DETERMINATION OF THE TEMPERATURE DEPENDENCE OF HEAT CAPACITY FOR SOME MOLECULAR CRYSTALS OF NITRO COMPOUNDS

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An analysis of the existing approximations used for describing the dependence of heat capacity at a constant volume on the temperature of a molecular crystal has been carried out. It is shown that the considered Debye and Einstein approximations do not enable one to adequately describe the dependence of heat capacity at a constant volume on the temperature of the molecular crystals of nitro compounds. This inference requires the development of special approximations that would describe both low-frequency and high-frequency parts of the vibrational spectra of molecular crystals. This work presents a universal dependence allowing one to describe the dependence of heat capacity at a constant volume on temperature for a number of molecular crystals of nitro compounds.

Keywords: *equation of state, molecular crystal, Helmholtz energy, Planck constant, Boltzmann constant, Debye approximation, Einstein approximation.*

Introduction. The promising use of explosive processes in a number of branches of modern engineering is closely linked with the development of the mathematical models that adequately describe the physics of fast processes. The laws of mass, momentum, and energy conservation serve as the basis of the mathematical models of the mechanics of continua, thermodynamics, electrodynamics, etc. The conservation laws do not, however, belong to a closed system. The dependences between the quantities entering into the conservation equations are required, namely, the equations of state. They determine the fundamental relationship between the thermodynamic parameters, which does not depend on the method of attaining particular values of these parameters. The mathematical models of the thermodynamic properties of substances in different areas of the phase diagram are being constantly improved. An analysis and checking of the adequacy of proposed mathematical models require the existence of experimental data in a wide range of temperatures and pressures. In spite of the fact that a rather great number of works, both experimental and theoretical, are devoted to the solution of this problem, the theory of the construction of the equations of state of the molecular crystals of nitro compounds is very far from complete. The reason for this is that theoretical determination of the dependences that characterize the behavior of solid explosives, which relate to molecular crystals, is complicated by a large number of internal degrees of freedom of the molecules entering into the composition of molecular crystals of nitro compounds.

In connection with the difficulty of calculating the interparticle interaction in molecular crystals, the description of thermodynamic characteristics is usually given within the framework of semiempirical approaches when the functional dependence of the thermodynamic potential is determined proceeding from theoretical considerations, whereas the choice of certain coefficients of this dependence is calculated from the condition of the best fit to experimental data.

The thermodynamic properties of a substance are determined entirely if one of the thermodynamic potentials is known. It is convenient to proceed from the determination of the free Helmholtz energy $F(V, T)$ which is most simply associated with the model of substance structure [1–3]:

$$F = U + E_0 + kT\sum_{\alpha} \ln\left(1 - \exp\left(-\frac{h\omega_{\alpha}}{kT}\right)\right), \quad E_0 = \frac{1}{2}\sum_{\alpha} h\omega_{\alpha} . \qquad (1)$$

[†]Deceased

Here U is the energy of interaction between atoms, V is the specific volume, T is the body temperature, h is the Planck constant, k is the Boltzmann constant, ω_α is the frequency of normal vibrations, and E is the energy of zero vibrations. Summation in formula (1) is made by both the frequencies of vibrations of the molecules that form the crystal and by the frequencies of vibrations of the atoms entering into the composition of the molecules.

If the form of the function of the free Helmholtz energy $F(V, T)$ is known and all the values of the parameters entering into the description have been determined, differentiation may yield expressions for all the measured and calculated thermodynamic quantities:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T, \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,$$

$$E = F + TS, \quad C_P = T\left(\frac{\partial S}{\partial T}\right)_P, \quad C_V = T\left(\frac{\partial S}{\partial T}\right)_V.$$

At the present time, it is thought that the equations of state of molecular crystals contain two components: thermal and "cold" [4, 5]. The thermal component is determined by the vibrational motion of the molecules that enter into the composition of the crystal, whereas the cold one depends on the change in the energy of interaction both inside the molecule and between the molecules entering into the composition of the crystal depending on the volume. The relationship between the thermal and cold components is described by the dependence of the Grüneisen coefficient on the specific volume and is one of the basic problems in constructing the equations of state of solid bodies. The dependence of the Grüneisen coefficient on the specific volume may be determined by the Landau–Slater, Dugdale–McDonald formulas, and others [1].

The first step in modeling the thermal component of the equations of state is the determination of the functional dependence of heat capacity on temperature. In view of the fact that organic molecular crystals are thermally low-resistant, easily fusible, and sublimable already at low temperatures, experimental dependences of heat capacity on temperature in a wide range are known for a narrow range of substances in a gas phase [6, 7]. At the same time, of interest for a wide variety of fast processes is the behavior of solid organic substances in the region of high pressures and temperatures, experimental data for which on the dependence of heat capacity on temperature are absent. The only possibility of estimating the behavior of heat capacity in this case is the development of different computational schemes [8, 9].

The aim of the present work is the development of a computational scheme for determining the dependence of heat capacity on temperature for molecular crystals of nitro compounds that would rely on the existing experimental data [10, 11].

Analysis of the Approximations Used for Describing the Dependence of Heat Capacity on Temperature for the Molecular Crystals of Nitro Compounds. To determine the dependence of heat capacity on temperature for solid bodies increasing use has been made of the Debye or Einstein approximations. The most simple method of obtaining the values of the characteristic Debye temperature is an analysis of the dependence of heat capacity on temperature. It is just here, however, that the problems start to arise. The Helmholtz potential easily allows one to determine heat capacity at a constant volume C_V, whereas experiment yields data on heat capacity at a constant pressure C_P. Since at the temperatures at which experiments are carried out, anharmonicity is present, the heat capacities at a constant volume and at a constant pressure do not coincide. It can easily be shown that the coupling between the heat capacities is determined by the equality

$$C_P - C_V = T\frac{\alpha^2}{\beta_T}V,$$

where α is the isobaric expansion coefficient and β_T is the isothermal compressibility. One can easily determine the relationship between heat capacities and compressibilities:

$$\frac{\beta_S}{\beta_T} = \frac{C_V}{C_P},$$

where β_S is the adiabatic compressibility. In view of the fact that the adiabatic compressibility is associated with the adiabatic speed of sound C_S by the relation of the form

$$C_S^2 = \frac{V}{\beta_S},$$

one can easily determine the connection of the adiabatic compressibility and adiabatic speed of sound with the thermodynamic parameters determined experimentally [12, 13]:

TABLE 1. Thermal Parameters for the Equation of State of the Crystal

Parameters	Name of compound			
	Hexogen	PETN	TATB	Trotyl
μ, kg/kmole	222.13	316.50	258.18	227.13
ρ_0, kg/m^3	1806.0	1778.0	1937.0	1653.0
C_P, kJ/(kg·K)	1.1260	1.0880	1.0054	1.1260
C_V, kJ/(kg·K)	1.0533	1.0105	0.9995	1.1222
T_0, K	298.0	293.0	293.0	293.0
C_{S0}, m/s	2650	2320	1.4390	2200
$\alpha \cdot 10^{-3}$, K^{-1}	0.1927	0.2300	0.0995	0.0516

$$\beta_S = \frac{V}{C_S^2} = \beta_T - \frac{T\alpha^2 V}{C_P} .$$

The above relations allow one to determine an expression for heat capacity at a constant volume that involves the heat capacity at a constant pressure, isobaric expansion coefficient, adiabatic speed of sound, and the temperature:

$$C_V = \frac{C_P^2}{C_P + T\alpha^2 C_S^2} .$$

As the initial data for determining the initial thermal state of the molecular crystal use was made of experimental values of the corresponding quantities cited in the handbook of the Livermore [10] and Los Alamos National Laboratories [11]. For some crystals of nitro compounds Table 1 presents the available experimental data of heat capacity at a constant pressure, isobaric expansion coefficient, and isobaric speed of sound. The experimental data from Table 1 allow one to determine the heat capacity at a constant volume and test various models used for describing its behavior depending on temperature.

Debye Approximation. Following the Debye theory, in the vibrational part of the free Helmholtz energy we will replace the real spectrum of vibrations by a parabola cutting it off at a certain frequency. For this purpose we will rewrite expression (1) for the free Helmholtz energy in the form

$$F = U + E_0 + 9NRT \left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \xi^2 \ln\left(1 - \exp\left(-\xi\right)\right) d\xi , \qquad (2)$$

where R is the universal gas constant divided by the molecular mass of the substance μ, N is the number of atoms in a molecule, and θ_D is the Debye characteristic temperature.

Integrating over parts the expression for the vibrational component of the free Helmholtz energy $F(V, T)$ (2) and introducing the Debye function $D(x)$ by the formula given in [12, 13]

$$D(x) = \frac{3}{x^3} \int_0^x \xi^3 \frac{d\xi}{\exp \xi - 1} ,$$

we obtain an expression for the component of the free Helmholtz energy in the terms of characteristic temperatures:

$$F = U + E_0 + 3NRT \left(\ln\left(1 - \exp\left(-x_D\right)\right) - \frac{Dx_D}{3}\right), \qquad (3)$$

where $x_D = \dfrac{\theta_D}{T}$. Differentiating expression (3) twice with respect to the temperature at a constant volume, we will obtain an expression for heat capacity at a constant volume in the Debye approximation in terms of characteristic temperatures:

TABLE 2. Values of Characteristic Temperatures in the Debye Approximation

Parameters	Name of compound			
	Hexogen	PETN	TATB	Trotyl
$D_C(x)$	0.4466	0.4417	0.4250	0.4866
x_D	4.40	4.41	4.55	4.11
θ_D	1311.2	1292.1	1333.1	1204.2

$$C_V = 3NR\left(4Dx_D - \frac{3x_D}{\exp x_D - 1}\right). \tag{4}$$

It can easily be shown that the expression in parentheses on the right-hand side of Eq. (4) is the result of the integration by parts of the Debye heat capacity function $D_C(x)$ defined by the following expression:

$$D_C(x) = \frac{3}{x^3}\int_0^x \xi^4 \frac{\exp \xi}{\exp \xi - 1}\, d\xi.$$

The Debye function $D(x)$ and the Debye heat capacity function $D_C(x)$ are tabulated and presented in the reference literature on statistical thermodynamics [12]. The values of the characteristic temperatures in the Debye approximation are presented in Table 2.

In accordance with the Debye theory, the characteristic temperatures are calculated from experimental values of the longitudinal and transverse speeds of sound [10], and for the crystals considered they lie in the range ~90–160 K. It is seen from Table 2 that the cited values of the characteristic temperatures are much higher than in the indicated range.

While from the physical point of view the Einstein model for a monoatomic substance seems unlikely to be true, for molecular crystals, each of whose molecule has its own set of frequencies, a part of the spectrum corresponding to optical frequencies can be described approximately by the Einstein model [12].

Einstein Approximation. Following the Einstein theory, we will consider that all of the vibrational modes have the same frequency, and in the vibrational part of the free Helmholtz energy we replace the real vibrational spectrum by one efficient frequency. In this case, the expression for the free Helmholtz energy has the following form:

$$F = U + E_0 + 3NRT\, \ln\left(1 - \exp\left(-\frac{\theta_E}{T}\right)\right), \tag{5}$$

where θ_E is the characteristic Einstein temperature. Differentiating twice expression (5) with respect to the temperature at a constant volume, we will obtain an expression for the heat capacity at a constant volume in the Einstein approximation:

$$C_V = \frac{3NRx_E^2 \exp x_E}{(\exp x_E - 1)^2},$$

where $x_E = \dfrac{\theta_E}{T}$. It is known [12] that the values of the heat capacity at a constant volume determined by the Debye and Einstein theories coincide in the case where $\theta_E = 0.775\, \theta_D$, i.e., the characteristic Einstein temperatures for the crystals of nitro compounds considered in the work must lie in the temperature range ~70–125 K. The values of the characteristic temperatures in the Einstein approximation determined from the experimental data for the capacities from Table1 are presented in Table 3. It is seen that the obtained values of the characteristic temperatures in the Einstein approximation do not get into the range indicated above.

The Kitaigorodskii Approximation. In the works of A. I. Kitaigorodskii [13] on the thermodynamics of molecular crystals an assumption was made that to describe the behavior of an organic molecular crystal it is worthwhile to split its thermodynamic functions into intermolecular and intramolecular ones. The intermolecular part of the spectrum consisted of six vibrations per molecule: three vibrations constitute the vibrations of the molecule′s center of gravity and three vibrations, the vibrations of the Eulerian angles. In this case, the expression for the free Helmholtz energy can be presented in the form of two components: intermolecular and intramolecular ones:

TABLE 3. Values of Characteristic Temperatures in the Einstein Approximation

Parameters	Name of compound			
	Hexogen	PETN	TATB	Trotyl
x_E	3.24	3.25	3.34	3.05
θ_E	965.5	952.3	978.6	893.6

$$F = U_K + U_M + E_0 + 18RT \left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \xi^2 \ln\left(1 - \exp\left(-\xi\right)\right)d\xi + RT\sum_{i=7}^{3N} \ln\left(1 - \exp\left(-x_i\right)\right), \qquad (6)$$

where $x_i = \dfrac{h\omega_i}{kT}$ and ω_i are the frequencies of the normal vibrations of atoms inside molecules cited for hexogen, trotyl, TATB (triaminotrinitrobenzene), and PETN (pentaerythritol tetranitrate) in works [3, 14], and U_K and U_M are the intermolecular and intramolecular energies of interaction.

Differentiating twice expression (6) with respect to the temperature at a constant volume, we will obtain an equation for the heat capacity at a constant volume in the form of two components:

$$C_{VM} = R\sum_{i=7}^{3N} \frac{x_i^2 \exp x_i}{(\exp x_i - 1)^2}, \qquad (7)$$

$$C_{VD} = C_V - C_{VM} = 6R\left(4Dx_D - \frac{3x_D}{\exp x_D - 1}\right), \qquad (8)$$

where C_{VD} is the heat capacity component at a constant volume dependent on the vibrations of a molecule as a whole (three vibrations of the center of mass and three vibrations of the Eulerian angles) and determined in the Debye approximation, and C_{VM} is the component of the heat capacity at a constant volume dependent on the intramolecular vibrations. Part of the heat capacity C_{VM} is called intramolecular. The limiting values of the heat capacity components that correspond to high temperatures for all degrees of freedom are equal to $6R$ and $(3N - 6)R$, respectively. By virtue of the fact that molecular crystals have low Debye characteristic temperature (~90–160 K), it is already at room temperatures that part of the heat capacity determined by the vibrations of the molecule as a whole approaches its limiting value $6R$.

The force constants for calculating the spectra of normal vibrations inside the molecule were determined with the aid of the quantum-mechanical methods PM-3 and DFT described in detail in [15, 16]. To ensure the validity of the calculated intramolecular vibrational spectra the conformations of molecules were determined from the data of x-ray structural analysis of the corresponding molecular crystals. The IR spectra for the hexogen, trotyl, TATB, and PETN agree well with the well-known experimental data [11]. While the errors of measurements of C_P, α, and C_S exerts a weak effect on the results contained in Tables 2 and 3, in the given case, in calculating C_V, this fact is necessarily to be taken into account. The reason for this is that the value of the heat capacity C_{VD} that describes the vibrations of the molecule as a whole constitutes only 7–10% of the value of the total heat capacity C_V and can be compared with the total error of measurements of C_P, α, and C_S. The well-known experimental data [10, 11] make it possible to determine the value of C_V in a certain range presented in Table 4. The table also contains the values of C_{VM} calculated by formula (7) and values of C_{VM} determined by formula (8). By virtue of the fact that the pressure values 10–20 GPa characteristic for the initiation of detonation in the majority of solid explosives practically do not influence the intramolecular vibrational spectrum of nitro compound [17], to calculate the part of heat capacity associated with the intramolecular vibrations, it is possible to use the vibrational spectrum obtained for a single molecule. The values of the total dimensionless heat capacity at a constant volume C_V/R, dimensionless heat capacities C_{VM}/R, and C_{VD}/R for hexogen, PETN, TATB, and trotyl determined by formulas (7) and (8) are presented in Table 4.

As follows from the results of calculations presented in Table 4, the value $C_{VD}/R = 6$ gets into the range that determines the value of the heat capacity, which depends on the vibrations of the molecule as a whole. Consequently, the A. I. Kitaigorodskii approximation can be used in calculations of the heat capacity of molecular crystals, and, taking into

TABLE 4. Values of Dimensionless Heat Capacities at Constant Volume

Parameters	Name of compound			
	Hexogen	PETN	TATB	Trotyl
C_V/R	28.14–29.48	38.42	30.60–31.8	27.25–30.66
C_{VM}/R	22.35	32.33	24.48	21.62
C_{VD}/R	5.79–7.13	6.09	6.12	5.63–9.04

TABLE 5. Dependence of Dimensionless Heat Capacity at Constant Volume C_V/R on Temperature

Temperature T, K	Hexogen		PETN		Trotyl		Tetryl		TATB	
	1	2	1	2	1	2	1	2	1	2
293	28.0336	1.0000	38.8859	1.0000	27.3300	1.0000	34.3759	1.0000	30.5916	1.0000
333	30.5213	1.0887	42.2531	1.0866	29.6198	1.0838	37.1202	1.0798	33.6959	1.0979
373	32.8353	1.1713	45.4409	1.1686	31.7955	1.1634	39.6961	1.1548	36.6647	1.1888
413	34.9681	1.2474	48.4126	1.2450	33.8453	1.2384	42.1007	1.2247	39.3797	1.2728
453	36.9221	1.3171	51.1520	1.3154	35.7628	1.3086	44.3348	1.2897	41.8432	1.3503
493	38.7066	1.3807	53.6590	1.3799	37.5466	1.3738	46.4021	1.3498	44.0675	1.4214
533	40.3348	1.4388	55.9438	1.4387	39.1994	1.4343	48.3099	1.4053	46.0704	1.4866
573	41.8208	1.4918	58.0222	1.4921	40.7271	1.4902	50.0671	1.4565	47.8727	1.5462
613	43.1791	1.5403	59.9130	1.5407	42.1368	1.5418	51.6840	1.5035	49.4959	1.6007
653	44.4227	1.5846	61.6350	1.5850	43.4370	1.5894	53.1715	1.5468	50.9606	1.6505
693	45.5638	1.6253	63.2063	1.6254	44.6362	1.6332	54.5402	1.5866	52.2858	1.6961
733	46.6129	1.6628	64.6432	1.6624	45.7425	1.6737	55.8001	1.6232	53.4886	1.7378
773	47.5792	1.6972	65.9606	1.6963	46.7639	1.7111	56.9610	1.6570	54.5839	1.7761
813	48.4709	1.7290	67.1713	1.7274	47.7078	1.7456	58.0315	1.6881	55.5847	1.8114
853	49.2953	1.7584	68.2867	1.7561	48.5808	1.7776	59.0197	1.7169	56.5021	1.8439
893	50.0584	1.7857	69.3164	1.7826	49.3891	1.8071	59.9329	1.7435	57.3457	1.8740
933	50.7659	1.8109	70.2691	1.8071	50.1383	1.8346	60.7778	1.7680	58.1236	1.9018
973	51.4226	1.8343	71.1521	1.8298	50.8335	1.8600	61.5604	1.7908	58.8430	1.9277
993	51.7	1.8454	71.5696	1.8405	51.1623	1.8720	61.9300	1.8016	59.0826	1.9313

account the fact that the characteristic Debye temperature of molecular crystals are small, we may write an expression that determines the dependence of the heat capacity at constant volume on temperature in the form

$$C_V = 6R + R\sum_{i=7}^{3N} \frac{x_i^2 \exp(x_i)}{(\exp(x_i) - 1)^2}. \tag{9}$$

Using expression (9), we will calculate the dependence of the dimensionless heat capacity at constant volume C_V/R on temperature. The results of calculations for hexogen, PETN, trotyl, tetrile, and TATB are presented in Table 5. The values of the relative heat capacity, i.e., the ratio of the heat capacity at a constant volume at the temperature T to the value of the heat capacity at the temperature 293 K, are cited in column 2 of the table. It is seen from the analysis of Table 5 that for hexogen,
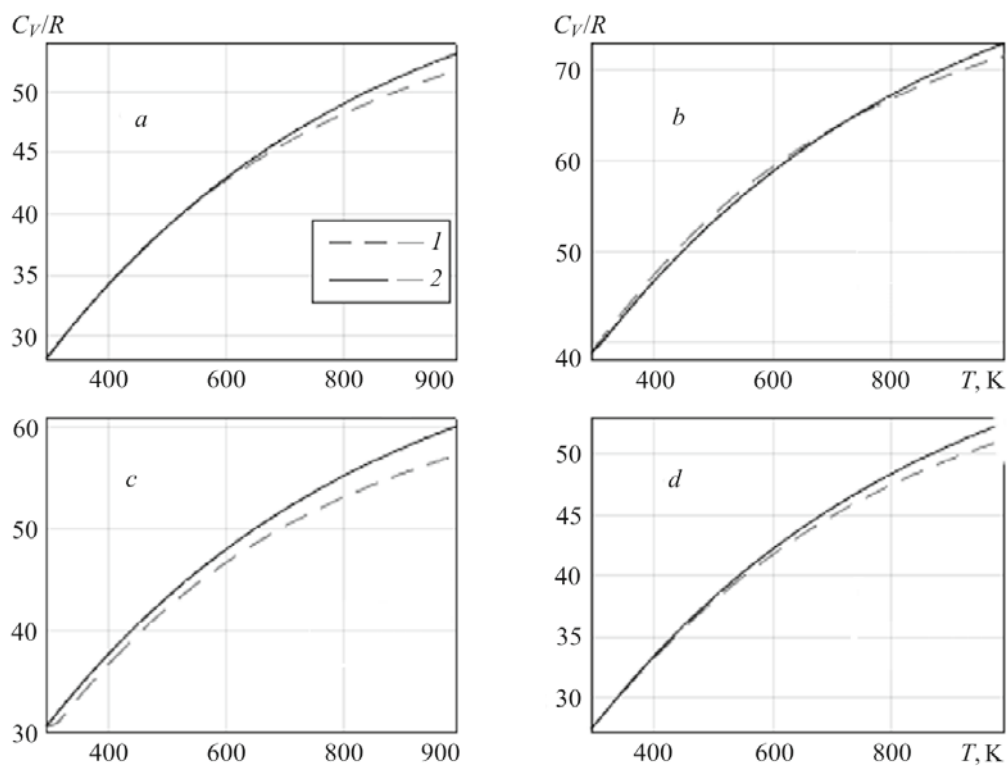
Fig. 1. Dimensionless heat capacity at onstant volume vs. temperature for hexogen (a), PETN (b), TATB (c), and trotyl (d): 1) data obtained by formula (9); 2) data obtained by formula (10).
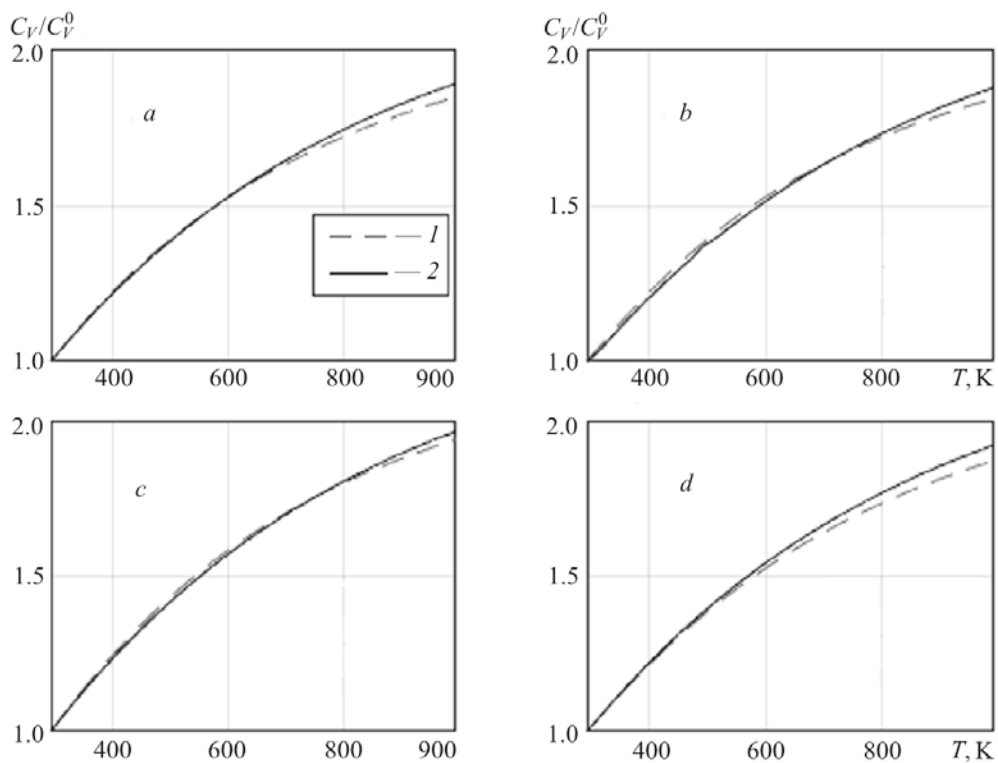

Fig. 2. Relative heat capacity at constant volume vs. temperature for hexogen (a), PETN (b), TATB (c), and trotyl (d): 1) data obtained by formula (9); 2) data obtained by formula (10).

TABLE 6. Relative Heat Capacities at Constant Volume vs. Temperature for Hexogen, PETN, TATB, and Trotyl

Temperature T, K	Hexogen			PETN			TATB			Trotyl		
	1	2	3	1	2	3	1	2	3	1	2	3
293	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
333	1.0887	1.0799	1.0861	1.0866	1.0816	1.0733	1.0979	1.0873	1.0933	1.0838	1.0842	1.0857
373	1.1713	1.1546	1.1663	1.1686	1.1579	1.1529	1.1888	1.1690	1.1802	1.1634	1.1629	1.1683
413	1.2474	1.2246	1.2409	1.2450	1.2292	1.2270	1.2728	1.2454	1.2611	1.2384	1.2366	1.2454
453	1.3171	1.2900	1.3103	1.3154	1.2960	1.2960	1.3503	1.3168	1.3364	1.3086	1.3055	1.3172
493	1.3807	1.3512	1.3749	1.3799	1.3585	1.3694	1.4214	1.3837	1.4065	1.3738	1.3700	1.3842
533	1.4388	1.4084	1.4349	1.4387	1.4169	1.4203	1.4866	1.4463	1.4718	1.4343	1.4303	1.4466
573	1.4918	1.4620	1.4908	1.4921	1.4716	1.4762	1.5462	1.5048	1.5326	1.4902	1.4867	1.5048
613	1.5403	1.5121	1.5429	1.5407	1.5228	1.5282	1.6007	1.5595	1.5892	1.5418	1.5395	1.5590
653	1.5846	1.5590	1.5913	1.5850	1.5706	1.5767	1.6505	1.6107	1.6419	1.5894	1.5889	1.6096
693	1.6253	1.6028	1.6363	1.6254	1.6154	1.6218	1.6961	1.6586	1.6910	1.6332	1.6351	1.6567
733	1.6628	1.6439	1.6782	1.6624	1.6572	1.6639	1.7378	1.7035	1.7366	1.6737	1.6783	1.7007
773	1.6972	1.6822	1.7172	1.6963	1.6964	1.7031	1.7761	1.7454	1.7792	1.7111	1.7187	1.7416
813	1.7290	1.7181	1.7535	1.7274	1.7331	1.7396	1.8114	1.7846	1.8188	1.7456	1.7565	1.7798
853	1.7584	1.7517	1.7872	1.7561	1.7674	1.7736	1.8439	1.8213	1.8556	1.7776	1.7919	1.8154
893	1.7857	1.7831	1.8186	1.7826	1.7994	1.8053	1.8740	1.8556	1.8899	1.8071	1.8250	1.8486
933	1.8109	1.8125	1.8479	1.8071	1.8294	1.8348	1.9018	1.8877	1.9219	1.8346	1.8560	1.8795
973	1.8343	1.8400	1.8750	1.8298	1.8575	1.8623	1.9277	1.9178	1.9517	1.8600	1.8850	1.9084
993	1.8454	1.8531	1.8878	1.8405	1.8708	1.8754	1.9313	1.9321	1.9658	1.8720	1.8987	1.9221

PETN, trotyl, tetrile, and TATB the values of the relative heat capacity at constant volume differ little, i.e., in this case the values of the relative heat capacity at constant volume can be described by a universal curve.

Another approach to the determination of the dependence of the heat capacity at constant volume on temperature was suggested in the work of V. G. Shchetinin [9]. In this work, for a number of crystals of nitro compounds it was shown that the function $C_V(T)$ is well described by an empirical expression of the form

$$C_V/C_{VH} = 1 - (1 - C_V^0/C_{VH}) \exp\left[-(T - T)/T_c\right],$$ (10)

where $C_{VH} = 3NR$, C_V^0 is the value of the heat capacity at the initial temperature, and T_c is the parameter determined in [9] for a number of organic compounds.

The results of calculations of the dependence of the dimensionless heat capacity at constant volume $C_V(T)/R$ and of the relative heat capacity $C_V(T)/C_V^0$ on temperature obtained by formulas (9) and (10) are presented in Figs. 1 and 2, respectively. As follows from the analysis of the results presented in Figs. 1 and 2, the data obtained by formulas (9) and (10) differ insignificantly within the limits of the measurement errors. The good coincidence of the dependences allows us to suggest the presence of a certain universal curve that describes the dependence of the dimensionless heat capacity at constant volume on temperature. The unification of the results of calculations performed by formulas (9) and (10) makes it possible to obtain an expression of the universal curve that describes the dependence of the dimensionless heat capacity at constant volume on temperature in the following form:

$$\frac{C_V}{C_V^0} = \frac{C_{VH}}{C_V^0} - \left(\frac{C_{VH}}{C_V^0} - 1\right) \exp\left[-(T - T_0)/T_*\right].$$ (11)

Table 6 presents the data of calculations of the relative heat capacities for hexogen, PETN, TATB, and trotyl performed by formula (9) (the results presented in column 1 of the table), formula (11) — the column numbered 2, and by formula (10) — the column numbered 3. As follows from the data of the table, the values of the relative heat capacity at constant volume calculated by formula (11) with the parameter T_* equal to 600 K lie in the range limited from below and from above by the values of the relative heat capacity at constant volume calculated by formulas (9) and (10), respectively.

CONCLUSIONS

As clearly follows from Tables 2–6, the results obtained permit the following conclusions:

1. The considered Debye and Einstein approximations do not provide the possibility to obtain correct values of the characteristic temperatures for the molecular crystals of nitro compounds.
2. The A. I. Kitaigorodskii approximation can be used in calculations of the dependence of the heat capacity at constant volume on temperature.
3. For hexogen, PETN, trotyl, tetrile, and TATB the values of the relative heat capacity at constant volume can be described by universal curve (11) with one parameter T_* equal to 600 K.

NOTATION

C_P, C_V, heat capacities at a constant pressure and volume, J/(kg·K); C_S, adiabatic speed of sound, m/s; C_{S0}, adiabatic speed of sound under normal conditions, m/s; C_{VD}, component of heat capacity at a constant volume dependent on the vibrations of the molecule as a whole and determined in the Debye approximation, J/(kg·K); C_{VM}, heat capacity component at a constant volume dependent on the intramolecular vibrations (intramolecular heat capacity at a constant volume), J/(kg·K); $C_{VH} = 3NR$, high-temperature limit for the total heat capacity at a constant volume, J/(kg·K); C_V^0, the value of the heat capacity at a constant volume at the initial temperature, J/(kg·K); $D(x)$, Debye function; $D_C(x)$, Debye heat capacity function; E_0, energy of zero vibrations, J/kg; E, internal energy, J/kg; $E(x)$, Einstein function; $F(V, T)$, free Helmholtz energy, J/kg; h, Planck constant, J·s; k, Boltzmann constant, J/K; N, number of atoms in a molecule; P, pressure, Pa; R, universal gas constant divided by the molecular mass of the substance μ, J/(kg·K); S, entropy, J/(kg·K); T, body temperature, K; T_0, temperature under normal conditions, K; T_c, T_*, parameters for formulas (10) and (11), K; U, energy of interaction between atoms, J/kg; U_K, U_M, intermolecular and intramolecular energies of interaction, J/kg; V, specific volume, m³/kg; $x_D = \dfrac{\theta_D}{T}$, $x_E = \dfrac{\theta_E}{T}$, dimensionless characteristic Debye and Einstein temperatures, K; α, isobaric expansion coefficient, K^{-1}; β_T, β_S, isothermal and adiabatic compressibilities, m·s²/kg; θ_D, θ_E, characteristic Debye and Einstein temperatures, K; μ, molecular mass of the substance, kg/kmole; ρ_0, density of the substance under normal conditions, kg/m³; ω_α, frequency of normal vibrations, m^{-1}.

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