liquid (table 10). The method applied here was the same as that used previously for biphenyl.⁽³⁸⁾ The sublimation vapor pressures were represented by the equation:

$$\ln(p/p_0) = 32.77 - 1.010 \times 10^4(T/\text{K})^{-1}, \quad (15)$$

in the temperature region 298.15 K to 355.3 K with $p_0 = 1$ Pa. Note that this equation is not valid for temperatures below the solid-phase transition near 292 K.

TABLE 15. Thermodynamic properties of dibenzofuran in the ideal-gas state ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and $p^\circ = 101.325 \text{ kPa}$)

T K	$\frac{\Delta_0^T H_m^\circ}{RT}$	$\frac{\Delta_{\text{imp}} H_m^\circ}{RT}^a$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_{\text{imp}} S_m^\circ}{R}^b$	$\frac{\Delta_f H_m^\circ}{RT}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{RT}$
298.15 ^{c,d}	45.74 ± 0.06	0.00	45.03 ± 0.07	0.00	22.30 ± 0.14	-38.40 ± 0.07	60.70 ± 0.12
300.00 ^{c,d}	45.59 ± 0.06	0.00	45.16 ± 0.07	0.00	22.11 ± 0.13	-38.44 ± 0.07	60.56 ± 0.12
320.00 ^{c,d}	44.08 ± 0.04	0.00	46.54 ± 0.05	0.00	20.29 ± 0.12	-38.90 ± 0.05	59.19 ± 0.12
340.00 ^{c,d}	42.82 ± 0.03	0.00	47.91 ± 0.04	0.00	18.69 ± 0.11	-39.32 ± 0.04	58.01 ± 0.11
360.00	41.76 ± 0.02	0.00	49.28 ± 0.04	0.00	17.27 ± 0.10	-39.71 ± 0.04	56.98 ± 0.11
380.00	40.89 ± 0.02	0.00	50.63 ± 0.04	0.00	16.03 ± 0.10	-40.06 ± 0.04	56.08 ± 0.10
400.00	40.16 ± 0.02	0.01	51.98 ± 0.04	0.01	14.92 ± 0.09	-40.37 ± 0.04	55.29 ± 0.10
420.00	39.56 ± 0.02	0.01	53.33 ± 0.04	0.01	13.93 ± 0.09	-40.65 ± 0.04	54.59 ± 0.10
440.00	39.06 ± 0.02	0.02	54.66 ± 0.04	0.01	13.05 ± 0.08	-40.91 ± 0.04	53.96 ± 0.09
460.00	38.67 ± 0.03	0.03	55.99 ± 0.04	0.02	12.26 ± 0.08	-41.14 ± 0.04	53.40 ± 0.09
480.00	38.35 ± 0.03	0.04	57.31 ± 0.05	0.03	11.54 ± 0.08	-41.35 ± 0.05	52.89 ± 0.09
500.00	38.09 ± 0.03	0.06	58.62 ± 0.05	0.05	10.89 ± 0.08	-41.54 ± 0.05	52.43 ± 0.09
520.00	37.90 ± 0.04	0.09	59.92 ± 0.06	0.07	10.31 ± 0.08	-41.70 ± 0.06	52.01 ± 0.09
540.00	37.76 ± 0.05	0.12	61.21 ± 0.06	0.09	9.78 ± 0.08	-41.85 ± 0.06	51.63 ± 0.09
560.00	37.67 ± 0.06	0.16	62.48 ± 0.08	0.11	9.30 ± 0.09	-41.99 ± 0.08	51.29 ± 0.09
580.00	37.61 ± 0.08	0.20	63.75 ± 0.09	0.14	8.86 ± 0.10	-42.11 ± 0.09	50.97 ± 0.10
600.00	37.58 ± 0.10	0.25	65.00 ± 0.11	0.18	8.46 ± 0.11	-42.21 ± 0.11	50.67 ± 0.12
620.00 ^c	37.59 ± 0.12	0.31	66.25 ± 0.13	0.22	8.09 ± 0.13	-42.30 ± 0.13	50.40 ± 0.13
640.00 ^c	37.63 ± 0.14	0.37	67.48 ± 0.15	0.26	7.77 ± 0.15	-42.37 ± 0.15	50.14 ± 0.15
660.00 ^c	37.70 ± 0.16	0.44	68.71 ± 0.17	0.32	7.47 ± 0.17	-42.43 ± 0.17	49.90 ± 0.16
680.00 ^c	37.79 ± 0.18	0.52	69.94 ± 0.19	0.37	7.21 ± 0.19	-42.46 ± 0.19	49.67 ± 0.18
700.00 ^c	37.90 ± 0.20	0.62	71.15 ± 0.21	0.44	6.98 ± 0.21	-42.48 ± 0.21	49.46 ± 0.19
720.00 ^c	38.03 ± 0.22	0.72	72.36 ± 0.23	0.52	6.77 ± 0.23	-42.49 ± 0.23	49.26 ± 0.21

^a Gas-imperfection correction to the ideal-gas enthalpy. The corrections were assumed accurate to 10 per cent of their value.

^b Gas-imperfection correction to the ideal-gas entropy. The corrections were assumed accurate to 10 per cent of their value.

^c Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted Cox coefficients.

^d Values at this temperature were calculated with graphically extrapolated values of the liquid-phase heat capacities.

4. Discussion

The standard energy of combustion $\Delta_c U_m^\circ/M$ of dibenzofuran had been measured twice previously.^(39,40) Cass *et al.*⁽³⁹⁾ measured $\Delta_c U_m^\circ/M$ to be $-(34844 \pm 25) \text{ J} \cdot \text{g}^{-1}$ with a conventional bomb calorimeter on a sample whose purity was not determined. Though this value is only 0.5 per cent different from that obtained here, it translates to a $\Delta_f H_m^\circ$ value of $-(5.3 \pm 4.2) \text{ kJ} \cdot \text{mol}^{-1}$, which is 550 per cent different.

Sabbah and Antipine⁽⁴⁰⁾ determined $\Delta_c U_m^\circ/M$ to be $-(34678 \pm 28) \text{ J} \cdot \text{g}^{-1}$ with a semi-micro bomb calorimeter (5 mg to 6 mg samples). This value is in excellent agreement with that obtained in this research: $-(34677.5 \pm 0.8) \text{ J} \cdot \text{g}^{-1}$. However, Sabbah and Antipine⁽⁴⁰⁾ reported $(29.2 \pm 4.8) \text{ kJ} \cdot \text{mol}^{-1}$ for the standard enthalpy of

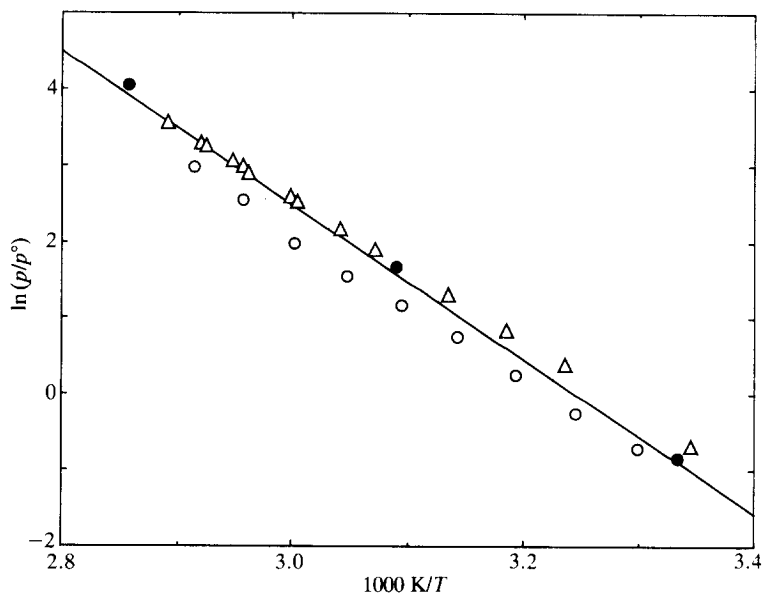


FIGURE 3. Sublimation pressures for dibenzofuran. —, Calculated from equation (15). ○, Hansen and Eckert;⁽⁴³⁾ △, Sato *et al.*;⁽⁴²⁾ ●, Rordorf.⁽⁴¹⁾

formation of crystalline dibenzofuran, but calculations using their results give a value of $-(29.2 \pm 4.8) \text{ kJ} \cdot \text{mol}^{-1}$. The error in sign was not typographical and significantly affects their subsequent discussion of the "conjugation energies" in dibenzofuran, carbazole, fluorene, and dibenzothiophene.

Sabbah and Antipine⁽⁴⁰⁾ reported measurements of the enthalpy of sublimation of dibenzofuran at 298.15 K, and listed a value $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = (76.46 \pm 0.16) \text{ kJ} \cdot \text{mol}^{-1}$. The corresponding value calculated in this research from tables 10 and 15 is $\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = (84.42 \pm 0.70) \text{ kJ} \cdot \text{mol}^{-1}$.

Vapor-pressure measurements on dibenzofuran have been reported for the solid⁽⁴¹⁻⁴³⁾ and liquid^(44, 45) phases. Figure 3 shows the sublimation vapor pressures reported in the literature. The line was determined from equation (15) of this research. Rordorf⁽⁴¹⁾ reported his results in equation form only. The three values shown in figure 3 span the range of his measurements. The results of Rordorf⁽⁴¹⁾ and Sato *et al.*⁽⁴²⁾ are in good agreement with the results of this research. The values measured by Hansen and Eckert⁽⁴³⁾ appear to be low.

Vapor pressures above the triple-point temperature have been reported twice by Kobayashi and co-workers.^(44, 45) Large deviations between their values and results reported here are shown in figure 4. We have observed similar large deviations between our results and those of Kobayashi and co-workers for acridine⁽⁴⁶⁾ and biphenyl.⁽³⁸⁾

Thermodynamic properties for dibenzofuran in the ideal-gas state were published in an American Petroleum Institute (API) monograph.⁽⁴⁷⁾ These values were calculated using the partial fundamental vibrational assignment of Bree *et al.*⁽⁴⁸⁾ with

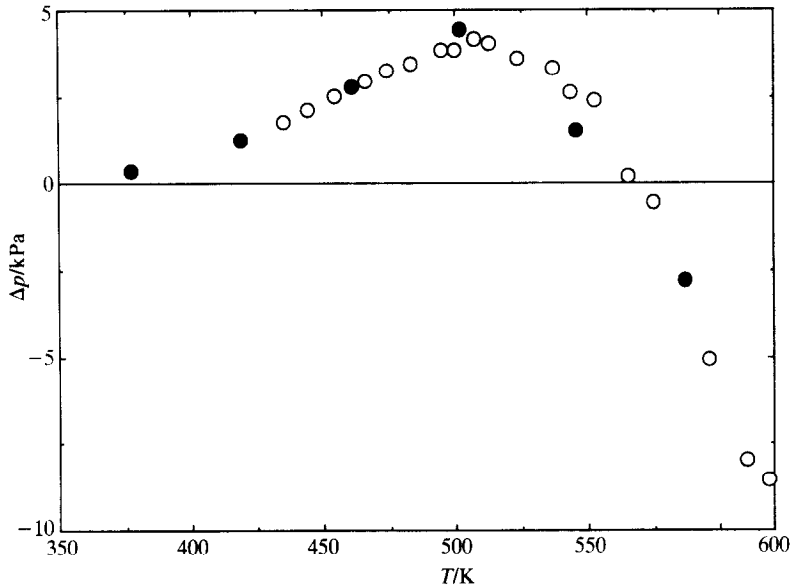


FIGURE 4. Deviation plot for dibenzofuran vapor pressures. $\Delta p = p(\text{lit}) - p(\text{Cox})$, where $p(\text{Cox})$ was calculated from the Cox equation coefficients given in table 5. ●, Nasir, Sivaraman, and Kobayashi;⁽⁴⁴⁾ ○, Sivaraman and Kobayashi.⁽⁴⁵⁾

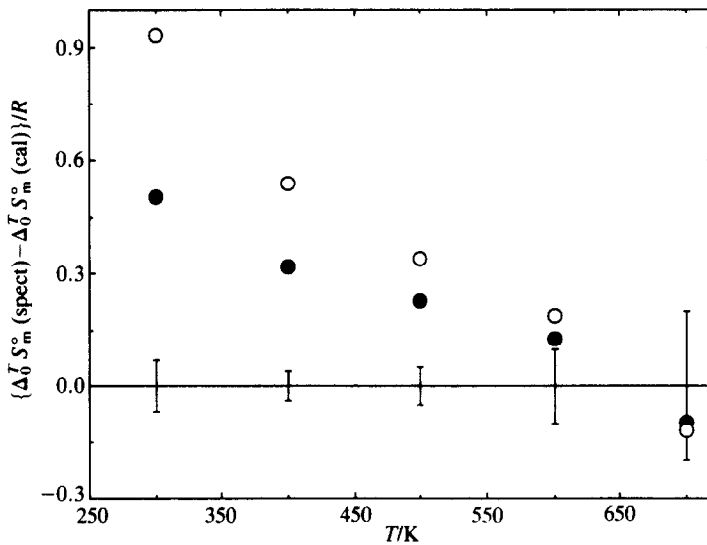


FIGURE 5. Deviation of ideal-gas entropy values calculated from vibrational frequencies and statistical mechanics (spect) from the calorimetrically (cal) derived values of this research. The error bars represent the uncertainty limits of the calorimetric results (one standard deviation). ○, Values based on the "corrected" API values⁽⁴⁷⁾ (see text); ●, values based on the combined results of Danchinov *et al.*⁽⁴⁹⁾ and Gastilovich *et al.*⁽⁵⁰⁾

TABLE 16. Comparison of experimental and estimated critical properties for dibenzofuran

	This research	Lydersen ⁽⁵¹⁾	Somayajulu ⁽⁵²⁾
T_c/K	824	807	826 ^a
$\rho_c/(\text{kg} \cdot \text{m}^{-3})$	340	345	337
p_c/MPa	3.64 ^b	3.20	3.65

^aThis value was calculated with equation (12) of reference 52. An alternative formulation, equation (11) of reference 52, yielded $T_c = 827.5$ K.

^bThis value was derived from the fitting procedure described in the text. T_c and ρ_c were obtained graphically from figure 2.

wavenumber estimates for the unassigned modes. The wavenumber estimates were not listed in the API monograph. Very large differences (approximately 9.2R in the ideal-gas entropies) are seen between the API values and those of this research given in table 15. Most of the discrepancy can be accounted for, if the moment-of-inertia value used in the calculation of the API values was 1×10^8 too small. The "corrected" API values used to calculate the differences represented by the open circles in figure 5 were determined based on this assumption.

Ideal-gas heat capacities and entropies for dibenzofuran also can be calculated using the results of Danchinov *et al.*⁽⁴⁹⁾ and Gastilovich *et al.*,⁽⁵⁰⁾ who calculated the fundamental vibrational frequencies for the in-plane and out-of-plane modes, respectively. Their analyses also were based on the partial assignment of Bree *et al.*⁽⁴⁸⁾ The difference between ideal-gas entropies calculated from their frequencies and those of this research are shown as solid circles in figure 5. The differences show the same trend as that observed for the "corrected" API values. The relatively large deviations at low temperature indicate that one or more fundamental vibrational modes were assigned frequencies that were too low.

No previous experimental determinations of the condensed-phase heat capacities for dibenzofuran could be found in the literature; however, these quantities were estimated as part of the API report.⁽⁴⁷⁾ The estimated liquid-phase heat capacities range from 3 per cent low near 300 K to 3 per cent high near 600 K.

The experimental critical-property values reported here are the first for dibenzofuran. Table 16 shows a comparison of the experimental results with values estimated by the widely used method of Lydersen.⁽⁵¹⁾ The Lydersen parameters were recently revised and updated by Somayajulu.⁽⁵²⁾ Estimates based on the Somayajulu parameters also are included in table 16. Agreement between the experimental values and those based on the revised parameters is excellent.

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REFERENCES

1. Tsonopoulos, C.; Heidman, J. L.; Hwang, S.-C. *Thermodynamic and Transport Properties of Coal Liquids*. Wiley: New York. **1986**.
2. Weisser, O.; Landa, S. *Sulfide Catalysts, Their Properties and Applications*. Pergamon: New York. **1973**.
3. Krishnamurthy, S.; Panvelker, S.; Shah, Y. T. *AIChE J.* **1981**, 27, 994.
4. La Vopa, V.; Satterfield, C. N. *Energy and Fuels* **1987**, 1, 323.
5. *Pure Appl. Chem.* **1983**, 55, 1101.
6. Cohen, E. R.; Taylor, B. N. *J. Phys. Chem. Ref. Data* **1988**, 17, 1795.
7. *Metrologia* **1969**, 5, 35.
8. McCrackin, F. L.; Chang, S. *S. Rev. Sci. Instrum.* **1975**, 46, 550.
9. Good, W. D. *J. Chem. Eng. Data* **1969**, 14, 231.
10. Good, W. D. *J. Chem. Eng. Data* **1972**, 17, 28.
11. Good, W. D.; Smith, N. K. *J. Chem. Eng. Data* **1969**, 14, 102.
12. Steele, W. V.; Archer, D. G.; Chirico, R. D.; Collier, W. B.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Gammon, B. E. *J. Chem. Thermodynamics* **1988**, 20, 1233.
13. Good, W. D.; Scott, D. W.; Waddington, G. *J. Phys. Chem.* **1956**, 60, 1080.
14. Good, W. D.; Douslin, D. R.; Scott, D. W.; George, A.; Lacina, J. L.; McCullough, J. P.; Waddington, G. *J. Phys. Chem.* **1959**, 63, 1133.
15. Smith, N. K.; Stewart, R. C. Jr.; Osborn, A. G.; Scott, D. W. *J. Chem. Thermodynamics* **1980**, 12, 919.
16. Chirico, R. D.; Hossenlopp, I. A.; Nguyen, A.; Strube, M. M.; Steele, W. V. *Thermodynamic Studies Related to the Hydrogenation of Phenanthrene*. NIPER-247. Published by DOE Fossil Energy, Bartlesville Project Office. Available from NTIS Report No. DE-8687001252. April, **1987**.
17. Goldberg, R. N.; Nuttall, R. L.; Prosen, E. J.; Brunetti, A. P. *NBS Report 10437*. U.S. Department of Commerce, National Bureau of Standards. June **1971**.
18. Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*. Rossini, F. D.: editor. Interscience: New York. **1956**, chap. 5, pp. 75-128.
19. Świątosławski, W. *Ebulliometric Measurements*. Reinhold: New York. **1945**.
20. Osborn, A. G.; Douslin, D. R. *J. Chem. Eng. Data* **1966**, 11, 502.
21. Chirico, R. D.; Nguyen, A.; Steele, W. V.; Strube, M. M.; Tsonopoulos, C. *J. Chem. Eng. Data* **1989**, 34, 149.
22. Antoine, C. *C.R. Acad. Sci.* **1888**, 107, 681.
23. Douslin, D. R.; McCullough, J. P. *U.S. Bureau of Mines. Report of Investigation 6149*. **1963**, pp. 11.
24. Douslin, D. R.; Osborn, A. G. *J. Sci. Instrum.* **1965**, 42, 369.
25. Huffman, H. M. *Chem. Rev.* **1947**, 40, 1.
26. Ruehwein, R. A.; Huffman, H. M. *J. Am. Chem. Soc.* **1943**, 65, 1920.
27. Scott, D. W.; Douslin, D. R.; Gross, M. E.; Oliver, G. D.; Huffman, H. M. *J. Am. Chem. Soc.* **1952**, 74, 883.
28. Knipmeyer, S. E.; Archer, D. G.; Chirico, R. D.; Gammon, B. E.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Steele, W. V.; Strube, M. M. *Fluid Phase Equilibria* **1989**, 52, 185.
29. Rossini, F. D. *Experimental Thermochemistry*. Rossini, F. D.: editor. Interscience: New York. **1956**, chap. 14, pp. 297-320.
30. *CODATA Key Values for Thermodynamics*. Cox, J. D.; Wagman, D. D.; Medvedev, V. A.: editors. Hemisphere: New York. **1989**.
31. Scott, D. W.; Osborn, A. G. *J. Phys. Chem.* **1979**, 83, 2714.
32. Cox, E. R. *Ind. Eng. Chem.* **1936**, 28, 613.
33. Gammon, B. E.; Callanan, J. E.; Hossenlopp, I. A.; Osborn, A. G.; Good, W. D. *Proceedings of the 8th Symposium on Thermophysical Properties*. National Bureau of Standards, Gaithersburg, MD. June 15-19, **1981**.
34. Pitzer, K. S.; Curl, R. F. Jr. *J. Am. Chem. Soc.* **1957**, 79, 2369.
35. Riedel, L. *Chem.-Ing.-Tech.* **1954**, 26, 259.
36. McCullough, J. P.; Waddington, G. *Anal. Chim. Acta* **1957**, 17, 80.

37. Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*. 3rd edition. Supplement No. 1 to *J. Phys. Chem. Ref. Data* **1985**, 14.
38. Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. *J. Chem. Thermodynamics* **1989**, 21, 1307.
39. Cass, R. C.; Fletcher, S. E.; Mortimer, C. T.; Springall, H. D.; White, T. R. *J. Chem. Soc.* **1958**, 1406.
40. Sabbah, R.; Antipine, I. *Bull. Soc. Chim. Fr.* **1987**, 392.
41. Rordorf, B. F. *Chemosphere* **1986**, 15, 1325.
42. Sato, N.; Inomata, H.; Arai, K.; Saito, S. *J. Chem. Eng. Jpn.* **1986**, 19, 145.
43. Hansen, P. C.; Eckert, C. A. *J. Chem. Eng. Data* **1986**, 31, 1.
44. Nasir, P.; Sivaraman, A.; Kobayashi, R. *J. Chem. Thermodynamics* **1984**, 16, 199.
45. Sivaraman, A.; Kobayashi, R. *J. Chem. Eng. Data* **1982**, 27, 264.
46. Steele, W. V.; Chirico, R. D.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Gammon, B. E. *J. Chem. Thermodynamics* **1989**, 21, 81.
47. Wilhoit, R. C.; Adler, S. *Benzofuran, Dibenzofuran, and Benzonaphthofurans*. API Monograph Series Publication 721. American Petroleum Institute: Washington D.C. **1983**.
48. Bree, A.; Vilkos, V. V. B.; Zwarich, R. *J. Mol. Spect.* **1973**, 48, 124.
49. Danchinov, K. M.; Rodionov, A. N.; Shigoren, D. N. *Russ. J. Phys. Chem.* **1981**, 55, 1442.
50. Gastilovich, E. A.; Danchinov, K. M.; Klimentko, V. G.; Mishenina, K. A.; Rodionov, A. N. *Russ. J. Phys. Chem.* **1984**, 58, 1681.
51. Lydersen, A. L. *Estimation of Critical Properties of Organic Compounds by the Method of Group Contributions*. College of Engineering; Engineering Experiment Station Report No. 3. University of Wisconsin: Madison, WI. **1955**.
52. Somayajulu, G. R. *J. Chem. Eng. Data* **1989**, 34, 106.