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The Entropy of Crystalline Naphthalene

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The entropy of naphthalene is calculated in the range 15–298° K., using characteristic lattice frequencies derived from X-ray and spectroscopic analyses. The results agree fairly well with the experimental entropy derived from Southard & Brickwedde's calorimetric measurements.

The preceding paper (Cruickshank, 1956) has given a theoretical account of the variation of the molecular vibration amplitudes with temperature in crystals of benzene, naphthalene and anthracene. The lattice frequencies used in that work may also be used to calculate thermodynamic properties of these crystals. In the present paper a comparison is made of the theoretical and experimental entropy of naphthalene in the range 15–298° K. No suitable calorimetric data appears to be available for anthracene (nor are the variations of its lattice frequencies with temperature known), while there are a number of disputed problems about the lattice vibrations of benzene, which accordingly requires separate discussion (Cruickshank, 1957).

Comparisons of experimental and theoretical thermodynamic functions of crystals are usually carried out in terms of specific heats, but, as Guggenheim (1949) has stressed, the entropy is really more suitable for such comparisons. It is the only simple thermodynamic function for which there is both a closed formula and an experimental value available from a single set of calorimetric measurements performed at constant pressure, whereas the comparison of specific heats involves the difference between C_p and C_v, which must be estimated from additional experiments.

Table 1. *Contributions to the entropy of naphthalene*

T (°K.)	$S_{\text{trans.}}$	$S_{\text{rot.}}$	$S_{\text{int.}}$	S_{total}
298·2	15·09	12·10	13·83	41·02
200	12·23	9·38	6·22	27·83
100	7·82	5·04	1·43	14·29
70	5·70	3·22	0·51	9·43
50	3·96	1·86	0·14	5·96
30	1·80	0·56	0·01	2·37
20	0·76	0·07	0·00	0·83
15	0·35	0·03	0·00	0·38

Following the assignment of lattice frequencies given in the preceding paper, the theoretical entropy of naphthalene may be estimated from the contributions of the vibrations in six translational branches, approximated by a Debye entropy function with

$$\Theta_D = 113-0{\cdot}076T \text{ °K.},$$

and six rotational optic branches, approximated by Einstein entropy functions with frequencies of (Ichishima, 1950)

$$\begin{aligned}\nu_4 &= 125-0{\cdot}0634T \text{ cm.}^{-1},\\ \nu_5 &= 145-0{\cdot}0633T,\\ \nu_3 &= 91-0{\cdot}0593T,\\ \nu_1 &= 60-0{\cdot}0433T,\\ \nu_2 &= 75-0{\cdot}0800T,\end{aligned}$$

ν_3 being taken twice. The entropy contributions of the internal molecular vibrations must also be included. The frequencies given in the recent vibrational assignment of naphthalene by McClellan & Pimentel (1955) will be used for this. Table 1 shows the contributions made to the calculated entropy at various temperatures by the lattice translational vibrations, the lattice rotational vibrations and the intramolecular vibrations. The last column gives the total calculated entropy.*

Table 2. *Experimental and calculated entropies of naphthalene*

(1) T (°K.)	(2) $S_{\text{calc.}}$	(3) ΔS	(4) $S_{\text{expt.}}$	(5) ΔS	(6) $S_{\text{calc.}}$ (adjusted)
298·2	41·02	−1·05	39·97	−1·02	40·99
200	27·83	−0·62	27·21	−0·75	27·96
100	14·29	−0·24	14·05	−0·52	14·57
70	9·43	+0·05	9·48	−0·32	9·80
50	5·96	+0·13	6·09	−0·16	6·25
30	2·37	+0·18	2·55	−0·06	2·61
20	0·83	+0·16	0·99	+0·03	0·96
15	0·38	+0·05	0·43	−0·02	0·45

Southard & Brickwedde (1933) have measured the specific heat C_p of naphthalene between 15·14° K. and 294·68° K. The experimental entropy obtained from their results by integrating C_p/T as a function of T is shown in column (4) of Table 2. Southard & Brick-

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* No difficulty arises through the lattice entropy being calculated from a model whose frequencies change with temperature. From one aspect, the statistical formulae may appear to give the calculated entropy at any temperature T_1 as

$$S(V(T_1), T_1)-S(V(T_1), 0),$$

whereas, with $S(V(T_1), T_1) \equiv S(P, T_1)$, the experimental entropy is ordinarily

$$S(P, T_1)-S(P, 0).$$

The two entropies are, however, the same, since, by the Third Law,

$$S(V(T_1), 0) = S(P, 0).$$

wedde gave the entropy only at 90° K. and 298·16° K. Their values, 12·52 and 39·89±0·12 e.u., differ slightly from those obtained in the present integration, 12·59 and 39·97 e.u., both integrations assuming a contribution of 0·43 e.u. from the unmeasured region below 15° K. The differences are not important for the present purpose and are probably due to the choice of slightly different smoothed curves through the measured C_p values.

The total calculated entropy is shown again in column (2) of Table 2, and the differences between the observed and calculated values are given in column (3). The differences are gratifyingly small considering the diverse sources from which the information about the lattice frequencies has been drawn. In detail, the calculated entropy is rather too small at low temperatures and rather too large at higher temperatures. Some adjustment of the discrepancy at low temperatures seems possible, for the temperature dependence of the translational lattice frequencies was only guessed from the known behaviour (Ichishima, 1950) of the rotational lattice frequencies. Θ_D is known from the X-ray results to be 91° K. at room temperature. If Θ_D is assumed to increase less quickly as T falls, and is taken as

$$\Theta_D = 106-0{\cdot}0512T\,,$$

a better fit of the experimental entropy between 15° K. and 30° K. can be obtained. The adjusted total calculated entropy is shown in column (6) of Table 2, and the new differences in column (5). The calculated entropy now gradually increases away from the experimental entropy as T rises above 50° K.

Possible causes of this slight discrepancy at higher temperatures are

(*a*) incorrect characteristic temperatures for the lattice frequencies;
(*b*) failure of the simple Debye theory;
(*c*) incorrect assignment of the internal frequencies.

We will discuss these in turn:

(*a*) To fit the observed and calculated entropies at 298·2° K., Θ_D would have to be about 111° K. This would imply a mean square translation vibration of the molecule at room temperature of $(\overline{u^2})_{\text{trans.}} = 2{\cdot}71\times10^{-2}$ Å^2, as compared with the X-ray value of $4{\cdot}03\times10^{-2}$ Å^2. The difference seems unallowably large. Errors in the rotational lattice frequencies might also cause the entropy discrepancy; however, the frequencies given by Ichishima agree closely with those given by Kastler & Rousset (1941) at room temperature.

(*b*) There is a slight difference between the characteristic temperature Θ_M occurring in the theory of the amplitudes of lattice vibrations and the Θ_D occurring in the thermodynamic theory (e.g. James, 1948). In the present work Θ_D has been assumed equal to Θ_M. The entropy discrepancy might be resolved if it could be shown that Θ_D should be rather larger than Θ_M. This seems unlikely to be so, for it is known for cubic crystals that Θ_M is slightly larger than Θ_D.

A more promising explanation is a partial failure of the Debye approximation itself as applied to a real monoclinic crystal. Even for cubic crystals the frequency distribution is markedly different from that assumed in the simple Debye theory (e.g. Born & Huang, 1954). Anharmonic effects are also probably of some importance. However, one would expect the failure of the simple theory to affect Θ_M and Θ_D in much the same way, so that the calculated entropy should be fairly reliable near room temperature, the temperature at which Θ_M was determined. But in view of the lack of quantitative knowledge, the failure of the simple theory must be set down as a possible explanation of the entropy discrepancy.

(*c*) The final possibility is of an error in the vibrational assignment made by McClellan & Pimentel. To remove the entropy discrepancy it would be necessary to raise substantially one of the low-frequency vibrations given by them, either 176 or 191 cm.$^{-1}$, or just possibly 285 cm.$^{-1}$. They discuss the possibility of omitting the 191 or the 285 cm.$^{-1}$ lines, but conclude against it.

Similar entropies are given by the slightly different vibrational assignment of Lippincott & O'Reilly (1955), as this also includes the same three low frequencies (though with the 191 cm.$^{-1}$ line attributed to a different symmetry species). Should any subsequent revision of the vibrational assignment remove one of these low-frequency lines, the present slight entropy discrepancy would probably disappear.

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