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Abstract

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G. V. BELYAKOV, G. G. VILENSKAYA

THE EQUATION OF STATE OF TRINITRO-TOLUENE

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This note considers the equation of state of a trinitrotoluene crystal, constructed by the Debye–Einstein–Grüneisen method.

The equation of state of a crystal of volume V with N molecules, each of which consists of s atoms, was represented in the form

$$P = -\frac{dE_x}{dV} + \frac{9}{8}Nk\gamma_{\mathrm{m}}\frac{\theta_{\mathrm{m}}}{V} + 3Nk\frac{\gamma_{\mathrm{m}}}{V}TD\left(\frac{\theta_{\mathrm{m}}}{T}\right) + \frac{1}{2}Nk\frac{\gamma_{\mathrm{a}}}{V}\sum_{i=1}^{f}\theta_{\mathrm{a}}^{i} + Nk\frac{\gamma_{\mathrm{a}}}{V}\sum_{i=1}^{f}\frac{\theta_{\mathrm{a}}^{i}}{e^{\theta_{\mathrm{a}}^{i}/T}-1}; \quad (1)$$

here $E_x(V/N)$ is the interaction energy between atoms when they are in equilibrium positions; k is Boltzmann' s constant; N is the number of molecules in 1 g; γ_{m} and γ_{a} are Grüneisen parameters for intermolecular and intramolecular frequencies, respectively; θ_{m} and θ_{a} are, respectively, the characteristic Debye temperature and the characteristic temperatures of the intramolecular (atomic) oscillators, including 3 characteristic frequencies associated with rotation of the molecule as a whole; $D(\theta_{\mathrm{m}}/T)$ is the Debye function.

In equation (1) three functions are unknown:

$$E_x = E_x(V/N), \qquad \gamma_{\mathrm{m}} = \gamma_{\mathrm{m}}(V/N), \qquad \gamma_{\mathrm{a}} = \gamma_{\mathrm{a}}(V/N).$$

The interatomic interaction energy E_x can be written as the sum of the interaction energies of atoms belonging to different molecules, which constitutes the intermolecular interaction energy E_x^{m}, and the interaction between atoms belonging to the selected molecule, E_x^{a}, i.e. $E_x = E_x^{\mathrm{m}} + E_x^{\mathrm{a}}$.

The intermolecular interaction energy was taken in the form of the empirical formula:

$$E_x^{\mathrm{m}} = \frac{N}{2}\Lambda_{\mathrm{m}}^{*}\left[\frac{m}{n-m}\left(\frac{V^*}{V}\right)^{n/3} - \frac{n}{n-m}\left(\frac{V^*}{V}\right)^{m/3}\right]. \quad (2)$$

Here Λ_m^* is the sublimation energy of the crystal per molecule, and V^* is the volume of the crystal at 0°K.

The interaction energy of atoms inside all molecules of the crystal was represented in a form analogous to equation (2), i.e.,

$$E_x^{\mathrm{a}} = N\Lambda_{\mathrm{a}}^* \left[\frac{l}{k-l} \left(\frac{V_{\mathrm{a}}^*}{V_{\mathrm{a}}} \right)^{k/3} - \frac{k}{k-l} \left(\frac{V_{\mathrm{a}}^*}{V_{\mathrm{a}}} \right)^{l/3} \right]. \tag{3}$$

Here Λ_{a}^* corresponds to the energy of rupture of all interatomic bonds in the molecule, and the ratio $V_{\mathrm{a}}^*/V_{\mathrm{a}}$ is the ratio of the atomic volume of the molecule at 0°K to the current atomic volume of the molecule.

The atomic size of the molecule was related to the volume of the crystal for comparatively small compressions by the relation:

$$V_{\mathrm{a}}^*/V_{\mathrm{a}} = 1/(1 - \delta(1 - V/V^*)). \tag{4}$$

Here δ is proportional to the ratio of the stiffnesses of the intermolecular bond to the total intramolecular one.

The Grüneisen coefficient γ_{M} was related to the volume of the crystal by the Slater relation

$$\gamma_{\mathrm{M}} \left(\frac{V}{N} \right) = -\frac{2}{3} - \frac{V}{2} \frac{d^2 P_x^{\mathrm{M}}/dV^2}{dP_x^{\mathrm{M}}/dV}. \tag{5}$$

Here $P_x^{\mathrm{M}} = -dE_x^{\mathrm{M}}/dV$. For comparatively small compressions, in view of the low compressibility of the atomic dimensions of the molecule, the coefficient γ_{a} was assumed constant.

Determination of the heat capacity of the TNT crystal requires knowledge of the characteristic Debye temperature and of the natural frequencies of the TNT molecule. The Debye temperature θ_{M}^0 was found from experimentally measured sound velocities in the TNT crystal (at $T = 291$°K and $V = V_0 = 0.599$) to be $\theta_{\mathrm{M}}^0 \simeq 75°$. Such a low Debye temperature of the crystal leads to the fact that already at room temperatures ~ 300°K the molecular heat capacity due to vibrations of the molecules as whole units may be regarded as saturated and equal to:

$$c_v^{\mathrm{M}} = 3Nk = 0.11 \cdot 10^7 \ \frac{\mathrm{erg}}{\mathrm{g} \cdot \mathrm{deg}}.$$

The temperature dependence of the intramolecular heat capacity of the crystal can be determined only if the complete set of natural frequencies of the TNT molecule is known. However, because of the absence of the complete spectrum of natural vibrations of the TNT molecule, it was assumed that in the TNT molecule all natural frequencies are equal to some mean frequency $\bar{\omega}_{\text{a}}$ (or, what is the same, to the mean temperature $\theta_{\text{a}} = \hbar\bar{\omega}_{\text{a}}/k$), which was determined from experimental data (1) on the dependence of the heat capacity of the TNT crystal on temperature. The best agreement with experiment in the temperature range $\Delta T = 273 \div 343^{\circ}$K is given by the calculated curve with characteristic temperature $\theta_{\text{a}} = 700^{\circ}$K (Fig. 2a) and number of effective vibrations $f = 51$.

To determine the interatomic interaction, the following experimental data were used: the isotherm (5) (at $T = 291^{\circ}$K) of TNT with initial density 1.63 g/cm^3, obtained up to a pressure of $22 \cdot 10^3$ atm; the heat capacity of TNT at $T = 291^{\circ}$K; the coefficient of volume expansion, measured in the temperature range $T = 243 \div 313^{\circ}$K; the sublimation energy of TNT (2) and the energy of rupture of all bonds in the molecule, equal to

$$\Lambda_{\text{a}}^{*} = 1.39 \cdot 10^{-10} \text{ erg/molecule.}$$

Let us write the Grüneisen relation for the crystal at the point $P = 1$ atm ($1/V_0 = 1.67$ g/cm^3) and $T = 291^{\circ}$K:

$$V_0\beta/K = \gamma_{\text{M}} c_v^{\text{M}} + \gamma_{\text{a}} c_v^{\text{a}}. \tag{6}$$

Here $V_0 = 0.599$ cm^3/g;

$$\beta = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P = 22.26 \cdot 10^{-5} \text{ deg}^{-1};$$

$$K = -\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_{T=291^{\circ}\text{K}} = 0.957 \cdot 10^{-11} \text{ s}^2 \cdot \text{cm/g};$$

$$c_v^{\text{M}} = 0.11 \cdot 10^7 \text{ erg/g} \cdot \text{deg}; \qquad c_v^{\text{a}} = 1.17 \cdot 10^7 \text{ erg/g} \cdot \text{deg}$$

is the heat capacity of the intramolecular part of the crystal.

At the point $V = V^{*} = 0.555$ cm^3/g (the specific volume of the crystal at $T = 0^{\circ}$K) the elastic pressure in the crystal is equal to 0. Therefore, at the point $(V = V^{*}, T = 291^{\circ}\text{K})$ the relation

$$P^{*}V^{*} = \gamma_{\text{M}}^{*} E_T^{\text{M}} + \gamma_{\text{a}} E_T^{\text{a}} \tag{7}$$

is valid.

Here $P^{*} = 13.3 \cdot 10^9$ dyn/cm^2 is the thermal pressure in the crystal, taken from the experimental isotherm for $T = 291^{\circ}$K;

$$E_T^{\mathrm{M}} = \frac{9}{8} Nk\theta_{\mathrm{M}}^* + 3NkTD\left(\frac{\theta_{\mathrm{M}}^*}{T}\right);$$

$$E_T^a = \tfrac{1}{2} Nkf\theta_a^* + NkTf\,\frac{\theta_a^*/T}{e^{\theta_a^*/T}-1};$$

θ_m^* and θ_a^* are taken at the point $V = V^*$, using the Slater equation (5).

Solving equations (6) and (7) simultaneously, while assuming γ_a = const, i.e., independent of the crystal density, and taking the density dependence of γ_m in the form (5), one can find the value of γ_a and the exponent n corresponding to the repulsive forces in the interaction of TNT molecules.

Fig. 1. P_g –Hugoniot adiabat; T_g –temperature along the Hugoniot adiabat; $D = 7.23 \cdot 10^5$ cm/sec –detonation velocity of TNT for $V_0 = 0.599$ cm^3/g

Fig. 2. Points are experimental data taken from work ([4])

When solving equations (6) and (7), the exponent m, which determines the attraction between molecules, was assumed equal to 6. The solution of equations (6) and (7), using (5), gives $\gamma_a = 0.74$ and $n = 15$.

Bearing in mind that $P_x^m = -dE_x^m/dV$ and $\gamma_m = -V/\theta_m \cdot d\theta_m/dV$, we find for $n = 15$

$$\theta_m = \theta_m^0\,(\sigma/\sigma_0)^{1/3}\sqrt{(2\sigma^3-1)/(2\sigma_0-1)}, \qquad \gamma_m = \tfrac{1}{3}(17\sigma^3-1)/(2\sigma^3-1), \quad (8)$$

$$P_x^m = N\Lambda_m^* \rho^{*\,5/3}/(\sigma^6-\sigma^3).$$

Here $\sigma = V^*/V$; $\sigma_0 = V^*/V_0$; $\Lambda_m^* = 3.07 \cdot 10^{-12}$ erg/molecule is the sublimation energy per molecule; $\rho^* = 1/V^* = 1.8$ g/cm^3 is the density of the crystal at $T = 0$°K.

In calculating the interaction energy E_x^a of the atoms in the molecule, it was assumed that in formula (3) $k = 12$, and $l = 6$. The constant δ was chosen so that the pressure on the isotherm ($T = 291$°K) at the point $\rho_0 = 1.67$ g/cm^3 was equal to 0. Thus, the selected δ was equal to 0.15.

In Fig. 1a the experimental and calculated isotherms are presented. The discrepancy between the calculated and experimental isotherms in the initial region is due to the fact that the experiments were carried out only for compressed TNT powder with an initial density of 1.63 g/cm^3, whereas in the calculated isotherm the initial density of TNT was 1.67 g/cm^3, corresponding to the density of a single crystal at $T = 291$°K. The fact that the isotherms must

coincide for high pressures $P \geq 10^4$ atm; this was associated with the experimental fact that powdered TNT compressed to pressures $P \geq 10^4$ atm, after removal of the load, has the density of a single crystal, i.e., the real isotherm for a TNT single crystal must coincide with the isotherm of powdered TNT beginning with pressures $P = 10^4$ atm.

An analogous calculation of the equation of state was also carried out by the "free-volume"method developed by Kirkwood (3). This method makes it possible to dispense with equation (5) and the Debye approximation, which leads to the possibility of calculating isentropes in the expansion of the substance.

As a result of calculating the equation of state by the "free-volume" method, the following were obtained: $n = 18$, $\gamma_a = 0.756$, $\delta = 0.137$.

The values of some thermodynamic quantities obtained as a result of the calculation are given in Figs. 1 and 2.

Institute of Physics of the Earth named after O. Yu. Schmidt
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.