PHYSICAL AND MATHEMATICAL SCIENCES

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MATHEMATICAL MODEL OF ENTHALPY OF CONDENSED SUBSTANCES USING AVERAGE MOLAR VOLUMES OF ELEMENTS

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Annotation: The mathematical dependence of the enthalpy of formation on the average molar volumes of chemical compounds, the number of atoms in the formula unit and the temperature for the condensed state in the widest possible temperature range is obtained. It is established that in contrast to entropy and heat capacity, it is necessary to take into account the initial enthalpy of formation, which can be calculated by the additive scheme. For this the value of atomic enthalpies for all elements is calculated and it is shown that the proposed mathematical model in this form allows to calculate the entropy of a compound with an average accuracy of up to 120 J/mol (R^2-0.9).

Keywords: average molar volume, enthalpy of formation, temperature dependence.

Although volume-based thermodynamics provides for the possibility of using the volumes of substances to estimate the enthalpy of their formation [1, 2], the actual data on the dependence of the enthalpy of formation of condensed substances on the average molar volumes give a much smaller multiple regression coefficient compared to the dependences for heat capacity and entropy [3].

This is explained by the fundamental difference of this value from heat capacity and entropy. In contrast, its value does not approach 0 when the temperature decreases to absolute zero, but approaches a certain value, which can be defined as the enthalpy of formation of a compound at 0K (initial enthalpy of creation).

$$H_T = \int_0^T C_P dT = H_0 + H_C \qquad (1)$$

where T– temperature, K;

H_T – enthalpy of compound formation for temperature T, J/mol;

C_p – heat capacity of the compound at temperature T, J/(mol·K);

H_0 – enthalpy of formation, depending on the composition of the compound, J/mol;

H_C – enthalpy of formation depending on heat capacity, J/mol;

Adding an extra member (H_0) to the dependence of enthalpy on the average molar volume and size of the compound (number of atoms), which was used for the dependence of entropy and heat capacity [4,5], the multiple regression coefficient R^2 increases to 0.91 (see fig.1).

At the same time, the processing of the same data set as for heat capacity and entropy from the NIST database and the HSC Chemistry 9.0 program showed that the calculation of the initial enthalpy of formation of a compound is possible according to the same additive scheme as for the average molar volumes [6].

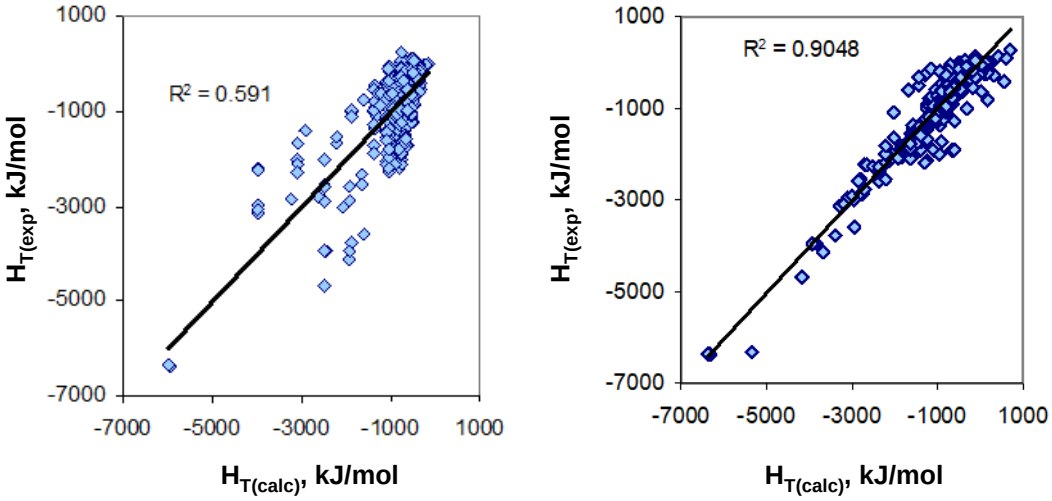

Fig. 1. Dependence of the isobaric heat capacity on the average molar volumes of substances without H_0 and with H_0

$$H_0 = \sum n_i H_{A,i}, \text{ для сполуки } A_a B_b C_c D_d \text{ або } E_{1n_1} ... E_{in_i} ... E_{kn_k} \quad (2)$$

where $H_{A,i}$ – initial enthalpy of compound formation;

$H_{A,i}$ – atomic (partial) enthalpy of formation;

A, B, C, D, E1, E_i, E_k – elements in the compound;

a, b, c, d, n_1, n_i, n_k – the number of elements in the compound.

As a result of using the values from table 1 the accuracy of the enthalpy of formation estimation is R^2=0.9 with an average error of 120 kJ/mol (fig.1) for temperature values from 200 to 900K.

As for entropy [4] with heat capacity [5], for the temperature dependence of enthalpy the dependence in the form of a linear function with three main members and one additional one was used

$$H_T = k_V \cdot V + k_N \cdot N + k_C + H_0 \quad (3)$$

where C_{pT} – entropy of a compound, J/(mol K);

V – average molar volume of the compound, cm^3/mol;

N – number of atoms in the compound;

k_V, k_N, k_C – coefficients of the equation;

H_0 – initial atomic enthalpy.

Table 1

Average atomic enthalpies of formation

Element	H_A, kJ/mol	Element	H_A, kJ/mol	Element	H_A, kJ/mol	Element	H_A, kJ/mol	Element	H_A, kJ/mol
H	13.7	Mn	-123.7	In	-141.9	Ta	-379.1	Bk	-409.8
He	819.6	Fe	-24.9	Sn	-112.7	W	-112.5	Cf	-409.8
Li	-174.7	Co	22.4	Sb	-37.4	Re	177.7	Es	-409.8
Be	-324.9	Ni	20.7	Te	3.1	Os	187.5	Fm	-409.8
B	46.1	Cu	-3.4	I	-65.8	Ir	187.5	Md	-409.8
C	80.4	Zn	-105.2	Xe	338.1	Pt	67.0	No	-409.8
N	307.4	Ga	-162.2	Cs	-218.7	Au	74.1	Lr	-543.1
O	-168.2	Ge	-133.2	Ba	-536.7	Hg	-6.5	Rf	-477.4
F	-270.7	As	3.7	La	-563.5	Tl	-112.7	Db	-394.4
Ne	614.7	Se	0.3	Ce	-598.8	Pb	-57.1	Sg	-180.3
Na	-237.6	Br	-105.8	Pr	-528.0	Bi	-9.4	Bh	122.9
Mg	-417.1	Kr	409.8	Nd	-505.6	Po	5.7	Hs	218.2
Al	-399.7	Rb	-202.2	Pm	-557.4	At	-20.5	Mt	190.6
Si	-254.8	Sr	-503.2	Sm	-562.3	Rn	204.9	Ds	99.4
P	-186.8	Y	-518.4	Eu	-489.7	Fr	-202.9	Rg	81.9
S	-26.2	Zr	-426.5	Gd	-532.5	Ra	-532.7	Cn	-28.7
Cl	-128.3	Nb	-318.2	Tb	-442.5	Ac	-563.5	Nh	-82.0
Ar	512.3	Mo	-54.6	Dy	-585.9	Th	-442.6	Fl	-43.1
K	-205.8	Tc	163.9	Ho	-534.2	Pa	-436.3	Mc	-35.9
Ca	-477.2	Ru	236.7	Er	-488.0	U	-417.8	Lv	12.9
Sc	-517.5	Rh	75.8	Tm	-558.2	Np	-409.1	Ts	-10.2
Ti	-380.8	Pd	50.2	Yb	-548.9	Pu	-413.5	Og	102.5
V	-214.3	Ag	67.1	Lu	-534.0	Am	-449.0		
Cr	-100.3	Cd	-27.4	Hf	-471.3	Cm	-409.8		

As shown in fig.2 the multiple regression coefficient R^2 for this equation reaches 90% even at temperatures of 100 K, but the most reliable values are in the temperature range of 220-800 K, which is connected with the use of polynomial equations to approximate the literature data.

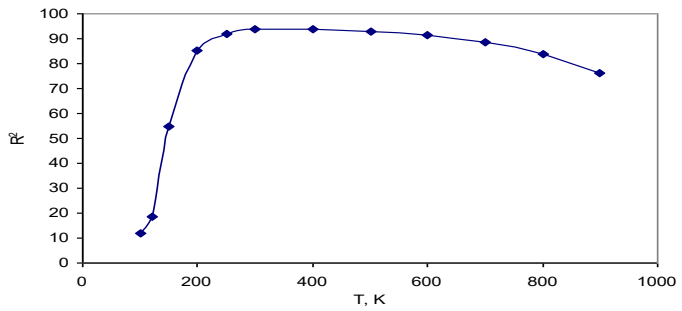

Fig. 2. Dependence of the multiple regression coefficient for the model according to equation (3) on temperature

The values of the coefficients of equation (3) can be approximated by the dependences obtained by integrating the dependences obtained earlier for the heat capacity [4], which ensures their consistency with theoretically justified values

$$k_V = 0.791 \cdot 10^{-3} \cdot \left\{ T \cdot \left(1 - 1.23 \cdot 10^{-4} \cdot \frac{T}{2} \right) - 27.1 \cdot \left[\arctan\left(\frac{T}{27.1}\right) + \frac{27.1 \cdot 1.23 \cdot 10^{-4}}{2} \ln\left(1 + \left(\frac{T}{27.1} \right)^2 \right) \right] \right\} \quad (4)$$

$$k_N = 13.7 \cdot 10^{-3} \cdot \left\{ T \cdot \left(1 + 1.09 \cdot 10^{-4} \cdot \frac{T}{2} \right) - 300.7 \cdot \left[\arctan\left(\frac{T}{300.7}\right) + \frac{300.7 \cdot 1.09 \cdot 10^{-4}}{2} \ln\left(1 + \left(\frac{T}{300.7} \right)^2 \right) \right] \right\} \quad (5)$$

$$k_C = 12.9 \cdot 10^{-3} \cdot \left\{ T \cdot \left(1 + 1.29 \cdot 10^{-3} \cdot \frac{T}{2} \right) - 116.5 \cdot \left[\arctan\left(\frac{T}{116.5}\right) + \frac{116.5 \cdot 1.29 \cdot 10^{-3}}{2} \ln\left(1 + \left(\frac{T}{116.5} \right)^2 \right) \right] \right\} \quad (6)$$

$$H_0 = H_A + 4.05 \cdot V - 79.35 \cdot N + 65.74 \quad (7)$$

Fig. 3 shows that the obtained dependences at temperatures above 250 K are very close to linear, which can simplify calculations for most cases. But at low temperatures their use is reasonable, because they give values that do not give gross deviations from theoretically justified values in contrast to polynomial dependences.

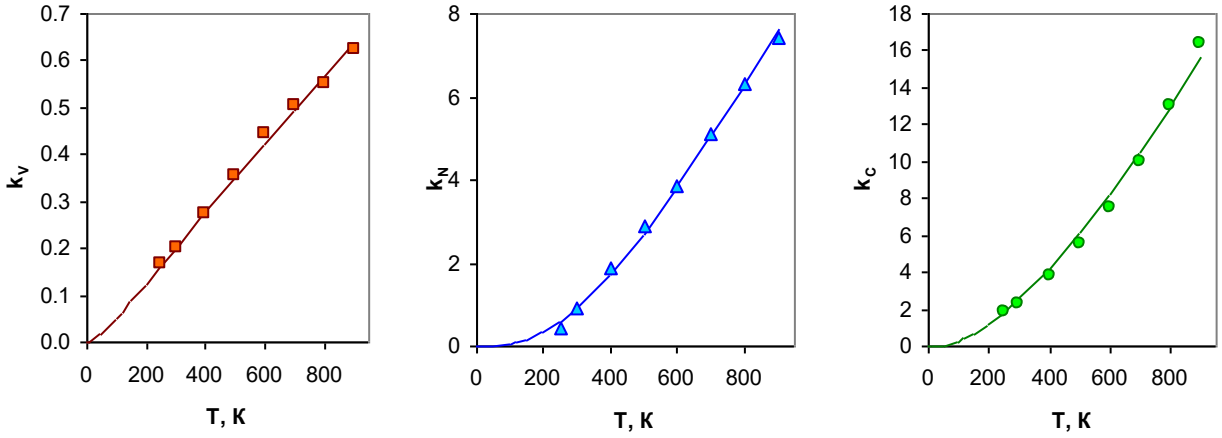

Fig. 3. Dependence of the model coefficients of equation (1) on temperature and their approximation by equations (4)-(6)

Comparison of the experimental data of the average heat capacity for the entire data array with the model for different values of the average molecular volume and the number of atoms in the formula unit of the compound (fig. 4), indicates a much greater influence of the size of the compound and its volume compared to temperature. The average values of these parameters for the array of experimental

data are N=4 and V=48 (marked by dots).

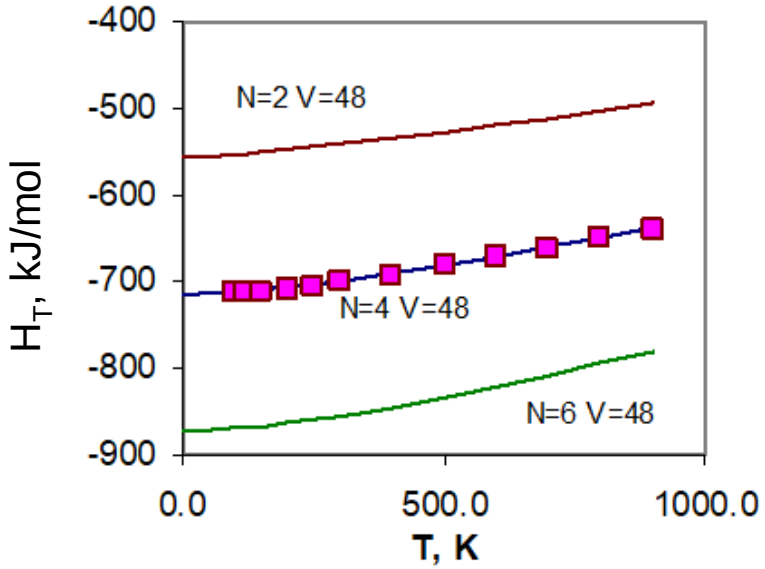

Fig. 4. Calculated entropy values by formulas (3)-(7)

As a result of additional studies, the mathematical dependence of the enthalpy of formation on the average molar volumes of chemical compounds, the number of atoms in the formula unit and the temperature for the condensed state in the widest possible temperature range was obtained. It is established that in contrast to entropy and heat capacity, it is necessary to take into account the initial enthalpy of formation, which can be calculated by the additive scheme. For this, the values of atomic enthalpies for all elements were calculated and it was shown that the proposed mathematical model in this form allows to calculate the enthalpy of a compound with an average accuracy of up to ±120 kJ/mol ($R^2 \approx 0.9$).

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