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USE OF AVERAGE MOLE VOLUMES OF ELEMENTS FOR CALCULATION OF THERMODYNAMIC PARAMETERS

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Annotation: The possibility of using molecular volumes of substances for prediction of heat capacity, entropy and enthalpy of formation of substances is analyzed. With the help of statistical data processing it is shown that the use of the additive model of average atomic molecular volumes does not reduce the accuracy of the obtained dependences. It is established that the accuracy of such calculations for the entropy and heat capacity of substances is close to the method of volume-based thermodynamics, but is simpler and more universal in use, and a similar dependence for calculating the energy of formation of substances is much less accurate and can be used only for its rough estimation.

Keywords: average molar volume, thermodynamic parameters, enthalpy, entropy, heat capacity, mathematical dependence.

One of the methods for estimating the thermodynamic parameters of substances is volume-based thermodynamics, which involves the use of molecular volumes of substances to predict their thermodynamic parameters [1].

The use of molecular volumes greatly simplifies the calculation of such important parameters as heat capacity, entropy and enthalpy of formation but there are many problems with obtaining the molar volumes. They can be obtained in different ways and none of them can be accepted as universal and exceptionally reliable [2-6].

Our studies have shown that the average molar volumes of substances calculated with the help of our proposed model [7-10] can be used for calculations of thermodynamic parameters similar to the volumes proposed in the literature.

For the analysis, data for more than 1000 inorganic and simple organic substances were taken, which were used earlier to obtain the average atomic molar volumes (table 1), which include at least 5 substances containing each of the chemical elements except for the new radioactive elements of the last period. The average accuracy of calculations of average molar volumes of substances according to this table using the additive model is 7% and for 90% of substances does not exceed 15%.

Thermodynamic parameters were taken from literature sources [11, 12] and open databases (NIST, CRCT, HSC) and their analysis showed that the difference between them reaches 10%, especially for relatively liquid compounds.

Table 1

Average molar atomic volumes

Element	Molar atomic volume, cm^3/mol		Element	Average molar atomic volume, cm^3/mol		Element	Average molar atomic volume, cm^3/mol	
	average	calculation		average	calculation		average	calculation
H	4.1	3.6	Nb	8.8	8.3	Tl	12.5	10.8
He	7.4	6.3	Mo	8.6	8.1	Pb	17.2	16.2
Li	5.4	5.4	Tc	9.3	8.6	Bi	20.4	21.6
Be	4.5	4.5	Ru	8.1	7.7	Po	24.5	27.0
B	4.4	3.6	Rh	7.8	7.4	At	30.0	32.4
C	5.7	5.4	Pd	8.3	7.2	Rn	36.9	37.8
N	5.9	7.2	Ag	11.3	10.8	Fr	30.0	32.4
O	6.7	9.0	Cd	13.0	12.6	Ra	25.0	27.0
F	8.2	10.8	In	11.5	9.0	Ac	17.3	17.1
Ne	13.3	12.6	Sn	15.5	13.5	Th	15.4	15.3

Na	10.9	10.8	Sb	19.1	18.0	Pa	13.8	13.5
Mg	7.8	9.0	Te	23.0	22.5	U	12.4	11.7
Al	7.4	5.4	I	27.5	27.0	Np	11.0	10.8
Si	8.7	8.1	Xe	31.0	31.5	Pu	11.7	11.7
P	10.3	10.8	Cs	27.2	27.0	Am	12.4	12.6
S	12.3	13.5	Ba	22.0	22.5	Cm	13.2	13.5
Cl	14.9	16.2	La	19.4	18.9	Bk	16.2	15.3
Ar	19.2	18.9	Ce	17.4	17.1	Cf	15.0	14.4
K	17.8	16.2	Pr	15.6	15.3	Es	14.9	14.4
Ca	14.5	13.5	Nd	14.1	13.5	Fm	14.8	14.4
Sc	7.9	7.2	Pm	12.6	12.6	Md	14.8	14.4
Ti	6.5	6.3	Sm	13.1	13.5	No	16.0	15.3
V	5.8	6.0	Eu	13.7	14.4	Lr	10.0	8.6
Cr	5.8	5.9	Gd	14.4	15.3	Rf	8.4	7.7
Mn	6.8	6.3	Tb	17.3	17.1	Db	7.6	7.4
Fe	5.5	5.4	Dy	16.0	15.3	Sg	8.0	7.2
Co	4.6	5.1	Ho	15.8	15.3	Bh	8.6	7.7
Ni	4.8	5.0	Er	15.5	15.3	Hs	7.5	6.8
Cu	7.9	7.2	Tm	15.3	15.3	Mt	7.5	6.5
Zn	9.4	9.0	Yb	16.3	17.1	Ds	8.5	6.3
Ga	9.2	7.2	Lu	10.4	9.9	Rg	17.5	18.0
Ge	11.5	10.8	Hf	8.8	9.0	Cn	20.0	19.8
As	14.1	14.4	Ta	7.7	8.7	Nh	14.0	12.6
Se	17.4	18.0	W	8.1	8.6	Fl	20.0	18.9
Br	21.1	21.6	Re	8.7	9.0	Mc	25.0	25.2
Kr	25.1	25.2	Os	7.7	8.1	Lv	30.0	31.5
Rb	21.3	21.6	Ir	7.6	7.8	Ts	36.0	37.8
Sr	16.6	18.0	Pt	8.6	7.7	Og	42.8	44.1
Y	11.4	9.5	Au	14.5	14.4			
Zr	9.8	8.6	Hg	16.4	16.2			

As a result of the previous regression analysis, it was found that the closest relationship of the average molar volume exists for the standard entropy, and the coefficient of determination R^2 when using the calculated average molar volumes almost does not differ from the experimental values.

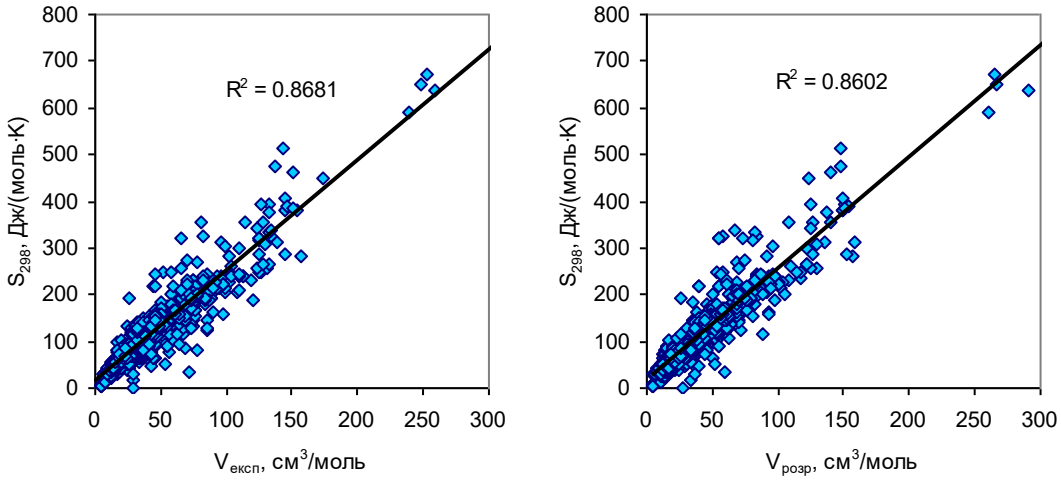

Fig. 1. Dependence of entropy on average molar volumes of substances

For calculations with an average accuracy of ±37 J/(mol K) the formula can be used

$$S_{298} = 2.37 \cdot V + 14.1 \qquad (1)$$

where

S_{298} – is the entropy of a substance at 298.15 K, J/(mol K);

V – average molar volume of a substance, cm3/mol.

It should be noted that significant deviations in the calculations are mainly observed for liquid substances, crystalline hydrates with a large number of water molecules and for substances with different crystal modifications.

A similar dependence, but with less accuracy, is present for the heat capacity (fig.2).

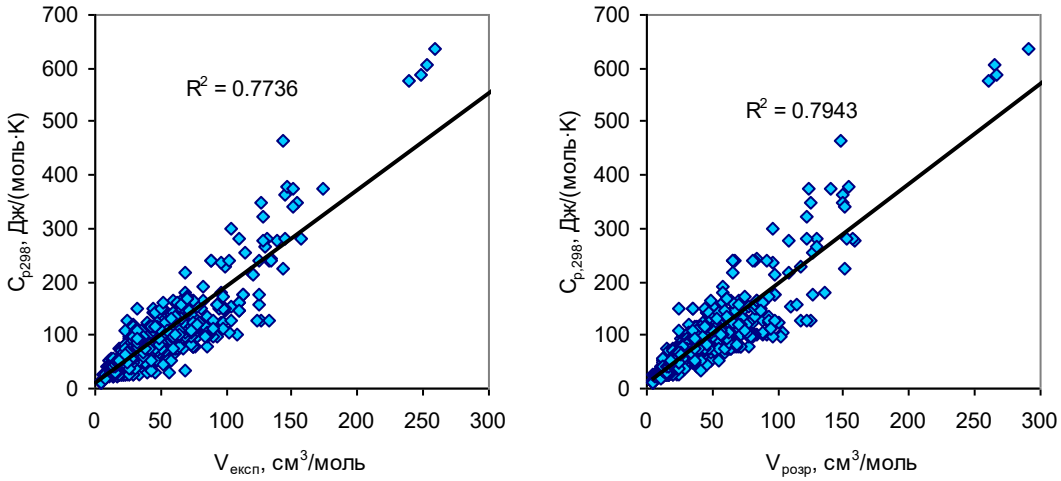

Fig. 2. Dependence of isobaric heat capacity on average molar volumes of substances

For calculations with an average accuracy of 47 J/(mol K) the formula can be used

$$C_{p,298} = 1.85 \cdot V + 8.34 \qquad (2)$$

where

$C_{p,298}$ – heat capacity of a substance at 298.15 K, J/(mol K);

V – average molar volume of a substance, cm3/mol.

The dependence for the enthalpy of formation has even lower accuracy and

does not confirm the dependence proposed in the literature (fig.3), and neither in the form of linear nor in the form of step dependence

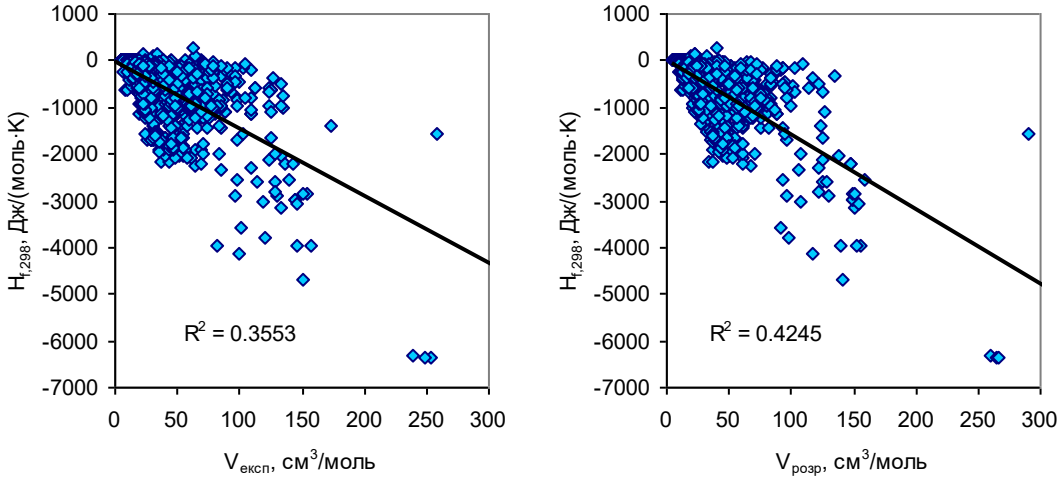

Fig. 3. Dependence of enthalpy of formation on average molar volumes of substances

However, even with its use, it is possible to estimate the enthalpy of formation of a substance using the formula

$$H_{f,298} = 12.6 - 15.2 \cdot V \qquad (3)$$

where

$H_{f,298}$ – enthalpy of formation at 298.15 K, J/(mol K);

V – average molar volume of a substance, cm3/mol.

Moreover, as can be seen from fig. 3, the accuracy of calculations of the enthalpy of formation when using the calculated values of molar volumes is higher (higher multiple regression coefficient R^2), which indicates a possible more complex dependence on the composition of the substance.

Thus, as a result of the studies, it was established that it is possible to use the average molar volumes of substances to calculate the thermodynamic parameters of substances using their average molar volumes based on the additive model of average atomic molar volumes. It is shown that the accuracy of such calculations for entropy and heat capacity of substances is close to the method of volume-based thermodynamics, but is simpler and more universal in use. It is also shown that such

dependence for calculations of energy of formation of substances is not accurate and can be used only for its rough estimation.

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