

Branched-chain organic compounds. Part 11: Validation of a new method for determination of the potential energy of cohesion of an organic crystal and deduction of the heat capacity of the vapour

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Abstract The cohesion energy of ethyl 3-cyano-3-(3,4-dimethoxyphenyl)-2,2,4-trimethylpentanoate, as obtained from the change of kinetic and potential energies in the heat of sublimation of the crystal, $E_{p,coh} = -46.7 \text{ kJ mol}^{-1}$ (78.6 °C), has been validated. A safe physicomathematic test based on the balance of entropy for the sublimation and Planck's equation for changes of state, extended to entropy, was devised to ascertain the kinetic energies of the crystal and the gas molecule. Entropic equations were developed for the phase equilibrium to find precisely and with simplicity the vibrational energy of the crystal by using the vapour pressure exclusively and independently from the internal rotational and vibrational motion of the gas molecule. The heat capacity of the vapour was determined in this way, which in this case releases the solid allowing vibrational movement in the gas phase to meet the pressure of sublimation, $C_p(T)/\text{J K}^{-1} \text{ mol}^{-1} = 1.268 T/\text{K} + 58.62$ (71.1–86.1 °C). An independent variational method of deducing the vibrational entropy, energy, or heat capacity of the gas molecule from each other was compared with the equations and was shown to yield the quantities with high accuracy. Values of the Nernst–Lindemann functions are tabulated.

Keywords Materials science · Phase transformations · Solid state · Thermodynamics

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Introduction

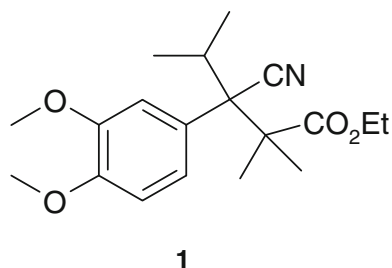
We have reported a method to find the potential energy of cohesion of the crystal of ester **1** (as a single enantiomer, Scheme 1) making use of the energy balance of the kinetic energies of the crystal and the vapour and the experimental energy of sublimation (Eq. 1, $E_p(\text{g}) = 0$, $\Delta_s U = \Delta_s H - RT$) [1]. The vibrational energy of the crystal was obtained from the heat capacity using Debye's theory of heat capacities of solids with its heat capacity and energy functions [2]. The vibrational energy of the gas molecule was, instead, obtained on the basis of the vibrational entropy. This was deduced by variation calculus from the vibrational heat capacity of the gas, because the Debye function for entropy in the solid state was suitable for the vibrational entropy of the gas, but the heat capacity function for the more calculus-exacting heat capacity (a derivative of either energy or entropy) was not as useful.

$$E_p(\text{cr}) = E_k(\text{g}) - E_k(\text{cr}) - \Delta_s U \quad (1)$$

Table 1 illustrates that, compared with energy or entropy, heat capacity is a worse fit for both the solid and gaseous states of ester **1**. The difficulty of theoretically describing C in an exact manner hinders reliable prediction of the energy by means of the approximate C function. In the organic material, E includes a prominent zero-point energy, and it is obtained solely from the small thermal rise ($E - E_0$).

The variational for the gas molecule based on S was proved correct in this work. The previous method also provided a means to obtain the absolute values of the thermodynamic functions for ester **1** in the three aggregation states, including chiral polymorphism. Absolute S and U for the gas state were disclosed, the latter with reference to the energy functions along the changes of state.

Scheme 1

**Table 1** Illustrative deviations from the Debye functions for ester **1** in the solid and gaseous states

	C (%)	$E - E_0$ (%)	S (%)
Solid	0.4	0.04	0.03
Gas	4	0.5	0.4

From information in Ref. [1]

We needed to reconsider essential points of our calculations concerning the conditions of applicability of Debye's theory to the crystal, being a molecular crystal instead of monoatomic, and the uncertainty in the vibrational energy of the gas molecule as it was obtained from an estimated C rather than the experimental value. Equation 1 demands the E_k values are known with high accuracy as they are much larger than the cohesion energy (ca. 800 vs. ca. -50 kJ mol^{-1} , so 1% errors will convert into 20%). Owing to such constraints we have checked some aspects significant to the cohesion energy of a basic molecular crystal such as ester **1**.

Factors relevant to the energies of the crystal and the molecule

Debye's theory refers only to monoatomic solids except at temperatures low enough that the theory is fulfilled by all kinds of solids because of the inactivity of high-frequency vibrations, which at ordinary T are active in organic ester **1**. For elasticity reasons, high frequencies with λ comparable to the distance between atoms are excluded from the fundamentals of the theory, but they become inactive more readily so that low frequencies become general for all solids (T^3 -law for heat capacity). In this proximity to 0 K this theory (but not other C theories) agrees with the Stefan–Boltzmann law (radiant energy proportional to T^4 , as regards the thermal energy) [2]. This has a consequence on this work, because the observable increase of the vibrational energy in a solid relates to E_0 , and this is mostly $E_k(\text{cr})$ for ester **1**, i.e. a 90% [1].

Schematically, the continuous distribution of frequencies in the Debye solid is given by Eqs. 2 and 2' (in the

elasticity formula $f(\rho, \kappa, \sigma)$: κ compressibility, σ Poisson's coefficient; total N atoms in the solid (each with three normal vibrations)) [2]. On the basis of this distribution the limit ν (ν from 0 to ν_D) can be obtained in two different ways: from the elastic coefficients only by use of the formula $f(\rho, \kappa, \sigma)$ followed by Eq. 2', or from the heat capacity only by solving the C function (at constant V : $C_V = f(\Theta_D/T)$, $\Theta_D = h\nu_D/k$), the function resulting from the distribution of frequencies by means of the Planck–Einstein formula for the thermal energy of a harmonic oscillator, and it was verified that the two procedures agreed for monoatomic solids.

$$dn_\nu = 3Vf(\rho, \kappa, \sigma)v^2 dv \quad (2)$$

$$f(\rho, \kappa, \sigma) = \frac{3N}{V\nu_D^3} \quad (2')$$

For actual heat capacities, the elastic restriction on the strongest frequencies was considered flexibly by Debye, verifying that diamond, with a high average frequency of 950 cm^{-1} ($\bar{\nu} = 3\nu_D/4$), followed the theoretical C_V function at all T . Ester **1**, with $\bar{\nu} = 759 \text{ cm}^{-1}$ [1], follows acceptably the function at ordinary T , as has been shown in this work.

On the other hand, the ester does not comply at all with theoretical C_V in the alternative manner, because it can be obtained from the elastic coefficients only, as has also been shown. The high actual Θ_D value for the ester (low C) is not within the range of these coefficients, not even if the crystal were as incompressible as Pt and more contractile than solid Ar. This procedure based on $f(\rho, \kappa, \sigma)$ is valid only for a weighed, non-assignable part of the heat capacity of the ester related to low frequencies (more or less saturated heat capacities, k per vibration, including lattice vibrations). Thus, the total heat capacity of this molecular crystal is not covered by the theory (in lacking the support of fundamental $f(\rho, \kappa, \sigma)$), in contrast with monoatomic solids and because the frequencies of the organic molecule are different from the frequencies associated with the elasticity of the crystal.

Despite this, the ν distribution in Eq. 2 and the resulting C_V function can be acceptable for the ester merely in an empirical manner. A corrected factor easily replaces theoretical factor $f(\rho, \kappa, \sigma)$. In addition, this factor is eliminated in the deduction of the function, although it subsides with ν_D or Θ_D . This practicality has precedents. The earlier Nernst–Lindemann C_V function for solids [3], which refers to only two frequencies (ν_{NL} and $\nu_{NL}/2$) for a material having very much frequencies and was found empirically, is practically identical with the Debye function (as it was examined, low T apart) [2]. Also, the Debye S function is adequate for calculation of the vibrational entropy of ester **1** in the gas state [1] despite the insignificant number of normal vibrations for the gas, 147 versus $153N_A$ for the crystal.

In a molecular crystal the continuous range of vibrations stretches throughout the molecule (the vibrations of the atoms in neighbouring molecules affect one another through forces in the crystal). This interactional continuum penetrating the molecule may affect the separability of the cohesion energy dealt with in this work, to the extent that this energy is associated with the outside of the molecule. The intermolecular vibrational interactions result in alteration of the frequencies. For the crystal of ester **1**, $\bar{\nu}$ decreases by 15% compared with the gas state [1]. In the crystal a very large number of cognate normal vibrations may be allotted to each normal vibration of the molecule (or degree of freedom) so that each is characterized by a $\bar{\nu}$ of statistical significance in the sense of thermodynamics. The six degrees of freedom for displacement of the centre of gravity and molecular orientation correspond to the lattice vibrations. Figure 1 shows a simulated allocation for ester **1**.

The lattice vibrations are thus separated formally from the internal molecular vibrations. Consequently, the energy of dissociation of the single, characteristic oscillator for the lattice vibrations is exactly the same as the potential energy of cohesion of the molecular crystal, or the potential energy of the crystal lattice ($D = -E_{p,coh}/6$). The separability of the cohesion energy (external to the molecule) is sustained in this manner. The cohesion energy may be approached with Morse's potential and lattice ν (Eqs. 3 and 3', $\beta = a/r_{eq}$, $D_{eq} = 8\pi^2 I \nu_{rot}^2$) (Refs. [5–7], part 4, p. 752).

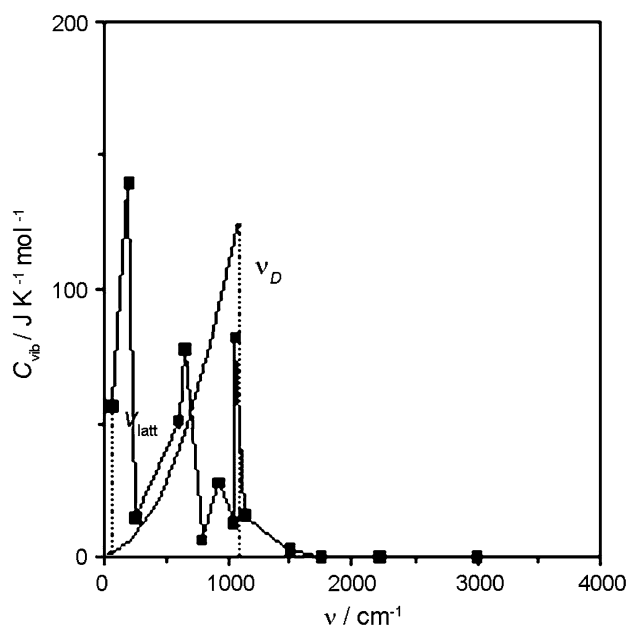


Fig. 1 Distribution of the heat capacity in the crystal of ester **1** with the vibrational frequency. The approximate allocation is from Ref. [4] for the isolated molecule

$$V(r) = D_{eq} \left(1 - e^{-\beta(r-r_{eq})} \right)^2 \quad (3)$$

$$D_{eq} = \frac{k_f}{2\beta^2} = \frac{2\pi^2 m r_{eq}^2 \nu^2}{a^2} \quad (3')$$

Doing away with the extensive spread of vibrations, a single molecule in a cavity of a medium characterized by the dielectric constant of the crystal may be taken for a basic molecular crystal. Thus the molecular dipole will oscillate about its equilibrium configuration in correspondence with the vibrations of the representative molecule, including those six extra in the crystal. The electrostatic interaction of an oscillating dipole with a surrounding dielectric results in alteration of the oscillator frequency (Ref. [8], p. 534), analogously with the coupled vibrations of nearby vibrators. The interaction should be independent of the cohesion energy (the lattice energy), because this concerns the motionless dipole (in addition to, at least, London forces).

The preceding vibrational and electrostatic descriptions may be regarded as equivalent, because the dielectric medium of the latter consists itself of the vibratory molecules of the crystal. These are the dielectric elements perturbed by the set-apart, neighbouring oscillating dipole, similarly to the exclusively vibrational picture. The separability of the cohesion energy is thus further supported.

A last point taken into account is the extent to which the change of frequencies on the condensation, and thus the change of force constants, may imply modification of the very large electronic energy of the molecule. Such modification will be unified with the cohesion energy in the overall $E_p(cr)$ value given by Eq. 1 ($E_p(cr) = E_{p,coh} + \Delta_g^{cr} E_{p,el}$), and a slight $\Delta_g^{cr} E_{p,el}$ change may hide a small $E_{p,coh}$ value.

This change of frequencies is not large (ca. 15% decrease for molecule **1**). A k_f refers to merely a transitory displacement of the covalently bound atoms from their equilibrium positions in the molecule, and it may occur in the end that a modification of k_f has an insignificant effect on the binding electronic energy (D). It would actually accord with Morse's potential on account of the variable β (Eq. 3', $\beta = a/r_{eq}$). Thus a weakening of k_f would be counterbalanced by a decrease in β , resulting in very consistent lengthening of r_{eq} . Such ideal conditions of separability of the vibrational and electronic energies may be justified by the Born–Oppenheimer approximation (the vibrational motion of the atoms is slower than the electronic motion). It may be less justifiable for the liquid state wherein the vibrational motion is slower than for the solid state (e.g. Ref. [1]), if the electronic motion also slows down and at such a rate that the two motions tend to converge. For a liquid however, the cohesion energy, as

such, is incorporated in the theory into the translational entropy, S , as an entropic $E_{p,\text{coh}}/T$ quantity.

The $E_p(\text{cr})$ value for ester **1** that has been obtained using Eq. 1 should agree with theoretical calculations, as it could be obtained by direct superposition of the molecular units of this basic molecular crystal, together with appropriate intermolecular potentials (Ref. [9], p. 693). The dielectric constant of the crystal could be introduced if the conformation of the electronic cloud of the molecule in the crystal were not the same as for the gas molecule, the actual cloud in the crystal serving as reference for calculating the cohesion energy. Disagreement of the calculated energy with the value obtained by use of Eq. 1 should result from dielectric modification of the energy of the molecule in the crystal, because the above-considered term $\Delta_g^{\text{ct}}E_{p,\text{el}}$ is not broken down in Eq. 1.

The frequency $\bar{\nu}$ obtained in practice with any of the meant C_V functions is, in statistical thermodynamics, the legitimate average frequency of the macroscopic system of molecular oscillators (Eqs. 4 and 4', n atoms in the molecule). However, the $\bar{\nu}$ values will not coincide for a given C_V because the ν distribution for the Planck–Einstein oscillator differs from one case to another and, in addition, neither distribution is exact. This thermodynamic concept of $\bar{\nu}$ is fully applicable to the isolated molecule, thus relating to the vibrations of one molecule, and when $\bar{\nu}$ is obtained for the gas state, as in the present case of molecule **1** using an S function. Frequency $\bar{\nu}$, and even if it were an exact value, will not anyway reproduce the energy of the macroscopic system when replaced on the basic Planck–Einstein formula, as a consequence of the quantization of the vibrational energy when this formula is used. Under quantum conditions every ν , including $\bar{\nu}$, takes its particular course from its ε_0 value. The principle of equipartition of the energy, in which ν does not affect $\varepsilon(kT)$, is not valid.

$$\bar{\nu} = \frac{2}{h} \varepsilon_0 = \frac{2}{h} \frac{E_0}{3nN_A} \quad (4)$$

$$E_0 = \frac{3nN_A h \nu_{PE}}{2} \equiv \frac{9nN_A h \nu_{NL}}{8} \equiv \frac{9nN_A h \nu_D}{8} \quad (4')$$

Objectives

In the previous calculations we used the experimental heat capacity of the crystal of ester **1** at constant pressure (C_p) in the Debye functions whereas the theory requires the heat capacity to be at constant volume for thermodynamic reasons ($dU = C_V dT$). This point of the calculations has been thoroughly examined. C_V can be determined experimentally and differs from C_p (Ref. [9], p 717; Refs. [10, 11], p 94), but it is not available for the crystal. First we found that the difference between C_V and C_p for the crystal could be greater than for ordinary ionic crystals or metals.

We then checked using an approximate C_V that the deviation of the crystal from the Debye C_V function could be larger than was previously indicated using the incorrect C_p [1]. This discrepancy of the function for the crystal posed a question about the reliability of $E_k(\text{cr})$ obtained from C_V .

In order to deal with this matter, a preliminary variational search was carried out on the set of heat capacities anchored in a normal manner to the experimental $C_p(T)$ of the crystal ($C = f \cdot C_p(T)$, $f \equiv$ parameter), so as to select a modified C_p with which $E_k(\text{cr})$ could be safely obtained. The search disclosed that the C which optimally fits the C_V function differs from C_V even farther than C_p . However, an extended search revealed that the optimum C could not be definitively selected because it did not persist as such in a full set of heat capacities derived from C_p . Despite this, the optimum C has subsequently been verified as satisfactory for overcoming the defectiveness of the Debye C_V function for the crystal, except for the high accuracy required for Eq. 1. The optimum C was also found for the Nernst–Lindemann and Planck–Einstein functions to make a comparison.

To settle the matter a safe and fine physicomathematic test was devised to find out the physically correct Θ_D value for the crystal, hence the correct $E_k(\text{cr})$. The test rested on the balance of entropy for the sublimation of the crystal (Eq. 5) and checked the translational entropy of the vapour as obtained by testing trial $\Theta_D(\text{cr})$ values against the actual value. This was obtained from the experimental vapour pressure (p_v) [1] with the Sackur–Tetrode equation [10]. The rotational entropy of the gas molecule was obtained with accuracy sufficient to test, using the X-ray structure of the molecule in the crystal [12] with regard to the pertinent rotational entropy formula (Ref. [8], p. 519).

$$S_{\text{tr}}(\text{g}) = S_{\text{vib}}(\text{cr}) + \Delta_s S - S_{\text{rot}}(\text{g}) - S_{\text{vib}}(\text{g}) \quad (5)$$

The test concerned a T interval, consistent with the requirement of two temperatures at least for contrasting the Debye S function with experiment. It was a small interval around the available temperature of sublimation of the crystal (T_s), which proved successful on account of the sensitivity of p_v to T . The modification of the entropy of sublimation with T in this interval was accounted for by Planck's equation for changes of state ($d\Delta_s H = \Delta_{\text{cr}}^g C_p dT$) [11, p 200], applied to entropy ($\Delta_s S = \Delta_s H/T$). The stepwise test will be described in detail.

The test cannot be performed on the energy instead of the entropy because the potential energy of the crystal is a second unknown, in addition to E_k . For consistency with the third law of thermodynamics, potential energy was not considered with regard to Eq. 5. E_p shares in the heat capacity ($C = C_k + C_p$), and the relevance of C_p concerning the energy will be discussed for the crystal of ester **1**.

The only $S_{\text{vib}}(\text{cr})$ value obtained by use of the test (at T_s) fully conformed to experiment, and the corresponding $E_{\text{k}}(\text{cr})$ value has been safely used in Eq. 1. The test also verified that the actual Θ_{D} value for the crystal closely corresponds with the optimum C variationally obtained from C_p . The actual Θ_{D} value departed to a significant extent from C_V , which pointed out that the significance of the Debye C_V function is empirical for this crystal.

By careful consideration of the equations of the test it was found that the quantities connected to the rotational and vibrational movements of the gas molecule cancel out in the equations. Using the resulting simplified equations, it was confirmed that the outcome of the test was reproduced with a high degree of numerical accuracy, which in turn freed the test from the uncertainty about C for the gas molecule. The simplified entropy equations, remaining subject to prior phase equilibrium, enable precise determination of the vibrational energy of the crystal by use of p_v , with complete exclusion of structural data and of thermodynamic data specifically relating to the polyatomic nature of the organic substance in the gas state.

The $E_{\text{k}}(\text{g})$ value in Eq. 1 has been readily obtained from the actual $S_{\text{vib}}(\text{g})$ value afforded by Eq. 5. Support for the reliability of the intermediary $\Theta_{\text{D}}(\text{g})$ value, itself untested, will be given. Using the test in an alternative manner, $C(T)$ for the gas molecule could be determined, making a complete check of heat capacities against $S_{\text{tr}}(\text{g})$. The simplified equations, analogous to the former, enable determination of C for the gas phase from p_v , dispensing with the solid phase.

With the availability of C_{vib} for the gas molecule a check on the previously reported variational method [1] was practicable, by comparison of the $S_{\text{vib}}(\text{g})$ value resulting from the method with the actual value provided by the test. By applying the method either in direct or reverse manner, S_{vib} and E_{vib} , or C_{vib} , were predicted with high accuracy. The results validate this variational method, and precedence was given to the values obtained by use of the test. On account of the accuracy provided by the test the error of the final $E_{\text{p}}(\text{cr})$ value is mostly reduced to the error in the experimental value of $\Delta_s U$.

Values of the Debye and Planck–Einstein functions for C_V , E , and S have been taken from those tabulated in Ref. [7] (part 4, p 736) and values of the Nernst–Lindemann functions for the intervals used in the work are tabulated in “Methods”.

Results and discussion

Deviation of the crystal from the Debye function for heat capacity

The relationship between heat capacity at constant p and at constant V is given by Eq. 6 (α isobaric expansion

coefficient, κ isothermic compressibility coefficient) (Ref. [9], p 717). For an organic crystal α may be estimated as $2.5\text{--}3.5 \cdot 10^{-4} \text{ K}^{-1}$, and κ $1\text{--}2 \cdot 10^{-10} \text{ Pa}^{-1}$ (Ref. [7], part 1, p 645). Using these ranges and Eq. 6, C_V for ester 1 is $10 \pm 4\%$ smaller than C_p (V : Ref. [12], C_p [1], collected in Table 3). This difference between C_p and C_V is greater than ca. 5% for ordinary ionic crystals and metals (Refs. [2, 9], p 717). This can be explained simply by the mean atomic heat capacity as the main factor ($C_{\text{at}} = C_p/n$, n atoms in the molecule, Eq. 6'). Thus this quantity is significantly smaller for the ester because of the large number of high-frequency vibrations that contribute little to C , e.g. C–H bonds (Fig. 1). The ratio α^2/κ in Eq. 6' may also favour the ester with respect to the other solids, while the lower V_{at} of the ester opposes the capability of C_{at} .

$$C_p - C_V = \frac{\alpha^2 VT}{\kappa} \quad (6)$$

$$\frac{C_p - C_V}{C_p} = \frac{\alpha^2 V_{\text{at}} T}{\kappa C_{\text{at}}} \quad (6')$$

To proceed, a value of C_V for the crystal was thus taken that was 10% lower than the experimental C_p , by multiplying $C_p(T)$ by 0.9 for the T interval (273.2–363.2 K, 0–90 °C). By use of this operation the relative displacement from $C_p(T)$ is the same for all points, becoming normalized. The Debye C_V function was solved for a sufficient number of C_V – T points (spaced regularly with regard to T), obtaining Θ_{D} as the average with the standard deviation (Table 2). For comparison, the deviations for diamond, KCl, and Ag were obtained for the same C_V region as for ester 1, using information on C_V values directly as given by Debye [2] and Nernst and Lindemann [3] (Table 2; footnote b). The deviation for the ester is larger than for the other solids, but acceptable.

On the other hand, the Θ_{D} value for the ester that is based on theory lies between 150 and 470 K, according to a calculation based on Eq. 2' using the α range above and a wide range of 0.1–0.4 for Poisson's coefficient ($0 < \sigma < 1/2$). The large difference between this basic Θ_{D} value with the value obtained by use of the C_V function (Table 2) indicates that the deviation of C_V from the function is not fundamental in nature, but merely a point of circumstantial

Table 2 Deviation of ester 1 from the Debye C_V function for C_V and C_p

	Θ_{D} (K)	Dev.	E_0 (kJ mol ⁻¹)	$(E - E_0)$ (kJ mol ⁻¹) ^a
C_V	1,562	$\pm 1.28\%$ ^b	745.2	49.4
C_p	1,456	$\pm 0.55\%$	694.6	57.2

^a 318.2 K

^b For a 15% interval of the C_V domain, diamond $\pm 0.33\%$, KCl $\pm 0.50\%$, Ag $\pm 0.80\%$

fitting. Thus, C_V may be modified, to refine its value. However, such modification of C_V is critical with regard to Eq. 1, in the manner that the $E_k(\text{cr})$ values from C_V and C_p (Table 2) differ by an amount similar to the cohesion energy. Because of this difficulty a search was undertaken in order to find a modified C that could be safely used for Eq. 1.

Figure 2 shows the effect of fitting C to the Debye C_V function on modification of the experimental C_p value. The optimum C does not lie within the likely range of C_V , being further from this range than C_p itself. As shown, the Nernst–Lindemann C_V function furnishes a better value for C_V than the Debye function (and this is true for the gas molecule also). Thus the former function should be chosen. However, these two C_V functions are, overall, practically identical [2] (also the expressions for E_0 (Eq. 4') are the same. The energy and the entropy for the two kinds of function are also similar, the values even crossing (selected $E - E_0$ and S values are given in “Methods” for verification; the corresponding Planck–Einstein functions lag at this stage).

Despite such likeness of the Debye and Nernst–Lindemann $E - E_0$ energies, the underlying disparity in E_0 (noted also in “Methods”) is not tolerable in this work because it is similar to the cohesion energy of the crystal. The Nernst–Lindemann energy in the proximity to 0 K, which is a direct consequence of backbone E_0 for the solid, does not agree with Stefan–Boltzmann law. This is not as would be expected for such decaying thermal energy [2].

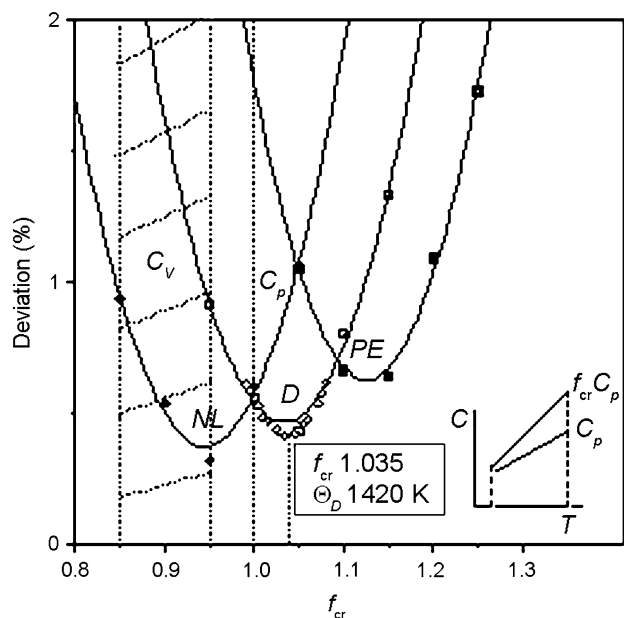


Fig. 2 Deviation of modified experimental C_p for ester **1** from the Debye, Nernst–Lindemann, or Planck–Einstein C_V function and as a function of the modification coefficient

For this purpose, E_0 values suitable for the present problem, the Debye functions (in general), and the Debye optimum C were preferred. Support for the preference will be given in discussing the $E_p(\text{cr})$ value for the crystal.

The modification of experimental C_p shown in Fig. 2 follows the normal path. The normal minimum that had been obtained could not represent an absolute minimum. In order to consider all possible heat capacities the slope of the normal values was varied by turning about the middle temperature. It was first observed that the Θ_D value for a normal $C(T)$ does not change with the turning angle. In turning successive normal slopes a series of consecutive minima was disclosed, without an absolute minimum. Figure 3 shows some sample minima. In this series the normal minimum (f_{cr} 1.035) was not shifted by the deflection, confirming the precision of the bidirectional variation. Because the C space was in general featureless, it was concluded that the normal optimum C was not defining but indicative, because it arose from the logical but somewhat arbitrary normalization in experimental C_p .

The Θ_D value that indeed conforms to the crystal (as will be discussed in next section) differs from the value for the optimum C by only 2%. On the other hand, this Θ_D value, which is still further displaced toward higher heat capacities, differs from the value for reference C_V (f_{cr} 0.9) by 11%. Consequently, ester **1** departs from the Debye C_V function to a significant degree, which is apparently a consequence of the empirical significance of the function, having no theoretical basis for this organic crystal as discussed above.

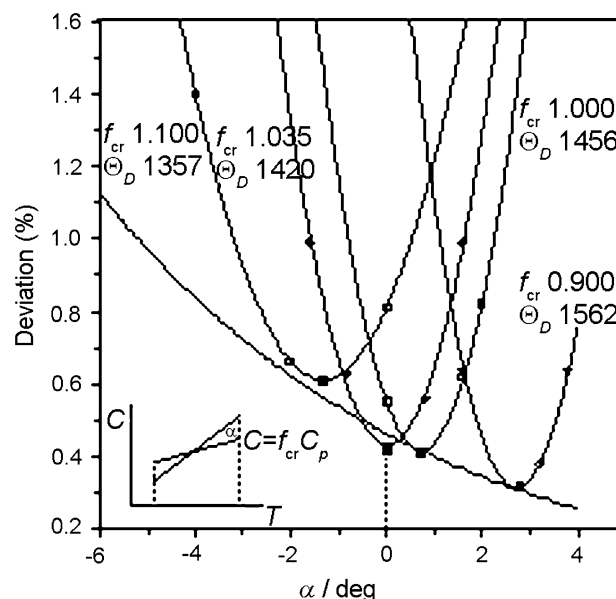


Fig. 3 Optimum fitting of the Debye C_V function by means of deflection

Test of the method: kinetic energy of the crystal

The test concerns a sufficiently wide trial interval of $\Theta_D(\text{cr})$ values, ensuring the outcome is unambiguous. As a preliminary procedure, it is obtained by the balance of entropy for the sublimation (Eq. 5) and, at the temperature of sublimation for the crystal (T_s 351.8 K), the $S_{\text{vib}}(\text{g})$ value that corresponds to a given trial Θ_D value, initially using in the equation the $S_{\text{vib}}(\text{cr})$ value conjugated with the Θ_D value at T_s . The $\Delta_s S$ value in the equation is known as the actual enthalpy of sublimation (collected in Table 3) [1]. This $\Delta_s H$ was determined from measurement of the sensitive vapour pressure for a small T range, and using Clausius–Clapeyron equation. In this manner, $\Delta_s H$ was given as an experimental constant for a p_v interval having significant amplitude (0.01–0.1 Pa) and it was referred to the middle temperature taken as T_s . The $S_{\text{tr}}(\text{g})$ value in Eq. 5 followed the experimental p_v value at T_s on the basis of the Sackur–Tetrode equation (Eq. 7, [10], footnote a in Table 3).

$$S_{\text{tr}}(\text{g}) = R \ln \frac{RT}{p_v} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} + \frac{3}{2}R + R(1 - \ln N_A) \quad (7)$$

The remaining $S_{\text{rot}}(\text{g})$ value was obtained by use of the formula for the rotational entropy of a polyatomic molecule as an asymmetric top (Eq. 8, Ref. [8] p. 519, symmetry-number 1, footnote d in Table 3). The product of the principal moments of inertia ($I_A I_B I_C$) was rigorously calculated by use of the exact Wilson–Hirshfelder method (Ref. [8], p. 509), using the coordinates of the atoms in the molecule as obtained by X-ray crystallography [12]. The $I_A I_B I_C$ value should not coincide with that applicable to Eq. 8 because of the existence of conformers in the ester. However, the two values should differ little considering that the value for a spheroid, as the molecule may be regarded by its general shape, does not change on equivalent spherification. For a substantial error of 10% in the $I_A I_B I_C$ value the $S_{\text{rot}}(\text{g})$ value would be affected by only 0.3% after use of Eq. 8, and the effect of this uncertainty on the final $E_p(\text{cr})$ value turned out in practice to be negligible.

$$S_{\text{rot}}(\text{g}) = R \ln(I_A I_B I_C)^{1/2} \left(\frac{8\pi^{7/3} kT}{h^2} \right)^{3/2} + \frac{3}{2}R \quad (8)$$

Continuing this preliminary work, the series of $S_{\text{vib}}(\text{g})$ values at T_s arrived at from the trial $\Theta_D(\text{cr})$ range is in turn brought into correlation with heat capacities for the gas molecule. The set of normal heat capacities ($C_p' = f_g \cdot C_p(T)$) derived from the Rihani–Doraiswamy C_p for the gaseous ester (quoted in Table 3) [1, 13] was used as a supply of C values. The $S_{\text{vib}}(\text{g})$ – C_p correlation was set up cursorily and in the usual manner on the basis of C , thus furnishing the average $\Theta_D(\text{g})$ value for a given vibrational C ($C_{\text{vib}} = C_p - 4R$, 273.3–363.2 K) by use of the theoretical C_V function and transferring the $\Theta_D(\text{g})$ value to the S function to assign the $S_{\text{vib}}(\text{g})$ value at T_s . The correlation is tabulated in “Methods”.

For particular refinements in the test, the $S_{\text{vib}}(\text{g})$ – C_p correlation was set up on the basis of S by use of the previously reported variational method (Eq. 9) [1]. Thus for a given $C_{\text{vib}}(T)$ the term $S_{\text{vib},351.8}$ was varied to obtain the best fit of $S_{\text{vib}}(T)$ to the Debye S function (273.2–363.2 K). Figure 4 shows several optimum $S_{\text{vib},351.8}$ values. In the variational method the deviation from the S function becomes lessened by one order of magnitude (to a 0.4%), which increases the reliability of C that was initially lacking.

$$S_{\text{vib}}(T) = \int_{351.8}^T \frac{C_{\text{vib}}(T)}{T} dT + S_{\text{vib},351.8} \quad (9)$$

To actually carry through the test, the T interval was used from which the experimental $\Delta_s H$ was worked out, designating a set of regularly spaced temperatures so that their average coincided with T_s . The test is summarized in Table 4 in reference to a selected $\Theta_D(\text{cr})$ value of the trial range and in its compliance to Eq. 5 for the T interval. The $S_{\text{vib}}(\text{cr})$ values in the table are conjugated with the $\Theta_D(\text{cr})$ value. The set of $\Delta_s S$ values was found by use of Eq. 10, which is an unmistakable consequence of Planck’s equation (as correctly approximated for sublimation; Ref. [11], p. 200). The $C_{p,g}(T)$ that matches the $\Theta_D(\text{cr})$ value using the foregoing cursory correlation is used in

Table 3 Summary of the quantities of ester **1** sufficient for the test and as experimental quantities (p_v in Pa, T in K, C in $\text{J K}^{-1} \text{mol}^{-1}$)

$p_v = f(T)$	$\Delta_s H$	$\Delta_s S$	$C_p(\text{cr})$	$I_A I_B I_C$
$\ln p_v = 38.7187 - 14760T^{-1}$ (344.0–359.6 K) ^a	$122.7 \pm 1.8 \text{ kJ mol}^{-1}$ (351.8 K) ^b	$348.8 \pm 5.1 \text{ J K}^{-1} \text{mol}^{-1}$ (351.8 K)	$C_{p,\text{cr}} = -1.017 \times 10^{-4} T^2 + 2.39T - 216.5^c$	$1.518 \times 10^{10} \text{ m}_0^3 \text{A}^{6d}$

^a $S_{\text{tr}}(\text{g})$ $307.4 \text{ J K}^{-1} \text{mol}^{-1}$ (351.8 K)

^b $\Delta_s U$ $119.8 \pm 1.7 \text{ kJ mol}^{-1}$ (351.8 K)

^c Discretional Rihani–Doraiswamy heat capacity: $C_{p,g} = -1 \times 10^{-3} T^2 + 1.741T - 26.9$

^d $S_{\text{rot}}(\text{g})$ $148.1 \text{ J K}^{-1} \text{mol}^{-1}$ (351.8 K)

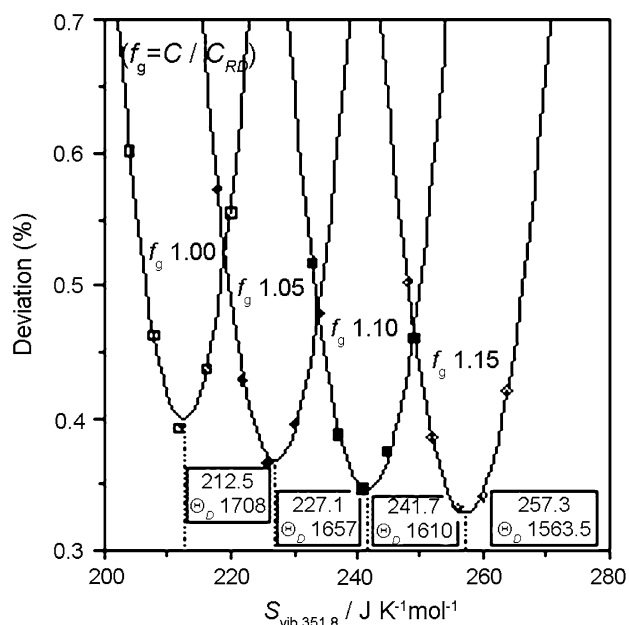


Fig. 4 Variational method. S_{vib} value at 351.8 K to optimally fit $S_{\text{vib}}(T)$ to the Debye S function (Θ_{D} relating to $S_{\text{vib}}(T)$); the standard errors for the optimum $S_{\text{vib},351.8}$ values on the second-order regressions are $\pm 0.3\text{--}0.6 \text{ J K}^{-1} \text{ mol}^{-1}$ ($r^2 = 0.995\text{--}0.999$)

Table 4 Test of the method

T (K)	$S_{\text{vib}}(\text{cr})$	$\Delta_{\text{s}}S$	$S_{\text{rot}}(\text{g})$	$S_{\text{vib}}(\text{g})$	$S_{\text{tr}}(\text{g})^{\text{a}}$	$S_{\text{tr}}(\text{g})$ (actual) ^b
344.3	323.20	358.82	147.79	220.44	313.79	314.56
347.3	328.65	354.78	147.90	224.39	311.14	311.67
350.3	334.23	350.77	148.01	228.33	308.66	308.82
353.3	339.82	346.80	148.11	232.27	306.24	306.02
356.3	345.25	342.87	148.22	236.20	303.70	303.27
359.3	350.82	338.97	148.32	240.13	301.34	300.57

Prediction of $S_{\text{tr}}(\text{g})$ by use of $\Theta_{\text{D}}(\text{cr}) = 1396 \text{ K}$; $S_{\text{vib},351.8}(\text{g}) = 230.3 \text{ J K}^{-1} \text{ mol}^{-1}$, $f_{\text{g}} = 1.072$; $C_{p,\text{g}} = -1.072 \times 10^{-3}T^2 + 1.866T - 28.84$; the error of the prediction in p_{v} is $4 \times 10^{-6} \text{ Pa}$ (0.01%) (all S values in $\text{J K}^{-1} \text{ mol}^{-1}$)

^a Regression for the initial data shown: $S_{\text{tr},\text{g}} = -0.82848T + 598.94$ ($r^2 = 1.000$)

^b Regression for the initial data shown: $S_{\text{tr},\text{g}} = -0.93286T + 635.66$ ($r^2 = 1.000$)

Eq. 10 together with the experimental $C_{p,\text{cr}}(T)$. Because Planck's equation gives $C_{p,\text{cr}}$ at the vapour pressure, it was estimated that modification of the experimental $C_{p,\text{cr}}$ value from 1 atm to 0 atm was negligible, 0.001% (the formula used is given in "Methods"). The $S_{\text{rot}}(\text{g})$ set was found by use of Eq. 8, and the $S_{\text{vib}}(\text{g})$ set by use of Eq. 9 (applying the $C_{p,\text{g}}$ function and the $S_{\text{vib},351.8}(\text{g})$ value). The actual $S_{\text{tr}}(\text{g})$ values are obtained by use of Eq. 7.

$$\Delta_{\text{s}}S(T) = \frac{\Delta_{\text{s}}H_{351.8}}{T} + \frac{1}{T} \int_{351.8}^T [C_{p,\text{g}}(T) - C_{p,\text{cr}}(T)] dT \quad (10)$$

The predicted and actual $S_{\text{tr}}(\text{g})$ values at T_{s} (351.8 K), omitted in the table, are of necessity coincident with each other by arithmetic, but become distinct in the manner afforded by the linear regressions (footnotes a, b). In these the $S(351.8)$ value shifts consistently with modification of the initial set of data. Thus, the difference between the $S(351.8)$ values in the regressions was taken as the error of the prediction, and related to the T interval. This error in S was converted into the heightened error in p_{v} by use of Eq. 7. The shift in T_{s} results from setting the regression $S(351.8)$ value for the experiment in the regression for prediction, and is 0.01 K.

The survey of the test is shown in Fig. 5. For each $\Theta_{\text{D}}(\text{cr})$ value a table similar to Table 4 was built. The variation in p_{v} is small, up to 1%, but the sensitivity is sufficient. The absolute minimum (1396 K) is definitely discernible from the most relative minimum, being ten times below in error and nearly touching the error bottom. The absolute minimum was refined using $C_{p,\text{g}}$ functions as provided by the variational method and is shown in Fig. 6a.

The absolute minimum persisted as such when modifying the $C_{p,\text{g}}(T)$ functions by deflection, which indicated that the test was independent of $S_{\text{vib}}(\text{g})$, which it should be because Eq. 9 can be regarded as embodied in Eq. 10. For reasons of numerical accuracy, it was, however, considered that the algebraic form of function $S_{\text{vib},\text{g}}(T)$ as worked out by use of Eq. 10 will not be the same as that worked out by use of Eq. 9, and that Eq. 10 is an approximation of the complete Planck's equation.

The independence of the test from $S_{\text{vib}}(\text{g})$ was verified by offsetting Eq. 9 in Eq. 10. For that, $C_{p,\text{g}}(T)$ was replaced by $4R$, and amount $351.8S_{\text{vib},351.8}(\text{g})$ (as a free-energy term)

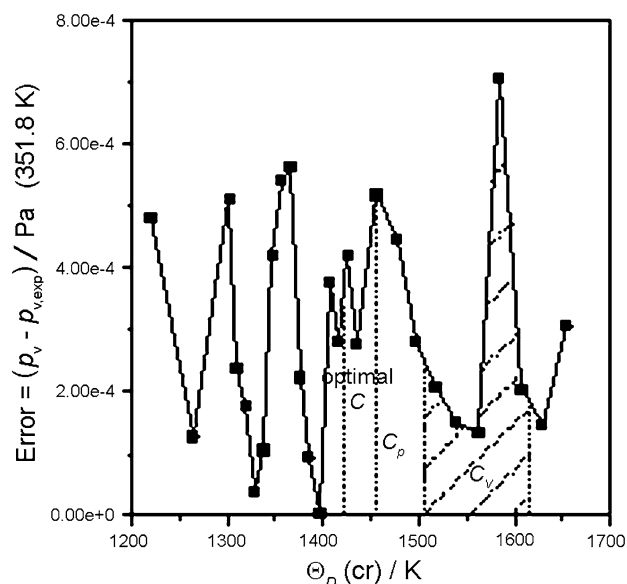


Fig. 5 Survey of the test

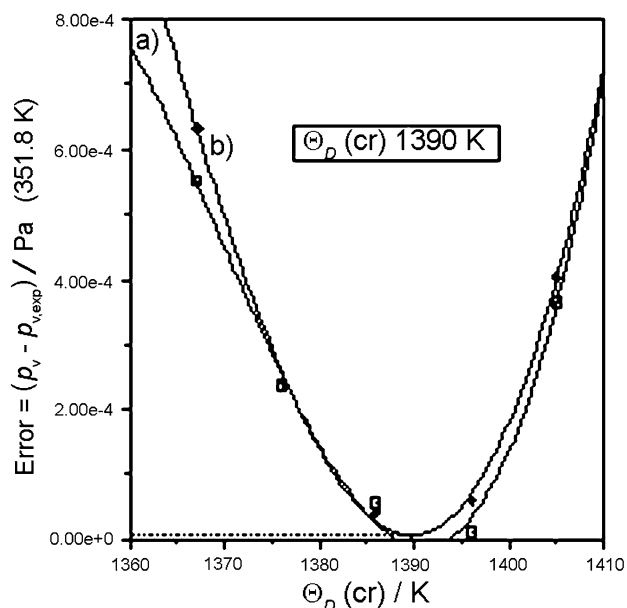


Fig. 6 Result of the test. Physical Θ_D value of the crystal for entropy and at 351.8 K: **a** associated with arbitrary $C_{p,g}(T)$, $\Theta_D(\text{cr}) = 1,392$ K; **b** unconditional value, $\Theta_D(\text{cr}) = 1,390$ K, the standard error for the third-order regression is ± 1 K ($r^2 = 0.998$), $S_{351.8} = 339.8$ J K $^{-1}$ mol $^{-1}$, $\bar{v}_{351.8} = 724$ cm $^{-1}$

was subtracted from $\Delta_s H_{351.8}$ to offset the last term in Eq. 9. Subsequently, Eq. 5 was used, eliminating the term $S_{\text{vib}}(\text{g})$. The results agreed within 0.1% (Fig. 6a, b). $S_{\text{rot}}(\text{g})$ was also omitted, leaving the gas molecule as if monoatomic, and with the same result ($\Theta_D(\text{cr})$ 1391 K). The most simplified equations for this case are Eqs. 11 and 12.

$$S_{\text{tr}}(\text{g}) = S_{\text{vib}}(\text{cr}) + \Delta_s S^* \quad (11)$$

$$\Delta_s S^*(T) = \frac{351.8 [S_{\text{tr},351.8}(\text{g}) - S_{\text{vib},351.8}(\text{cr})]}{T} + \frac{1}{T} \left[\int_{351.8}^T \left[\frac{5}{2}R - C_{p,\text{cr}}(T) \right] dT \right] \quad (12)$$

Thus, the test can be carried out with reference to only the entropy of the crystal and the translational entropy of the vapour (or p_v), without recourse to the molecular structure or knowledge of the heat capacity of the gas molecule, even though it implies artificial modification of Planck's equation for the phase equilibrium of the organic polyatomic substance. This entropic conversion of vibrational into free translational motion requires the prior permanence of the equilibrium of the whole transformation in its entirety (Eq. 12 referring to the real T_s). Eqs. 11 and 12 enable determination of the entropy of the solid phase solely from the pressure of the equilibrium gas phase, and they should be applicable to other organic crystals also.

The achieved S value, apparent in Fig. 6, corresponds in terms of the test exactly with the physical Θ_D value. The

S value is freed from theoretical or empirical defects and conforms precisely with experimental values in this T range. In this interval, deviation of the entropy of the crystal from the S function should be disregarded in any event. Here only the entropy at 351.8 K is known, and the proper heat capacity C_V is not available; this would be required for comparison in a manner consistent with the function at least one extended value of the available S value.

In passing to the $E_k(\text{cr})$ value through Θ_D , the level of confidence was maintained, because the rank of the fitting of S and E to the functions is the same, and very high (Table 1, solid). Furthermore, an increment of energy is directly built in proportion to the increment of entropy with the individual temperature ($dU = TdS_V$). The $E_k(\text{cr})$ value was 746.3 kJ mol $^{-1}$ (351.8 K).

The average vibrational frequency of the crystal ($153N_A$ normal vibrations), equivalent to the physical Θ_D value (Eqs. 4 and 4'), is quoted in Fig. 6. The optimum Θ_D value that was obtained by variational modification of experimental C_p (Fig. 2) is nearer the tested value by 2.2%, and similarly for $E_k(\text{cr})$, by 1.5%. This shows the suitability of the variational procedure on the crystal for approaching the correct values. This small deviation in E , however, represents 24% in the cohesion energy of the crystal.

The change in the total energy of the crystal with T at constant p may be expressed by Eq. 13 for the considered interval. The involved enthalpic term $p\Delta_{344.3}^{359.3}V$ can be neglected considering the expansivity and the pressure. Removing this term from the equation would be possible except for the change in potential energy on expansion of the crystal ($\Delta_{344.3}^{359.3}E_p$ on the left-hand side, $C_p = C_{p,k} + C_{p,p}$).

$$\Delta_{344.3}^{359.3}E_k = \int_{344.3}^{359.3} C_p dT \quad (13)$$

In order to confront the two sides of the equation the tested Θ_D value (supposed unaltered at the interval limits) and experimental C_p were used. The left-hand side was in excess by 0.542 kJ mol $^{-1}$. This small amount of energy would need to be counterbalanced by 5% by an unreasonable replacement of the tested Θ_D value. The lack of conformity may be amended by the actual non-constancy of Θ_D with T , on account of its relationship with density and coefficients κ and σ , as indicated in the "Introduction". The tested Θ_D value properly refers to $\Delta_{344.3}^{359.3}E_k$ at constant V and not at constant p . On expansion of the crystal, however, \bar{v} (and hence Θ_D) should decrease, because of the weakening of the lattice vibrations with increasing intermolecular distance. Thus modification of the tested Θ_D value by less than 1 K at both interval limits, so that Θ_D decreased with T , was sufficient to balance Eq. 13 ($\Theta_{D,344.3} = 1,390.8$ K, $\Theta_{D,359.3} = 1,389.2$ K).

Otherwise, the equation can be balanced with a larger decrease in Θ_D together with a decrease in cohesion energy ($\Delta_{344.3}^{359.3}E_p > 0$), e.g. a decrease of 3 K with a decrease of 0.555 kJ mol⁻¹. The latter represents a 1% decrease in cohesion energy for the 15 K expansion of the crystal. However, in no event can the seeming disagreement with Eq. 13, which concerns ΔT , affect the precision of the Θ_D and $E_k(\text{cr})$ values as tested in respect of one value of T .

Vibrational energy of the gas molecule

The vibrational entropy of ester **1** in the gas state was directly obtained by setting the actual entropy of the crystal in Eq. 5, which gave 233.1 J K⁻¹ mol⁻¹ (351.8 K). With the corresponding Θ_D value by the Debye S function, $\Theta_{D,351.8}$ 1,641 K, the vibrational energy was 810.6 kJ mol⁻¹, with a total $E_k(\text{g})$ value of 819.4 kJ mol⁻¹ (351.8 K). The frequency $\bar{\nu}$ for molecule **1** (147 normal vibrations) was 855.6 cm⁻¹, according to the Θ_D value (Eqs. 4, 4').

The actually untested $\Theta_D(\text{g})$ value, even though it is obtained solely from the right entropy, does not warrant the value of the vibrational energy. However, this is supported by the high and similar degree of fitting of S and E for the gas molecule to the functions, i.e. 0.09 and 0.14% deviations, respectively, and for the 15 K interval around 351.8 K. These deviations relate to actual C_{vib} for the gas molecule (presented in the next section), which was used to extend the single $S_{\text{vib},351.8}$ and $E_{\text{vib},351.8}$ values with T .

Equation 13 in this case gives exact values of E_{vib} and C_{vib} for the gas molecule, by using a value of $\Theta_D(\text{g})$ that is unconditioned by supramolecular factors and, in theory, also independent of T . Using the actual C_{vib} , the equation was satisfied by replacement of the untested $\Theta_D(\text{g})$ value by 1,710 K, a change of 4%, handling the value duly as if independent of T . Allowing, however, for flexibility in the value only a modification of $\pm 0.04\%$ was required, which would validate the value. Stronger support was subsequently found in checking C_{vib} against experimental p_v .

With Eq. 1 the $E_p(\text{cr})$ value was -46.7 kJ mol⁻¹ (351.8 K), which is the potential energy of cohesion if the quantity $\Delta_g^{\text{cr}}E_{p,\text{el}}$ is zero (as indicated in the "Introduction"; for $\Delta_s U$, see footnote b in Table 3). The value is, accidentally, practically coincident with the value previously obtained by use of the inappropriate value of C_p for the crystal and an indiscriminate C_p value for the gas (-47.7 kJ mol⁻¹) [1].

Table 5 gathers approximate $E_p(\text{cr})$ values obtained by using the three types of functions considered without testing, each type for both the crystal and the gas molecule. The involved $E_k(\text{cr})$ values are related to the optimum but approximate C rendered by the respective C_V function (Fig. 2). The $E_k(\text{g})$ values involved were obtained from the respective $S_{\text{vib}}(\text{g})$ values (Eq. 5) using $S_{\text{vib}}(\text{g}) - C_p$

Table 5 Potential energy of the crystal of ester **1** as obtained cursorily with the Debye, Nernst–Lindemann, or Planck–Einstein functions (kJ mol⁻¹)

D	NL	PE
-38.8 (-13.2^a , -123.8^b)	-8.9	-56.1

^a Using, alternatively, the NL functions for the gas molecule

^b Using, alternatively, the PE functions for the gas molecule

correlations for the respective type of functions and in the cursory manner described above. The Debye $E_p(\text{cr})$ value is in between, and is also obtained by using the other functions for the gas molecule only. This supports a preference for the Debye functions.

Heat capacity of the gas molecule

The heat capacity of ester **1** in the gas state was obtained by using the foregoing test in an alternative manner, to check trial heat capacities for the gas molecule against $S_{\text{tr}}(\text{g})$ once the $S_{\text{vib},351.8}$ values for the crystal and the gas had been established. $S_{\text{rot}}(\text{g})$ was directly removed from the equations, giving Eqs. 14 and 15.

$$S_{\text{tr}}(\text{g}) = S_{\text{vib}}(\text{cr}) + \Delta_s S^* - S_{\text{vib}}(\text{g}) \quad (14)$$

$$\Delta_s S^*(T) = \frac{\Delta_s H_{351.8} - 351.8 S_{\text{rot},351.8}(\text{g})}{T} + \frac{1}{T} \left[\int_{351.8}^T \left[\left(C_{p,\text{g}}(T) - \frac{3}{2}R \right) - C_{p,\text{cr}}(T) \right] dT \right] \quad (15)$$

Initially, the foregoing incomplete supply of heat capacities was tested over a sufficiently wide range (up to an 18% modification of parent C_p , $f_g = 1.01$ – 1.18 , in increments of 0.01). The results of the test are listed in Table 6. The $S_{\text{vib}}(\text{cr})$ and $S_{\text{vib}}(\text{g})$ sets depend on the

Table 6 Test for the heat capacity of ester **1** in the gas state

T (K)	$S_{\text{vib}}(\text{cr})$	$\Delta_s S$	$S_{\text{vib}}(\text{g})$	$S_{\text{tr}}(\text{g})^a$	$S_{\text{tr}}(\text{g})$ (actual) ^b
344.3	326.00	207.59	222.40	311.19	314.56
347.3	331.45	204.81	226.61	309.65	311.67
350.3	337.03	202.05	230.80	308.28	308.82
353.3	342.62	199.31	235.14	306.79	306.02
356.3	348.05	196.59	239.36	305.28	303.27
359.3	353.60	193.88	243.78	303.70	300.57

Prediction of $S_{\text{tr}}(\text{g})$ by use of $C_{p,\text{g}} = -1.09 \times 10^{-3}T^2 + 1.898T - 29.32$ (f_g 1.09); $\Theta_D(\text{cr}) = 1,390$ K, $\Theta_D(\text{g}) = 1,641$ K; the error of the prediction in p_v is 3×10^{-6} Pa (0.008%) (all S values in J K⁻¹ mol⁻¹)

^a Regression for the initial data shown: $S_{\text{tr},\text{g}} = -0.49571T + 481.87$ ($r^2 = 1.000$)

^b Regression for the initial data shown: $S_{\text{tr},\text{g}} = -0.93286T + 635.66$ ($r^2 = 1.000$)

previously determined Θ_D values and were held unchanged through the survey of heat capacities. The general prospect of the test is most similar to Fig. 5. The absolute minimum was at $f_g = 1.09$, and the most relative minimum at $f_g = 1.13$, which is probably a too large C_p for this gas. The absolute minimum was accurately located using a number of surrounding points for the third-order regression and lay at $f_g = 1.093 \pm 0.003$.

The test was not independent of the slope of $C_{p,g}(T)$, in contrast with the previous version wherein $C_{p,g}$ has no effect. For a linear $C_{vib}(T)$ and by geometry, ΔE_{vib} cannot change with a deflection of $C_{vib}(T)$ about the middle T , but not so into proportion to ΔS_{vib} with T ($dS_{vib} = dE_{vib}/T$) because there are two limit temperatures for Δ , not just one T as required (compare $dE_{vib} = C_{vib}dT$).

In the test, the deflection represented a second-order modification, but was perceivable, enabling a complete trial set of heat capacities to be accounted for, and enabling determination of the change in C_p with T . Thus the slope of the remaining $C_{p,g}(T)$ obtained was in turn checked in the usual way for the test for a wide scope of deflection about the test middle T (approximating $C_{p,g}(T)$ as linear). The assay is summarized in Fig. 7. The slope of the refined C_p is further inclined by 12%. With the errors at the remaining middle T and in the slope, the final error of prediction of C_p values is $\pm 1.3\%$. Corresponding $C_{vib}(T)$ is quoted in the figure. Table 7 collects heat capacities for ester 1 as obtained by different methods. These values are close to

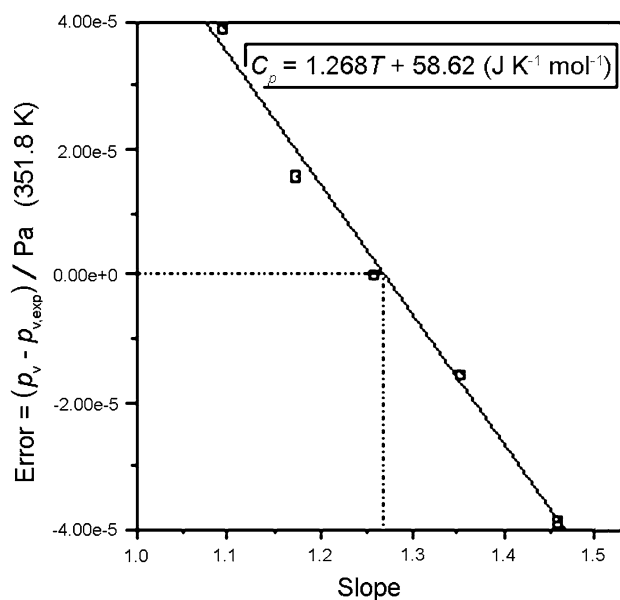


Fig. 7 Heat capacity of ester 1 in the gas state (344.3–359.3 K) as determined by deflection about 351.8 K. Reference for deflection: $C_p/\text{J K}^{-1} \text{mol}^{-1} = 1.133 T/\text{K} + 106.1$ ($f_g = 1.093$); the standard error for the slope axis on the linear regression is ± 0.016 ($r^2 = 0.991$); $C_{vib}/\text{J K}^{-1} \text{mol}^{-1} = 1.268 T/\text{K} + 25.36$

Table 7 Heat capacities for ester 1 in the gas state at constant pressure (in $\text{J K}^{-1} \text{mol}^{-1}$)

Method	318.2 K	351.8 K
Rihani–Doraiswamy [13]	425.8	461.8
Dobratz–Meghbrelan [4]	432.8	470.8
Benson [14]	458.3	496.4
This work	462.1	504.7

the values obtained by use of Benson's method and set aside from the other values (7–9%).

A defect in the test was the extrapolation of the tested $\Theta_D(\text{cr})$ value for a set of real $S_{vib}(\text{cr})$ values, and resulted from the natural drift of the theoretical S function (from one real anchor value). This indeterminacy was readily solvable, because experimental $C_{p,\text{cr}}(T)$ perfectly matches in Eq. 15 the real $S_{vib}(\text{cr})$ values at p_v ($\Delta_{0\text{atm}}^{\text{atm}} C_{p,\text{cr}} \approx 0$). Applying the elimination gives Eqs. 16 and 17. Thus these most simplified equations enable determination of C for the gas molecule from the pressure of the gas phase equilibrated with the solid phase.

$$S_{\text{tr}}(\text{g}) = \Delta_s S^* - S_{vib}(\text{g}) \quad (16)$$

$$\Delta_s S^*(T) = \frac{351.8 [S_{\text{tr},351.8}(\text{g}) + S_{vib,351.8}(\text{g})]}{T} + \frac{1}{T} \left[\int_{351.8}^T \left[C_{p,g}(T) - \frac{3}{2}R \right] dT \right] \quad (17)$$

The remaining and isolated $\Theta_D(\text{g})$ value, similarly defective, is necessary for the subsistence of the test itself as is sustaining any trial $C_{p,g}(T)$. That imperfection affects the performance of C in the test. When the test was used with the most simplified equations the absolute minimum was not displaced, but its depth decreased significantly (20-fold). From this point, and holding the optimum $C_{p,g}(T)$ unchanged, the depth was restored by perturbing the $\Theta_D(\text{g})$ value by as little as 0.05 K (0.003%). This represented a rate of 8×10^2 K per Pa (as a depth unit), while the rate for the reverse and usual modification of $C_{p,g}(T)$ (with the $\Theta_D(\text{g})$ value fixed) is 1.5×10^5 K per Pa, i.e. 200-fold. This indicates that the mathematical unfitness of the $\Theta_D(\text{g})$ value for the T interval has been removed. Under these conditions, the above-given value of vibrational energy that followed the $\Theta_D(\text{g})$ value is accurate.

Check on the variational method for the gas molecule

With the actual C_{vib} of the gaseous ester, a test for the variational method could be carried out, checking the predicted $S_{vib,351.8}(\text{g})$ value (from C_{vib}) versus the actual value, given above. Making use of $C_{vib}(T)$ as extrapolated to the usual interval in the variational method (273.2–363.2 K),

the optimum $S_{\text{vib},351.8}$ value was found at 237.0 ± 0.4 $\text{J K}^{-1} \text{mol}^{-1}$, in the manner of Fig. 4. The value differs by 1.7% from the actual value. The Θ_{D} value of 1,626 K resulting from the variational method and the corresponding vibrational energy of $804.8 \text{ kJ mol}^{-1}$ differs by 0.9 and 0.7% from the values of the actual entropy. For the energy the deviation represents 12% of the $E_{\text{p}}(\text{cr})$ value.

In a reverse manner, the $C_{\text{vib}}(T)$ for the gaseous ester that is predicted by the variational method from the actual $S_{\text{vib},351.8}$ value was directly obtained by interpolation in Fig. 4. This gave $f_{\text{g}} = 1.071$ together with $\Theta_{\text{D}} = 1,638$ K. However, this outcome was ambiguous because of the limited number of heat capacities used for the method.

In order to ensure these values were correct, two features of the variational method were examined. It was found that both an optimum $S_{\text{vib},351.8}$ value and its Θ_{D} value are independent of the deflection of the involved $C_{\text{vib}}(T)$ about the middle T . These two features in conjunction ensured the correctness of the Θ_{D} value. However, it also follows that the correctness of $C_{\text{vib}}(T)$ can be ensured only at the middle T . Therefore, taking this single C value obtained by the reverse variational method, i.e. $C_{\text{p}} = 456.1 \text{ J K}^{-1} \text{mol}^{-1}$ ($f_{\text{g}} = 1.071$, 318.2 K), it deviates by 1.3% from the value obtained by use of the test (Table 7). It is concluded on the whole that the accuracy achieved in practice with the variational method was approximately 1%.

Error of the method

Concerning the $E_{\text{k}}(\text{cr})$ value only the last error of correlation was considered (Fig. 6), other uncertainties having been dropped in the test, and it amounted to $\pm 0.4 \text{ kJ mol}^{-1}$. In the $E_{\text{k}}(\text{g})$ value, as obtained by means of Eq. 5, allowance was made for the experimental uncertainty in $S_{\text{tr}}(\text{g})$ (from p_{v}), $\pm 0.07\%$, and for the above-mentioned uncertainty in $S_{\text{rot}}(\text{g})$, $\pm 0.3\%$, which together represented $\pm 0.6 \text{ kJ mol}^{-1}$. These energy errors used in Eq. 1 together with the experimental error of $\Delta_{\text{s}}U$, $\pm 1.7 \text{ kJ mol}^{-1}$ (Table 3), added up to $\pm 1.9 \text{ kJ mol}^{-1}$ ($s = (\sum s_i^2)^{1/2}$, s_i standard deviation). Thus, the error of the $E_{\text{p}}(\text{cr})$ value, $\pm 4\%$, mainly results from experimental $\Delta_{\text{s}}U$ value.

Table 8 Closeness between the Debye and Nernst–Lindemann functions for energy or entropy and their difference from the Planck–Einstein functions

$f_{\text{cr}} (C/C_{\text{p}})$	$(E-E_0) (\text{kJ mol}^{-1})^{\text{a}}$			$S (\text{J K}^{-1} \text{mol}^{-1})^{\text{a}}$		
	D	NL	PE	D	NL	PE
0.85	45.9	< 46.2	38.5	200.0	194.9	153.3
0.90	49.4 ^b	> 47.6 ^c	41.9	216.8	201.6	168.1
0.95	53.3	< 54.1	45.6	234.4	> 232.1	184.1
1.00	57.2	58.4	49.3	252.7	≅ 252.4	200.5
1.05	61.3	62.8	53.3	274.2	> 273.3	218.0

^a 318.2 K

^b $E_0 = 745.2 \text{ kJ mol}^{-1}$, $\Theta_{\text{D}} = 1,562$ K

^c $E_0 = 792.9 \text{ kJ mol}^{-1}$, $\Theta_{\text{NL}} = 1,662$ K

In conclusion, the potential energy of cohesion of the crystal of ester **1** and the heat capacity of the vapour have been determined by means of thermodynamics and elemental statistical thermodynamics together with simple variational procedures. Equations wherein the vibrational entropy of a solid or a gas wholly reverts to the translational entropy for the corresponding sublimation have been derived for determination of the vibrational energy of the crystal and the vibrational heat capacity of the vapour.

Methods

General

Deviations and errors generally refer to the standard values. Linear, second-order, and third-order regressions were obtained by use of the software Cricket Graph, version 1.3.2. The standard error of the x estimate on the regressions was obtained by use of $s_x[(1-r^2)(n-1)/(n-1-a)]^{1/2}$, where s_x is the standard deviation of the x data and a the order of the regression. The values used for constants were: $R = 8.315 \text{ J K}^{-1} \text{mol}^{-1}$, $h = 6.626 \times 10^{-34} \text{ J s}$, $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$, $c = 2.998 \times 10^8 \text{ m s}^{-1}$, $N_{\text{A}} = 6.022 \times 10^{23} \text{ mol}^{-1}$, $m_{\text{u}} = 1.661 \times 10^{-27} \text{ kg}$, $M(\mathbf{1}) = 333.42 \text{ g mol}^{-1}$ (Tables 8, 9, and 10).

The modification of C_{p} with pressure was estimated by using the approximate equation Eq. 18, which is valid at

Table 9 Correlation of entropy with heat capacity by use of the Debye functions

$S (\text{J K}^{-1} \text{mol}^{-1}) (351.8 \text{ K})$	130.7	143.0	155.5	168.3	181.6	195.3	209.3	223.7
$f_{\text{g}} (C/C_{\text{RD}})$	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.05
$\Theta_{\text{D}} (\text{K})$	2,103	2,028	1,959.5	1,895	1,834.5	1,777.5	1,723	1,672
$S (\text{J K}^{-1} \text{mol}^{-1}) (351.8 \text{ K})$	238.6	253.8	270.0	286.4	303.1	320.8	338.9	
$f_{\text{g}} (C/C_{\text{RD}})$	1.10	1.15	1.20	1.25	1.30	1.35	1.40	
$\Theta_{\text{D}} (\text{K})$	1,623	1,576	1,530	1,486	1,444	1,402.5	1,363	

Table 10 Values of the Nernst–Lindemann functions for heat capacity, energy, and entropy (with $R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$, for one degree of freedom)

Θ/T	0	1	2	3	4	5	6	7	8	9
$C_v = \frac{R}{2} \left[\frac{(\Theta/T)^2 e^{\Theta/T}}{(e^{\Theta/T} - 1)^2} + \frac{(\Theta/2T)^2 e^{\Theta/2T}}{(e^{\Theta/2T} - 1)^2} \right]$										
3.	5.5216	5.3900	5.2595	5.1302	5.0025	4.8763	4.7520	4.6295	4.5090	4.3907
4.	4.2745	4.1606	4.0490	3.9397	3.8328	3.7283	3.6261	3.5264	3.4290	3.3340
5.	3.2413	3.1510	3.0629	2.9771	2.8935	2.8121	2.7328	2.6556	2.5804	2.5073
6.	2.4361	2.3668	2.2994	2.2337	2.1699	2.1077	2.0473	1.9884	1.9312	1.8755
7.	1.8213	1.7686	1.7173	1.6673	1.6187	1.5715	1.5255	1.4807	1.4372	1.3948
$\frac{E-E_0}{T} = \frac{R}{2} \left[\frac{\Theta/T}{e^{\Theta/T} - 1} + \frac{\Theta/2T}{e^{\Theta/2T} - 1} \right] (E_0 = \frac{9R\Theta}{8})$										
4.	1.6117	1.5466	1.4842	1.4244	1.3671	1.3123	1.2597	1.2094	1.1611	1.1148
5.	1.0705	1.0280	0.9872	0.9481	0.9106	0.8746	0.8401	0.8070	0.7753	0.7448
6.	0.7155	0.6874	0.6604	0.6345	0.6096	0.5857	0.5628	0.5407	0.5196	0.4992
$S = \frac{R}{2} \left[\frac{\Theta/T}{e^{\Theta/T} - 1} - \ln(1 - e^{-\Theta/T}) + \frac{\Theta/2T}{e^{\Theta/2T} - 1} - \ln(1 - e^{-\Theta/2T}) \right]$										
4.	2.2931	2.1890	2.0901	1.9961	1.9067	1.8218	1.7410	1.6640	1.5908	1.5211
5.	1.4547	1.3914	1.3311	1.2735	1.2187	1.1663	1.1164	1.0687	1.0232	0.9797
6.	0.9381	0.8984	0.8605	0.8242	0.7896	0.7564	0.7247	0.6943	0.6653	0.6375
7.	0.6109	0.5855	0.5611	0.5377	0.5154	0.4940	0.4735	0.4538	0.4350	0.4170

350 K, and in which V is the molar volume, $\alpha = (1/V)(\partial V/\partial T)_p$, and $\kappa = -(1/V)(\partial V/\partial p)_T$.

$$\Delta C_p \cong \frac{\alpha V}{\kappa} (1 - e^{\kappa \Delta p}) \quad (18)$$

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