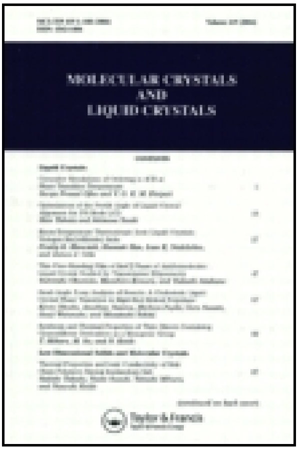

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Calculation of Thermodynamic Functions of Solid Napthalene and Pyrene

Yu. P. Ivanov [a], M. Yu. Antipin [a], A. J. Perstsin [a] & Yu. T. Struchkov [a]

[a] Institute of Organo-Element Compounds, Academy of Sciences of USSR, Moscow, 117312, Vavilov Str. 28, U.S.S.R.

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Calculation of Thermodynamic Functions of Solid Naphthalene and Pyrene

YU. P. IVANOV, M. YU. ANTIPIN, A. J. PERTSIN† and YU. T. STRUCHKOV

Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Moscow 117312, Vavilov Str. 28, U.S.S.R.

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By using the cell model as a statistical mechanical basis and the atom-atom potential scheme as an approximation to intermolecular potential, the thermodynamic properties of the pyrene and naphthalene crystals are calculated at some temperatures between 100 and 300 K. The partition functions of the crystals are computed by the importance sampling (Monte Carlo) method. The literature and own experimental data on thermal expansion are used. The calculated thermodynamic functions show good agreement with experiment. For some temperatures the calculation results are compared with those obtained in the quasiharmonic approximation.

INTRODUCTION

In 1975, one of the authors[1] has shown that the thermodynamic properties of a molecular organic crystal can be computed with a rather high accuracy by using a method combining the cell model,[2] as a statistical mechanical basis, with the atom-atom potential approximation[3] as an approximation to intermolecular potential. The method (hereafter referred to by the abbreviation CMAP) has been successfully used to calculate the thermodynamic functions of the benzene,[1] anthracene and naphthalene[4] crystals, as well as the plastic-phase transition in adamantane[5] and the high-pressure orthorhombic-monoclinic phase transition in benzene.[6,7] In all the cases the calculated thermodynamic properties showed good agreement with experiment only when the authors used experimental thermal expansion data.[1,4,5] When the equilibrium unit cell parameters were determined by minimizing the free

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† To whom all correspondence should be addressed.

energy of the system the calculations resulted in somewhat overestimated densities and gave thermodynamic functions really observed at higher pressures.[6,7]

The present paper is intended to provide further verification of CMAP method when used together with experimental thermal expansion parameters. We present more detailed data on the naphthalene crystal and compare the data with those obtained via the quasiharmonic approximation.[8] Besides, we report the unit cell parameters of the pyrene crystal at six temperatures between 133 and 293 K and use these parameters to calculate the thermodynamic properties of the crystal.

METHOD

The first assumption of the CMAP method is that the total free energy of a molecular crystal can be separated into its intra- and intermolecular (or crystalline) constituents

$$F_{\mathrm{tot}} = F_{\mathrm{mol}} + F_{\mathrm{cryst}} \tag{1}$$

This is usually the case for rigid molecules such as naphthalene and pyrene. The CMAP method proper is intended to calculate F_{cryst} only. The corresponding experimental quantity is readily derived from the calorimetric free energy by subtracting its intramolecular contribution calculated from internal mode vibration frequencies.

The CMAP method treats an organic molecular crystal as a classical system of N rigid molecules, each having three translational and three rotational degrees of freedom. The configurational integral of the system is written in the form

$$Q_N = \left[\exp\left\{-\frac{E(0)}{2kT}\right\} \int_\Delta \exp\left\{-\frac{E(q)-E(0)}{kT}\right\} dq\right]^N \tag{2}$$

where $E(q)$ is the potential energy of interaction of the molecule at q with its neighbours at their equilibrium positions; the six-dimensional, vector q describes displacements of the initial molecule from its equilibrium position ($q = 0$); Δ is the volume of the configurational space per molecule.

As seen from Eq.(2), Q_N is proportional to the N-th power of the configurational integral of a molecule as it wanders in the potential field exerted by its neighbours, the latters assumed fixed at their equilibrium sites. The formulas for all thermodynamic functions can be readily deduced from Eq.(2) using the expression

$$F = f(T) - kT \ln Q_N \tag{3}$$

and the known differential equations for the entropy, internal energy, heat capacity and other functions. In all the cases the problem reduces to evaluation of sixfold integrals of the form

$$\int_{\Delta} g(q) \exp\left\{-\frac{E(q)-E(0)}{kT}\right\} dq \qquad (4)$$

where $g(q)$ is some function of the molecular coordinates (for instance, $g(q) = E(q)$).

A sufficiently accurate estimate of the integrals can be obtained using the importance sampling (Monte Carlo) method (see Ref. 1,7 for details). Our experience shows that by sampling as low as $\sim 10^3$ random points in Δ it is possible to estimate the free and internal energies with an accuracy of ~ 0.02 kcal mole^{-1} and entropy and heat capacity with accuracies of 0.2 and 0.3–0.4 cal $\cdot$ $\text{mole}^{-1} \cdot \text{K}^{-1}$ respectively. For a computer such as CDC–6600 it takes 5–7 min, a time much shorter than that needed to compute the thermodynamic functions via solution of the lattice dynamics problem.

The energy $E(q)$ in Eqs.(2,4) is calculated by the atom-atom potential method[3] as the sum of atom-atom interactions of the form

$$\varphi(z) = -Az^{-6} + B\exp\{-\alpha z\} \qquad (5)$$

The empirical parameters A, B and α used in this paper are those suggested for H . . . H, H . . . C and C . . . C non-bonded interactions by Mirskaya *et al.*[9]

EXPERIMENTAL

A commercial grade pyrene labelled 99 per cent pure was recrystallized two times from a toluene-xylene-benzene mixture and further purified by five passes of zone-refining. X-ray data were obtained on a Syntex P–2_1 four circle automatic diffractometer using CuK_α radiation and a graphite monochromator. For low-temperature work, a Syntex LT–1 attachment was employed to maintain the desired temperature to ±2°.

Pyrene crystals grown from a toluene-xylene-benzene mixture are monoclinic, space group $P2_1/a$, $Z = 4$. Unit cell parameters of the crystal at six temperatures are listed in Table I. The room temperature data show good agreement with those reported by Camerman and Trotter.[10]

RESULTS

1 Naphthalene

Table 2 summarizes observed and calculated thermodynamic properties of the naphthalene crystal at four temperatures. Under the observed thermo-

TABLE I
Unit cell parameters of the pyrene crystal at six temperatures (given in parentheses are standard deviations).

T(K)	a(Å)	b(Å)	c(Å)	$\beta°$	V(A^3)
293	13.644(2)	9.255(1)	8.469(1)	100.27(1)	1052.4(3)
244.5	13.600(2)	9.214(1)	8.440(1)	100.30(1)	1040.6(3)
213	13.574(1)	9.195(1)	8.442(1)	100.29(1)	1034.3(2)
191	13.558(2)	9.182(1)	8.409(1)	100.27(1)	1030.0(2)
155	13.530(2)	9.168(2)	8.390(2)	100.22(1)	1024.1(3)
133	13.520(1)	9.161(1)	8.382(2)	100.20(2)	1021.8(3)

TABLE II
Comparison between experimental and calculated properties of naphthalene. (* - calculated using the quasiharmonic approximation)

	$-F$ kcal/mole	$F_{78} - F_T$ kcal/mole		S cal/mol·K		C_v cal/mole·K	
$T(K)$	calc	calc	obs	calc	obs	calc	obs
78	12.16	0.00	0.00	8.7	9.1	10.4	9.5
120	12.70	0.54	0.58	13.6 18.1*	14.3	9.8 11.4*	10.1
173	13.55	1.39	1.47	18.5	18.6	10.7	10.5
296	16.25	4.09	4.22	25.7 30.1* 27.5*	25.7	9.8 11.9* 11.8*	10.1

dynamic quantities we imply here their intermolecular contributions derived from calorimetric data[11] and internal mode vibration frequencies.[12] Since calorimetric measurements do not provide absolute values for F, as do the CMAP calculations, this thermodynamic function is given in Table II with reference to its value at 78 K, the lowest temperature we dealt with. The intermolecular contribution to the heat capacity C_v, presented in Table II, was taken from Ref. 3.

Marked by asterisks in Table II are the quantities obtained in the quasiharmonic approximation via calculation of the density of phonon states (these calculations were carried out by E. F. Sheka using the Pawley's lattice dynamics program[13]). Also listed (the lowest row) are the values for S and C_v obtained by Filippini *et al.*[14] following the same approach.

As seen from Table II, the thermodynamic properties of the naphthalene crystal, calculated by the CMAP method, are in good agreement with experiment, especially at higher temperatures. True, the calculation fails to reproduce the correct behavior of C_v between 78 and 120 K. This is not, however, very surprising because C_v is estimated with a rather large statistical error (~0.4 cal·mole^{-1}·K^{-1}), while the observed C_v increases, in this temperature range, only by 1 cal·mole^{-1} · K^{-1}.

The quasiharmonic approximation yields on the whole much worse results. The advantage of the cell model over the quasiharmonic approximation has been explained by Barker.[2] At high temperatures (usually, above $\theta_D/2$, 50–100 K for most organic crystals) the main portion of the intermolecular contribution to the free energy is accounted for by high vibration frequencies which are close to the frequency corresponding to independent motion of molecules. The cell model completely ignores the correlations in molecular motion but, in return, takes into account anharmonicity of the lattice energy, which becomes important just at high temperatures.

2 Pyrene

Table III presents the observed thermodynamic properties of the pyrene crystal in the temperature range 130 to 300 K. The total values for F and S were derived from calcorimetric data[15] and their internal mode contributions from fundamental frequencies reported by Bree *et al.*[16] No reliable estimate could be obtained for C_v because of the lack of compressibility data needed to calculate C_v from C_p. (Though the pressure-volume curve for the solid pyrene

TABLE III

Free energy and entropy of the pyrene crystal and their internal (mol) and external (cryst) mode constituents in the temperature range between 130 and 300 K.

	$F_O - F_T$, kcal/mole			S, cal/mole K		
T(K)	tot	mol	cryst	tot	mol	cryst
130	1.42	0.20	1.22	23.2	5.2	18.0
140	1.66	0.26	1.40	24.9	6.1	18.9
150	1.92	0.32	1.60	26.6	7.0	19.6
160	2.19	0.40	1.80	28.3	7.9	20.3
170	2.49	0.48	2.00	29.9	8.9	21.0
180	2.79	0.58	2.22	31.5	9.9	21.6
190	3.12	0.68	2.44	33.2	11.0	22.2
200	3.45	0.80	2.66	34.8	12.1	22.7
210	3.81	0.92	2.89	36.5	13.2	23.3
220	4.19	1.06	3.13	38.2	14.4	23.8
230	4.58	1.21	3.37	39.9	15.6	24.3
240	4.98	1.37	3.61	41.6	16.8	24.8
250	5.41	1.55	3.86	43.3	18.1	25.2
260	5.85	1.73	4.11	45.0	19.3	25.7
270	6.31	1.93	4.37	46.7	20.6	26.1
280	6.78	2.15	4.64	48.5	21.9	26.6
290	7.28	2.37	4.91	50.2	23.2	27.0
300	7.79	2.61	5.18	52.0	24.6	27.4

TABLE IV
Comparison between experimental and calculated thermodynamic properties of pyrene (* – calculated using the quasiharmonic approximation[14]).

T(K)	$-F$ kcal/mole	$F_{133}-F_T$ kcal/mole		S cal/mole K	
	calc	calc	obs	calc	obs
133	24.33	0.00	0.00	17.8	18.2
155	24.74	0.41	0.43	19.6	20.0
191	25.41	1.08	1.14	22.1	22.2
213	25.93	1.60	1.69	23.8	23.4
244.5	26.74	2.41	2.47	25.8	25.0
293	27.93	3.60	3.74	28.6	27.2
298				29.5*–30.3*	27.3

was available,[17] the low-pressure compressibility could not be had from this curve in view of the phase transition occurring in the crystal at ~2.7 kbar).

Table IV compares observed and calculated values for the free energy and entropy of the crystal (as with naphthalene, we present only intermolecular contributions to these thermodynamic functions). As seen from Table IV, the calculated values are again in good agreement with experiment. Marked by asterisks in Table IV are the entropy values obtained by Filippini *et al.*[14] via lattice dynamical calculations. As with naphthalene, his results show worse agreement with experiment.

Thus, the results of the present work together with those reported in previous papers[1,4–7] suggest that the CMAP method provides a very reliable means for calculating thermodynamic functions of molecular organic crystals at high temperatures. This is of great importance from the view-point of practical applications of low-molecular-weight organic compounds.

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