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Thermodynamics of Crystalline Benzene in the Self-Consistent Field Approximation

The Atom–Atom Potential Method

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The self-consistent field approximation of the classical statistical mechanics has been used to compute the thermodynamic functions of crystalline benzene. The configuration integral of the system was estimated by "importance sampling" (Monte-Carlo) method. The calculations were carried out in the atom–atom approximation for intermolecular interactions. The calculated thermodynamic functions showed good agreement with experimental data.

INTRODUCTION

During the last few years a new semiempirical method for calculating the interaction energy of neutral molecules, the atom–atom potential method,[1] has received much attention and a number of various applications of the method have been reported.

The calculation of the thermodynamics of a molecular crystal by atom–atom potential method may be carried out, in principle, through the normal vibration analysis.[1] There being considerable computational difficulties involved in such a procedure, we attempted to use an alternative approach. Our calculations are based on classical self-consistent field (SCF) theory developed for the most part by Kirkwood,[2] a first approximation of the theory being used. (In this approximation the theory may be easily reduced to the well known Lennard-Jones-Devonshire theory by making some additional assumptions).[3] Up to now, this approach has been used mostly for calculating the thermodynamics of solids and liquids constituted by spherical molecules. The atom–atom approximation for intermolecular interactions enables the SCF calculations to be extended to cover non-spherical molecules.

DESCRIPTION OF METHOD

We consider a crystal as a classical system containing N rigid molecules with three translational and three rotational degrees of freedom per molecule. Let $P(q_1, \ldots, q_N)\,\mathrm{d}q_1 \ldots \mathrm{d}q_N$ be the probability that molecule 1 is in $\mathrm{d}q_1$ at q_1, 2 in $\mathrm{d}q_2$ at q_2, etc., where q's are (generalized) molecular coordinates. In the SCF approximation $P(q_1, \ldots, q_N)$ assumed to be a product of independent single particle probability densities. That is,

$$P(q_1, \ldots, q_N) = \prod_{i=1}^{N} \rho_i(q_i) \tag{1}$$

The best possible P of the form in Eq. (1) may be found by minimizing the configurational free energy expressed in terms of $\rho_i(q_i)$.[3] The condition that the configurational free energy be stationary to variation of ρ_i is easily shown to be

$$\rho_i(q_i) = \exp\{-\psi_i(q_i)/kT\}\left[\int \exp\{-\psi_i(q_i)/kT\}\mathrm{d}q_i\right]^{-1} \tag{2}$$

where $\psi_i(q_i)$ is an effective potential in the field of which molecule i moves:

$$\psi_i(q_i) = \sum_{j \neq i}^{N} \int E(q_i, q_j)\rho_j(q_j)\mathrm{d}q_j \tag{3}$$

($E(q_i, q_j)$ denotes the energy of coupling of molecules i and j as a function of their coordinates q_i and q_j).

The consistency Equations (2–3) are usually solved by iteration method. As a zeroth approximation $\rho_j(q_j)$ is taken to be sharply peaked at $q_j = q_j^{\mathrm{eq}}$, where q_j^{eq} are equilibrium coordinates of molecule j. That is, $\rho_j^{(0)} = \delta(q_j - q_j^{\mathrm{eq}})$. If we now substitute $\delta(q_j - q_j^{\mathrm{eq}})$ for ρ_j in Eq. (3), we obtain as a first approximation (SCF-1)

$$\psi_i^{(1)}(q_i) = \sum_{j \neq i}^{N} E(q_i, q_j^{\mathrm{eq}}) \equiv E(q_i) \tag{4}$$

the potential energy of interaction of molecule i at q_i with its next neighbours at their equilibrium positions. In the SCF-1 approximation the configuration integral (partition function) of a system may be written as

$$Z_{\mathrm{SCF-1}} = \left[\exp\{-E(q^{\mathrm{eq}})/2kT\} \int_{\Delta} \exp\{-[E(q) - E(q^{\mathrm{eq}})]/kT\}\mathrm{d}q\right]^N \tag{5}$$

where Δ is the volume of configurational phase space per molecule. This expression enables the calculation of the thermodynamic functions to be made.

In the present work the orientation of a molecule was described by Euler angles θ, φ, and ψ. Thus, $\mathrm{d}q = \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,\mathrm{d}\psi\cdot\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$ (x, y, z are the Cartesian coordinates of the center of gravity of a molecule).

The integral in Eq. (5) is the so-called "free volume." It was estimated by "importance sampling" (Monte-Carlo) method (for details see).[4] It can be rewritten as

$$\int_\Delta \frac{f(q)}{g(q)}\cdot q(q)\mathrm{d}q, \tag{6}$$

where $f(q)$ denotes $\exp\{-[E(q) - E(q^{\mathrm{eq}})]/kT\}$.

Let $g(q)$ be some positive valued function such that

$$\int_\Delta g(q)\mathrm{d}q = 1. \tag{7}$$

If $q^{(1)}, q^{(2)}, \ldots, q^{(n)}$ are independent random points distributed within the volume Δ with the probability density function $g(q)$ then the quantity

$$\lim \frac{1}{n}\sum_{i=1}^{n} f(q^{(i)})/g(q^{(i)}) \tag{8}$$

may be used as an estimation of integral (6).

The object in "importance sampling" is to concentrate the distribution of the sample points in the parts of Δ that are of most "importance." That is, one should choose $g(q)$ as being approximately proportional to $f(q)$. In our calculations the molecular states were generated by computer with the probability density of

$$g(q) = \prod_{s=1}^{6}\exp\{-(q_s - q_s^{\mathrm{eq}})^2/2\sigma_s^2\}(\sqrt{2\pi}\cdot\sigma_s)^{-1} \tag{9}$$

That is, the coordinates q_s ($s = 1, 2, \ldots, 6$) of the initial molecule each were generated independently. The parameters σ's of the distribution Eq. (9) were obtained by least square fitting $g(q)$ to $f(q)$. To judge the effectiveness of the choice of $g(q)$ distribution of the quantity $p^{(i)} = \ln[f(q^{(i)})/g(q^{(i)})]$ over its magnitude was computed. In all cases the distribution had a sharp maximum in the vicinity of zero, about 60% of the points $p^{(i)}$ being within the range of $|p^{(i)}| < 0.5$. Convergence of the sum (8) proved to be rather rapid: it took about 700–800 computations of the energy $E(q^{(i)})$ to obtain the value of the free energy with an accuracy of 0.03–0.05 kcal. mol^{-1}.

Summing up (8) it is reasonable to compute $E(q^{(i)})\cdot f(q^{(i)})$ and $E^2(q^{(i)})\cdot f(q^{(i)})$ in each state $q^{(i)}$ since, having done it, one can evaluate the non-ideal part of the internal energy, U, and heat capacity, C_v, by the formulas

$$U = \langle E(q) \rangle - \tfrac{1}{2} E(q^{\mathrm{eq}}), \tag{10}$$

$$C_v = \frac{Nk}{(kT)^2} [\langle E^2(q) \rangle - \langle E(q) \rangle^2] \tag{11}$$

where the brackets $\langle \quad \rangle$ denote statistical averaging over the states of the initial molecule:

$$\langle \varphi(q) \rangle = \frac{\int_\Delta \varphi(q) f(q) \mathrm{d}q}{\int_\Delta f(q) \mathrm{d}q} = \lim_{n \to \infty} \frac{\sum_{i=1}^{n} \varphi(q^{(i)}) \cdot f(q^{(i)}) / g(q^{(i)})}{\sum_{i=1}^{n} f(q^{(i)}) / g(q^{(i)})} \tag{12}$$

for some function $\varphi(q)$.

The formulas (10–11) result from the fact that the SCF-1 approximations to the entropy, S, internal energy, and heat capacity are to be thermodynamically consistent with the SCF-1 approximation to the free energy

$$F = -kT \ln Z_{\mathrm{SCF}-1}. \tag{13}$$

That is, the following relations should hold:

$$S = -\left(\frac{\partial F}{\partial T}\right)_v, \tag{14}$$

$$U = F - \left(\frac{\partial F}{\partial T}\right)_v \cdot T, \tag{15}$$

$$C_v = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_v. \tag{16}$$

Using Eq. (5), Eqs. (15–16) can be readily reduced to Eqs. (10–11).

In addition it is to be noted that the choice of $g(q)$ of the Gaussian form in Eq. (9) is no more than a means for estimation of the integral in Eq. (5). Our calculations are, therefore, free from the assumption of harmonicity of the potential $\psi(q)$, even though only quadratic in q_s terms are presented in the expression for $g(q)$. (The harmonic approximation of the SCF theory has been discussed in).[5]

RESULTS AND DISCUSSION

The thermodynamic functions of crystalline benzene were calculated with potential functions for interatomic interactions derived by Mirsky from elasticity moduli of naphtalene.[6] Unit cell parameters of the benzene crystal and equilibrium values of Euler angles at three temperatures: 138°, 218°, and 270°K were taken from.[7]

The results of calculations are summarized in Table I. (Given in Table I are whole values of the thermodynamic functions, that is, the ideal part is included.) Experimental data on the lattice part of the free energy and entropy as calculated from a calorimetric experiment[8] and frequencies of intramolecular vibrations[9] are also presented. The experimental and calculated values of the free energy are given relative to the corresponding values at zero temperature. The calculation of zero free energy, which coincides in the SCF approximation with the potential energy $\frac{1}{2}E(q^{eq})$, was performed with unit cell parameters obtained in[1] by extrapolation of the structural data[7] to 0°K.

TABLE I

The thermodynamic functions of the benzene crystal calculated for three temperatures

	$F^0 - F$ kcal·mol^{-1}		S cal·mol^{-1}·grad^{-1}		C_v cal·mol^{-1}·grad^{-1}	
T°K	calc.	exp.	calc.	exp.	calc.	exp.
138	0.5	1.1	15.9	16.0	10.8	10.5 (170°)
218	2.1	2.7	22.5	22.5	10.6	10.6 (220°)
270	3.5	4.1	26.1	26.3	10.5	10.2 (250°)

Experimental data on the heat capacity C_v are not available. A crude estimation of C_v from data on C_p was made in the following way: The compressibility, α, as determined from sound velocity measurements over the temperature range of 170° to 250°K was borrowed from Heseltine *et al.*[10] We choose the temperature values as close to our own ones as possible: 170°, 220°, and 250°K. The thermal expansion of the benzene crystal was found by graphical differentiation of the specific volume curve reproduced from the structural data at 77°, 138°, 218°, 253°, and 270°K.[7,11] The thermal expansion coefficient, β, at 170°, 220°, and 250°K proved to be 444, 525, and $622 \cdot 10^{-6}$ grad^{-1} respectively. Finally, the heat capacity was evaluated from the equation

$$C_p - C_v = -V \cdot T \cdot \alpha^2/\beta \tag{17}$$

and after excluding the intramolecular part resulted in the values given in Table I above.

As is seen from Table I, our results agree very closely with experiment. The difference between calculated and observed free energy does not depend on temperature and may be attributed to inaccuracy of calculating the free energy at zero temperature. As to heat capacity, the error of determining the thermal expansion coefficient at different temperatures seems to be too large to reveal true temperature dependence of C_v.

In conclusion we should like to recall the main assumptions used in our calculations:

1) The multiplicity for probability density function (1). The approximation actually means the neglect of correlations between the states of different molecules. To some extent this is justified by the fact that the displacements of molecules from their equilibrium positions are small compared to intermolecular distances in crystals. (On the same reason a first approximation of the SCF theory is approximately valid.)

2) The atom–atom approximation for intermolecular interactions. The approximation has comprehensively been discussed in[1] where the possibility of predicting the structure and heats of sublimation of molecular crystals has been demonstrated. Other papers have shown this approach to be fruitful for calculating the properties of polyatomic gases and liquids.[12] It is beyond doubt that regarded as purely empirical functions the atom–atom potentials are capable of describing intermolecular interactions with reasonable accuracy. We believe the results of our calculations to provide support for this view.

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