

HEAT CAPACITY: EXPERIMENTS AND CALCULATIONS

Ways of Estimating the Heat Capacity of Crystalline Phases

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Abstract—A brief review is presented of contemporary ways of estimating heat capacity and determining their main advantages and disadvantages. Incremental schemes that predict the temperature dependences of heat capacity are considered in detail. Results of estimating the heat capacity of $(\text{InAs})_{1-x}(\text{GaAs})_x$ solid solutions using specially selected mixing rules are presented.

Keywords: heat capacity, ways of estimating heat capacity

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INTRODUCTION

Heat capacity is a key quantity for determining temperature dependences of the thermodynamic properties of different substances. Isobaric heat capacity is measured in a number of ways, including relaxation (used in physical property measuring systems (PPMS)), vacuum adiabatic calorimetry, differential scanning calorimetry (DSC), drop calorimetry, etc. The first three ways yield values of $C_p(T)$; in the last, we must differentiate the thermal effect with respect to temperature to obtain this dependence. All of these techniques differ in the temperature range of measurement, the accuracy of the data obtained, and the complexity of experiments. Adiabatic calorimetry has the smallest error (from 0.2% at 298 K to 10–15% near 0 K), while the upper range of such measurements does not exceed 300–350 K. DSC and drop calorimetry are characterized by large errors but allow measurements at fairly high temperatures. Another problem associated with measuring heat capacity is that the advantages of high-precision experimental techniques cannot be enjoyed for some substances since the error in measuring a property is determined by the reproducibility of a sample's properties rather than the accuracy of the procedure.

The question therefore arises of the possibility of predicting both low- and high-temperature values of $C_p(T)$ with errors comparable to the accuracy of an experiment.

The aim of this work is to give a brief overview of modern ways of estimating the heat capacity of crystalline phases. The focus is on the most popular ways of estimating, and we refer to existing reviews of alternative ways of predicting $C_p(T)$ that include numerous correlation relationships.

Ways of estimating the heat capacity of inorganic substances proposed before the 1990s were described in monographs [1–3] and review paper [4], while [5–10] are of special note in the works of subsequent decades. The main difference between the ways of estimating now being developed and those proposed in the mid-20th century is their authors' attempts to estimate accurately the temperature dependences of $C_p(T)$ beyond predicting $C_p(298.15 \text{ K})$.

THE NEUMANN–KOPP RULE AND MODIFICATIONS OF IT

Molar heat capacity $C_p(T)$ of a compound is often estimated using the Neumann–Kopp rule (NKR) by summing at a given temperature the molar heat capacities $C_{p,i}^\circ(T)$ of individual components multiplied by their amounts n_i in a compound:

$$C_p(T) = \sum_i n_i C_{p,i}^\circ(T), \quad (1)$$

thereby ignoring the change in heat capacity during as a compound forms from components [11].

Leitner et al. [6–8] gave a detailed analysis of the applicability of this rule to describe the heat capacities of different substances. The authors of [8] noted that the Neumann–Kopp rule can be used to describe mainly those substances in which the lattice contribution to the heat capacity of both the substance itself and its constituent components predominates. The undoubted advantage of [8] was an attempt to test the predictive ability of the Neumann–Kopp rule in a wide range of temperatures and analyze the factors that determine the deviation of experimental data from additivity.

Mixed oxides were used to show that at low temperatures, the nonzero value of $\Delta_{\text{ox}}C_p$ is due to the difference in the lattice contribution to the heat capacity of a mixed oxide caused by a change in the vibrational spectrum during the formation of the compound [8]. Analysis of the phonon spectrum of BaZrO_3 perovskite revealed a notable difference between the low-frequency acoustic modes of BaZrO_3 and BaO , which in the opinion of the authors results in positive deviation from the Neumann–Kopp rule.

At high temperatures, the deviation from additivity is associated with the difference between the values of molar volumes and thermal coefficients. The authors of [8] therefore proposed introducing correction ΔC_{dil} into the equation for calculating the heat capacity of a compound containing several components:

$$C_{p,m}(A_{x_A}B_{x_B}O_z) = x_A C_{p,m}(AO_a) + x_B C_{p,m}(BO_b) + \Delta C_{\text{dil}}. \quad (2)$$

To estimate the value of the last term in Eq. (2), we must have information about thermal coefficients (α_i , β_i) and molar volumes $V_{m,i}$ of a substance and its constituent components:

$$\Delta C_{\text{dil}} = -Tx_A x_B \frac{\beta_A \beta_B V_{m,A} V_{m,B}}{\beta_{AB} V_{m,AB}} \left(\frac{\alpha_A}{\beta_A} - \frac{\alpha_B}{\beta_B} \right)^2.$$

Consideration of the volume factor when using the Neumann–Kopp rule correlates with the conclusions of Meyer [12], who once showed that NKR satisfactorily holds for those solid compounds whose molar volume is approximately equal to the stoichiometric sum of the atomic volumes of the elements that form this compound. Meyer concluded that $C_{p,m}(\text{compound}) > C_{p,\text{at}}(\text{elements})$, if $V_m(\text{compound}) > V_{\text{at}}(\text{elements})$, and vice versa.

The proposal to improve the description of experimental data by introducing an additional term into Eq. (1) was not completely new. For example, Hurst and Harrison [13] recommended a similar solution that used the below ratio to estimate heat capacity:

$$C_p(T) = \sum_i n_i C_{p,i}^{\circ}(T) + n_{\text{misc}} C_{\text{misc}},$$

where the first sum is calculated with allowance for the properties of individual substances, and the second term is the product of two variable parameters. The main problem was in this case estimating the numerical value of this additional term.

Zimmermann et al. [14] proposed introducing a correction factor to improve the quality of heat capacity estimates using the NKR. For example, a correction factor of 0.982 was introduced for the sum of the terms on the right side of Eq. (1) in order to match results from estimating the heat capacity of $\text{Y}_2\text{Cu}_2\text{O}_5$ and the measured $C_p(T)$ values. The value of this factor was found using enthalpy increments $\{H^{\circ}(873 \text{ K}) -$

$H^{\circ}(T_{\text{ref}})\}$ of yttrium cuprate, measured in the same work.

To improve the accuracy of the Neumann–Kopp technique, it was proposed that properties of larger pseudo-components be summed [7, 15]. It was recommended that $C_p(T)$ of binary compounds AC_{c_1} and BC_{c_2} be used to calculate the heat capacity of compound $\text{A}_a\text{B}_b\text{C}_{c_s}$, rather than components A, B, and C:

$$C_{p,m}(\text{A}_a\text{B}_b\text{C}_{c_s}) = aC_{p,m}(\text{AC}_{c_1,s}) + bC_{p,m}(\text{BC}_{c_2,s}).$$

According to the authors, such an approach improves the reliability of predictions and expands the possibilities of obtaining adequate estimates when simple substances cannot exist in the solid state under the conditions of interest (e.g., one of the components is a volatile substance like O_2 , N_2 , or Hal_2).

INCREMENTAL SCHEMES

All incremental schemes for estimating heat capacity are based on the assumption that function $C_p(T)$ of a substance of interest can be presented as the sum of the corresponding contributions from individual structural fragments ($\hat{C}_{p,i}(T)$):

$$C_p(T) = \sum_i \hat{n}_i \hat{C}_{p,i}(T), \quad (3)$$

where \hat{n}_i is the amount of the i th component in the chemical formula of the compound. If we use only data at room temperature to determine the values of increments, the estimated heat capacity does not depend on temperature.

The specific form of functions $C_p(T)$ and thus $\hat{C}_{p,i}(T)$ varies in different works. For example, Robie et al. [16] used the dependence

$$C_p(T) = a + bT + cT^{-2} + dT^2 + e/\sqrt{T}$$

and expressions based on it with zero values of some parameters. Mostafa et al. [5] proposed describing the heat capacity with a polynomial:

$$C_p(T) = a + bT + cT^{-2} + dT^2.$$

A more complex dependence is used for crystalline substances in the ASPEN PLUS software package [17]:

$$C_p(T) = a + bT + cT^{-2} + dT^2 + fT^{-1} + g/\sqrt{T^3}.$$

Voronin and Uspenskaya [18, 19] were guided by [20] when selecting the type of temperature dependence of the heat capacity of mixed oxides. The recommendation was to use the below expression with non-negative values of coefficients k_1 and k_2 to describe $C_p(T)$ above 250 K:

$$C_p(T) = k_0 + k_1 T^{-0.5} + k_2 T^{-2} + k_3 T^{-3}.$$

Table 1. Heat capacity increments (J/(mol K)) for structural units U^{z+} ($z = 4, 5, 6$), La^{3+} , Th^{4+} , and O^{2-} [5]

Structural unit	$\hat{C}_{p,a,i}$	$\hat{C}_{p,b,i}$	$\hat{C}_{p,c,i}$	$\hat{C}_{p,d,i}$	N
U^{4+}	26.669	-29.923	-0.066	2.171	7
U^{5+}	13.890	-31.178	0.627	-2.126	4
U^{6+}	-14.769	50.875	1.654	-14.399	11
Th^{4+}	20.291	-28.458	0.351	-1.633	11
La^{3+}	15.803	-11.296	0.458	3.344	8
O^{2-}	28.152	12.043	-0.747	-4.023	1155

N is the frequency of this fragment being in the compounds that was considered during parameterization.

Depending on the form of the selected $C_p(T)$ function, the expressions for estimating the heat capacity can also differ. Mostafa et al. [5] used the ratio

$$C_p(T) = \sum_i n_i \hat{C}_{p,a,i} + \left(\sum_i n_i \hat{C}_{p,b,i} \right) 10^{-3} T + \left(\sum_i n_i \hat{C}_{p,c,i} \right) 10^6 T^{-2} + \left(\sum_i n_i \hat{C}_{p,d,i} \right) 10^{-6} T^2, \quad (4)$$

while it was assumed in [19] that

$$C_p(T) = \sum_i n_i \hat{C}_{p,k_0,i} + \left(\sum_i n_i \hat{C}_{p,k_1,i} \right) T^{-0.5} + \left(\sum_i n_i \hat{C}_{p,k_2,i} \right) T^{-2} + \left(\sum_i n_i \hat{C}_{p,k_3,i} \right) T^{-3}.$$

Mostafa's scheme can be considered the most popular incremental scheme now in use. In this work, we consider the main advantages and disadvantages of this approach using this scheme as an example.

The main advantage of any incremental scheme is the possibility of estimating a priori the heat capacity of a compound of interest. The quality of prediction depends directly on the amount and accuracy of the data used in the parametrization. In [5], the values of O^{2-} increments were calculated by allowing for this fragment being present in 1155 compounds. Na^+ was in 91 compounds; Cr^{2+} and Cr^{6+} , only in four compounds. The reliability of estimates were higher for those phases that contained structural fragments in a larger number of different compounds. Expanding the range of substances according to which the properties of the numerical values of the contributions from structural units are estimated increases the number of substances whose heat capacity can be predicted. However, the quality of a prediction often deteriorates, compared to schemes that use a narrower range of substances with similar structural characteristics [19].

The main disadvantages of incremental schemes include a system of invariants being created for parameters that correlate with one another according to $\hat{C}_{p,i}$. Under these conditions, ill-conditioned systems of equations must be solved numerically, and the depen-

dences of properties on temperature and composition cannot be effectively separated [19]. This affects the reliability of estimates in general. The predicted dependence can even turn out to be physically contradictory (e.g., with a maximum in the $C_p(T)$ curve calculated from ionic contributions).

One indicator of the quality of any thermodynamic model is its ability to reproduce properties not used in model parameterization. In [5], salts of calcium, magnesium, zinc, and manganese were selected as test objects. The discrepancy between the calculated and measured values varied from 0.63% for $CaCO_3$ to 7.63% for $CaSO_4 \cdot 2H_2O$. In this work, we decided to check selectively the possibility of predicting the properties of mixed oxides that form stoichiometric phases and solid solutions if experimental data for them were not considered when estimating the values of increments in [5]: $(U_{1-x}Th_x)O_2$ [21] and $(U_{1-x}La_x)O_{1.95}$ [22].

For $(U_{1-x}Th_x)O_2$ solid solutions, we verified the reproducibility of the experimentally measured values of enthalpy increment $H_T^\circ - H_{298.15}^\circ$ using the heat capacity increments recommended in [5] (Table 1). The results from the comparison of experiments and calculations for two compositions ($x = 0.5$ and 0.1) are shown in Fig. 1. The values of $\Delta H^\circ(T)$ agree below 700 K, and the discrepancy grew along with temperature (Fig. 1). The average value of deviations for three solid solutions ($x = 0.1, 0.5,$ and 0.9) was $\sim 5\%$; the maximum was 10%.

A somewhat different pattern is observed for $(U_{1-x}La_x)O_y$ solid solutions. The difference between these solutions and earlier ones is the different degrees of uranium oxidation, which must be considered when determining the properties of these phases. When calculating the heat capacity and the enthalpy increment, we used the numerical values of the parameters for the corresponding structural units (Table 1). The calculated results are illustrated by the graphs in Fig. 2. Function $\Delta H^\circ(T)$ of these solid solutions is characterized by the same patterns that were observed in uranium oxide doped with thorium. For the phases presented in Figs. 2b, 2d, the mean value of deviations in enthalpy $H^\circ(T) - H^\circ(298.15 \text{ K})$ taken modulo is 3.8

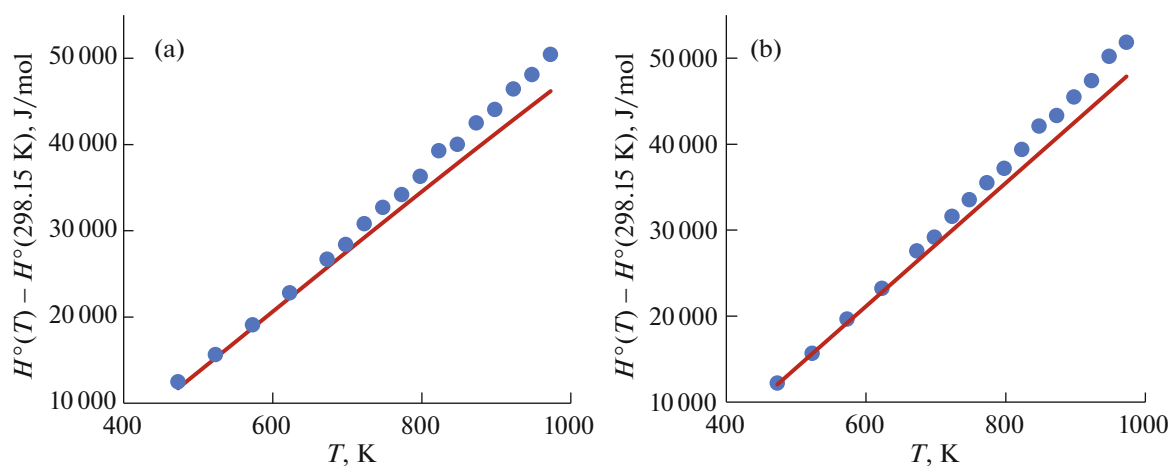


Fig. 1. Comparison of the calculated and measured values of the enthalpy increment for phases (a) $(U_{0.5}Th_{0.5})O_2$ and (b) $(U_{0.9}Th_{0.1})O_2$. Dots are experimental data from [21]; the line presents calculations using increments from Table 1.

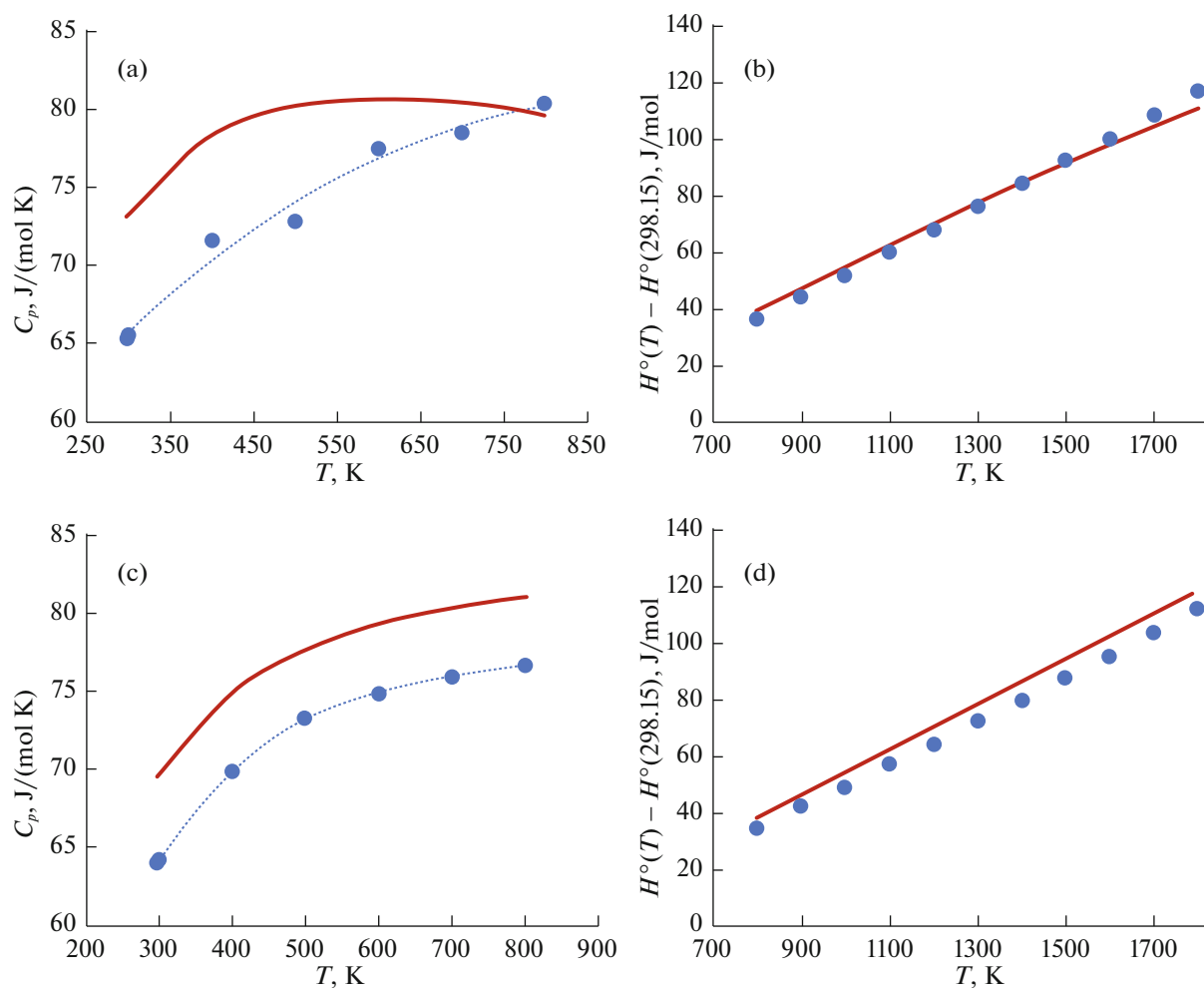


Fig. 2. Comparison of calculated and measured values of heat capacity and enthalpy increments for phases (a, b) $(U_{0.8}La_{0.2})O_{1.95}$ and (c, d) $(U_{0.6}La_{0.4})O_{1.87}$. Dots are the experimental data from [22]. The dotted curve shows the smoothed $C_p(T)$ values; the solid curve, calculations using increments from Table 1.

and 9.4% at uranium mole fractions of 0.8 and 0.6, respectively.

However, the somewhat non-physical behavior of the calculated heat capacity of the $(U_{0.8}La_{0.2})O_{1.95}$ phase is noteworthy. We must consider this artifact, since it is not an isolated case. Similar behavior was observed for the stoichiometric compound $Y_2Cu_2O_5$ [19] when using the increments from [5].

We also determined the possibility of extrapolating the predicted results to temperatures below 298.15 K using the example of ZrO_2 . Attempts to extrapolate the proposed model dependences to lower temperatures were unsuccessful. If the difference between the calculated and measured values was 0.1% for zirconium oxide at 298.15 K, it reached 1% at the temperature fell to 278 K and continued to grow (at 238 K, it was 5.6%). The quality of prediction deteriorated when ZrO_2 was doped with 0.08 mol % of Y_2O_3 , and the difference between $C_p(298.15)$ values was ~1%. At 278 K, however, the deviations were similar to those observed for pure zirconium oxide (i.e., they grew by 1%, relative to 298.15 K). Data from [23] were used in our calculations.

Besides the type of functional dependence $C_p(T)$, the choice of structural fragments (e.g., ions, ionic or neutral forms, associates) is also vital for developing an incremental scheme. The selected increments may not correspond at all to real structural elements of the described compounds or any existing individual substances. Ions are usually taken as pseudo-components because of the limited set of experimental data and the possibility of using it for averaging over large samples of experimental data. As was noted in [19], however, if individual atoms or ions rather than groups of atoms are selected as structural units for constructing an additive scheme, the consistent use of this way of calculating properties assumes there are zero formation functions for obtaining more complex phases from individual oxides (e.g., halides and sulfides).

GLASSER–JENKINS TECHNIQUE

The possibility of improving the predictive ability of the Neumann–Kopp rule by introducing an additional term $\Delta C_{p,dil}$, calculated using information on the volumetric properties of substances, was already discussed above.

The way of estimating heat capacity proposed in the works of Glasser and Jenkins [9, 10] is based on the correlation between heat capacity and the molar volume of ionic compounds. This approach allows us to predict C_p only at one temperature (298.15 K). To calculate heat capacity $C_p(298.15\text{ K})$, we propose using the expressions

$$C_p(298.15\text{ K}), \text{ J}/(\text{mol K}) \approx k_1 V_m + c,$$

$$C_p(298.15\text{ K}), \text{ J}/(\text{mol K}) \approx k' \left(\frac{M}{\rho} \right) + c,$$

where V_m is the molar volume (nm^3), calculated per formula unit of the compound; M is the molar weight (g/mol); ρ is density (g/cm^3); and k_1 , k' , and c are parameters of the equation. For a large number of ionic compounds, $k_1 = 1322\text{ J}/(\text{mol K nm}^3)$, and $c = -0.8\text{ J}/(\text{mol K})$. The values of the heat capacity increments for individual ions (cations and anions) and neutral particles (to determine the properties of hydrates) were refined in these works and can be combined with the set of increments proposed by Spencer in [24].

ESTIMATING HEAT CAPACITY WITH COMBINATIONS OF PLANCK–EINSTEIN FUNCTIONS

In 2013, Voronin and Kutsenok [25] proposed using a combination of Planck–Einstein functions to describe the temperature dependences of heat capacity in the range of 0 K to the melting temperature:

$$C_p(x, T) = \sum_{i=1}^m \alpha_i(x) C_E \left(\frac{\theta_i(x)}{T} \right),$$

$$\frac{C_E \left(\frac{\theta}{T} \right)}{R} = \frac{3 \left(\frac{\theta}{T} \right)^2 e^{\frac{\theta}{T}}}{\left(e^{\frac{\theta}{T}} - 1 \right)^2}, \quad (5)$$

where α_i and θ_i are variable parameters that generally do not have a strict physical meaning but ensure physically correct limiting behavior of the $C_p(T)$ function and an adequate description of results from measuring heat capacity.

This technique was subsequently developed and is now actively used in presenting $C_p(T)$ for substances of different natures [26, 27]. The first successful attempt to develop a way of determining thermodynamic properties using this approach was made in 2019 [28], with zeolites selected as the objects of study. To describe the heat capacity of this class of substances, the authors proposed using the expression

$$C_p(\vec{\alpha}^{(1)}, \dots, \vec{\alpha}^{(m)}, \vec{\theta}^{(1)}, \dots, \vec{\theta}^{(m)}, \vec{n}, T)$$

$$= \sum_{i=1}^m f_i(\vec{n}) \sum_{j=1}^{m_i} \alpha_j^{(i)} C_E \left(\frac{\theta_j^{(i)}}{T} \right),$$

where f_i are functions that depend on the composition of the zeolite, expressed in terms of the amounts of components (determined by vector \vec{n}); $\vec{\alpha}^{(i)}$ and $\vec{\theta}^{(i)}$ are the vectors of empirical parameters, optimized using least squares; m_i is the number of terms of the

Table 2. Types of the dependence of parameters $\alpha_i(x)$ and $\theta_i(x)$ on composition; Eqs. (6) were used to determine mixed parameters α_{2x} and θ_{2x}

i	$\alpha_i(x)$	$\theta_i(x)$
1	$\alpha_1(x) = (\alpha_1(1) - \alpha_1(0))x + \alpha_1(0)$	$\theta_1(x) = (\theta_1(1) - \theta_1(0))x + \theta_1(0)$
2	$\alpha_2(x) = \alpha_2(0)(1-x)^2 + 2\alpha_{2x}(1-x)x + \alpha_2(1)x^2$	$\theta_2(x) = \theta_2(0)(1-x)^2 + 2\theta_{2x}(1-x)x + \theta_2(1)x^2$
≥ 3	$\alpha_i(x) = (\alpha_i(1) - \alpha_i(0))x + \alpha_i(0)$	$\theta_i(x) = \theta_i(0) = \theta_i(1)$

i th increment; m is the number of increments; and C_E is the Planck–Einstein function calculated with Eq. (5). The contributions were estimated based on results from experimental studies of 46 different zeolites containing water and Li, Na, K, Tl, Ca, Mg, Sr, Ba, Fe, Al, and Si oxides at $T = 0–1000$ K. Anomalies in the heat capacity curves that were associated with phase transitions were excluded using the specially developed approach described in [29].

We made the next step in developing ways of estimating thermodynamic functions (particularly heat capacity) using a combination of Planck–Einstein functions. Using solid solutions $(\text{InAs})_{1-x}(\text{GaAs})_x$ as an example, we tested the possibility of using different mixing rules to estimate the heat capacity of solid solutions. This particular system was selected because of the availability of fairly accurate measurements of $C_p(T)$ at different phase compositions in a wide range of temperatures below 298 K, up to the temperature of melting for boundary compositions [30, 31]. It is also essential that ways of estimating the thermodynamic properties of alloys are extremely scarce, in contrast to those of mixed oxides or salt systems. Having a successful solution to the problem, we could propose a new way of estimating the thermodynamic properties of alloys.

Several versions of mixing rules for parameters α and θ were tested during our calculations. We obtained a satisfactory description of the experimental data by varying the dependence of the characteristic temperatures on the composition of only the first two largest parameters: θ_1 and θ_2 , while the remaining characteristic temperatures θ_i ($i \geq 3$) were fixed and independent of composition (this did not significantly affect the accuracy of the data described within the limits of their measuring errors). All parameters α_i ($i \neq 2$) and characteristic temperature θ_1 can be taken as linearly dependent on the composition. For characteristic temperature θ_2 and parameter α_2 , we must consider at least a parabolic dependence on composition. Without this, it is impossible to reproduce typical anomalies on the curves of excess heat capacities versus temperature (Fig. 3).

Allowing for these limitations, we calculated the heat capacities of the solid solution using Eq. (5) with the dependences of the parameters on the composition presented in Table 2. Mixed parameters α_{2x} and

θ_{2x} were calculated using relations with single empirical parameter $z = 1/24$, obtained by optimization using all available experimental data:

$$\begin{aligned}\alpha_{2x} &= \frac{\alpha_2(0) + \alpha_2(1)}{2}(1-z), \\ \theta_{2x} &= \frac{\theta_2(0) + \theta_2(1)}{2}(1-z).\end{aligned}\quad (6)$$

Four pairs of Planck–Einstein functions were sufficient for an adequate description of the temperature dependences of the heat capacities of the components. One more pair of parameters, α_1 and θ_1 , had to be kept when expanding the range of temperatures to the melting point, (a count was made again, starting from the pair of parameters that had the highest value of characteristic temperature θ_i). Parameters θ_i with $i \geq 3$ were forcibly equalized when optimizing, which simplified the procedure for applying the mixing rules. Numerical values of the parameters for the components (Table 3) are given with an excess number of significant figures for the correct reproduction of the dependences shown in Fig. 3.

When analyzing the dependence of the excess heat capacity of the solid solution (ss) ($C_p^{\text{ex}} = C_{p,\text{ss}} - (1-x)C_{p,\text{InAs}} - xC_{p,\text{GaAs}}$) on temperature (Fig. 3), two items attract our attention: (a) the absence of significant residual anomalies in dependences $C_p^{\text{ex}}(T)$ for the boundary components and the systemic presence of extrema in similar dependences for solid solutions and (b) fairly low values of the excess heat capacity, which

Table 3. Parameters α and θ of the Planck–Einstein functions for individual InAs and GaAs compounds

i	InAs		GaAs	
	α_i	θ_i	α_i	θ_i
1	0.353146	3453.40	0.318291	4187.68
2	0.535623	331.677	0.633299	358.682
3	0.274842	130.221	0.339065	130.221
4	0.199201	67.2747	0.042965	67.2747
5	0.003273	21.1449	0.00092034	21.1449

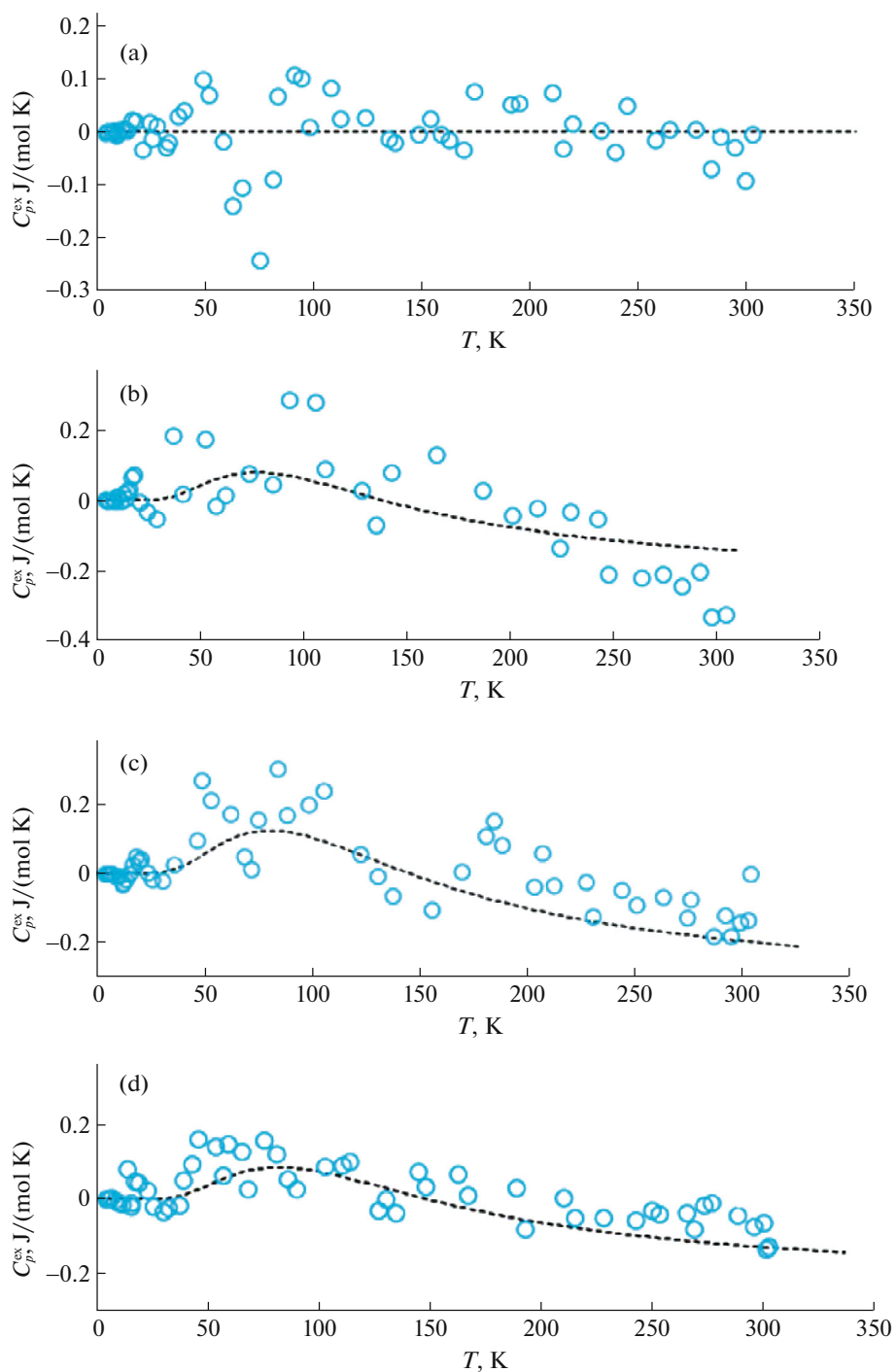


Fig. 3. Dependences of excess heat capacity on temperature for different compositions of $(\text{InAs})_{1-x}(\text{GaAs})_x$ solid solutions: $x =$ (a) 0, (b) 0.4, (c) 0.6, and (d) 0.8. Dots are data from [30]; the dashed curve presents our calculated results.

impose certain requirements on heat capacity measurements since their errors should be lower than C_p^{ex} . The mixing rules (the calculated curve with allowance for the mixing rules is indicated in Fig. 3 by a dashed curve) allow us to describe satisfactorily both the shape of the curves and the numerical values of the

excess heat capacity of solid solutions in the temperature range of 5–300 K.

CONCLUSIONS

Analysis of our calculations and the literature data show that incremental schemes generally describe the

experimental data better than the conventional Neumann–Kopp rule. However, we should check for non-physical anomalies in the $C_p(T)$ curves before using estimated values of heat capacity in calculating phase and chemical equilibria.

With a successful selection of mixing rules, we can develop schemes for estimating the thermodynamic properties of phases of variable composition, based on using combinations of Planck–Einstein functions. The main factor hindering the development of this kind of work is the limited high-precision data obtained via adiabatic calorimetry for a series of solid solutions in systems of different natures.

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