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MATHEMATICAL MODEL OF HEAT CAPACITY OF CONDENSED SUBSTANCES USING AVERAGE MOLAR VOLUMES OF ELEMENTS

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Annotation: The mathematical dependence of the isobaric heat capacity on the average molar volumes of chemical compounds and the number of atoms in the formula unit for the condensed state in the widest possible temperature range is obtained. It is established that, in contrast to entropy, the influence of the size of the compound (number of atoms of the formula unit) is less than the influence of the average molar volume. It is shown that the proposed mathematical model allows calculating the entropy of a compound with an average accuracy of ±8 J/(mol K).

Keywords: average molar volume, isobaric heat capacity, temperature dependence.

The molar isobaric heat capacity of substances in the condensed state is a necessary component for calculations of thermodynamic parameters of reactions and, as for entropy, its estimation is possible on the basis of volume-based thermodynamics [1, 2]. And using the molecular volumes of substances to predict the

values of heat capacity allows to obtain their estimates even with greater accuracy than the estimates of entropy values [3].

For entropy it is not even the values for standard conditions (295.15 K) that are important but rather the temperature dependence of the heat capacity over as wide a temperature range as possible.

To obtain this relationship we used the experience of creating a similar dependence for the entropy of compounds [4]. To create a mathematical model, data from the NIST database and the HSC Chemistry 9.0 program were used to develop a model of average molar volumes for different temperatures and the temperature dependence of entropy.

As a result, it was found that for any temperature, the dependence of isobaric enthalpy on the average molar volume is more significant than for entropy and for temperatures above 250 K the determination coefficient R^2 reaches 0.94, which provides an average error of the estimate ±8 J/(mol·K).

As for entropy for each temperature this dependence can be represented by a linear function with three variables

$$C_{p_T} = k_V \cdot V + k_N \cdot N + k_C \qquad (1)$$

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.

As can be seen from Fig. 1, the multiple regression coefficient R^2 for this equation almost does not change with increasing temperature and decreases very strongly at temperatures below 250 K. This is due to the use of standard polynomial dependencies in the program to approximate entropy values, which give an error of more than 3000 J/mol for some compounds, and even negative values at low temperatures.

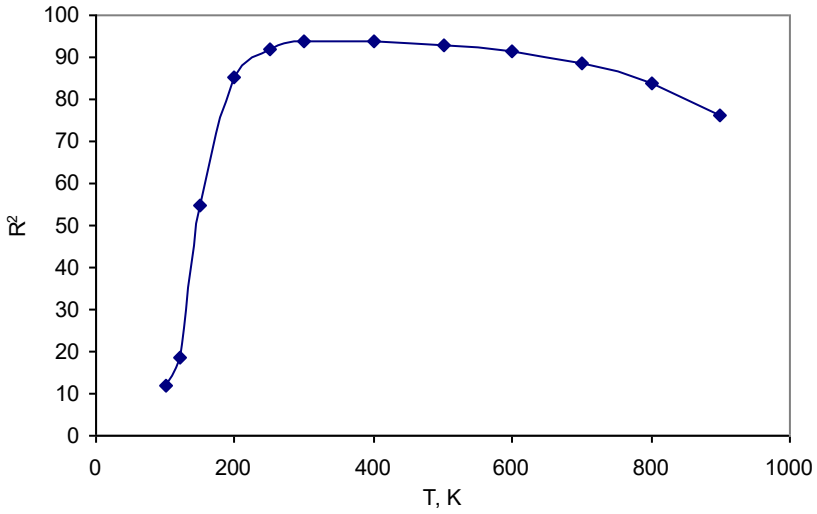

Fig. 1. Dependence of the multiple regression coefficient for the model according to equation (1) on temperature

As can be seen from fig. 2 for temperatures above 250 K the multiple regression coefficient remains almost unchanged. At lower temperatures, the multiple regression coefficient decreases rapidly which is caused by the use of polynomial dependences for enthalpy calculations in these databases.

At temperatures above 250 K the values of the coefficients of equation (1) change sequentially and can be approximated by quite simple dependences which as for enthalpy follow from the previously established general temperature dependence of entropy and isobaric heat capacity for condensed compounds [5].

$$k_V = 0.663 \cdot \left(\frac{T^2}{T^2 + 62.5^2} \right) \cdot \left(1 - 3.37 \cdot 10^{-4} \cdot T\right) \quad (2)$$

$$k_N = 15.03 \cdot \left(\frac{T^2}{T^2 + 152.5^2} \right) \cdot \left(1 + 4.50 \cdot 10^{-5} \cdot T\right) \quad (3)$$

$$k_C = 15.69 \cdot \left(\frac{T^2}{T^2 + 260.3^2} \right) \cdot \left(1 + 1.00 \cdot 10^{-3} \cdot T\right) \quad (4)$$

where T – temperature, K.

Fig. 2 shows a different character of the influence on the value of isobaric enthalpy of the average molar volume the number of atoms in the formula unit and the free term of dependence (1).

A temperature increase of 600 K reduces the effect of the average molar volume by about 20%. The temperature dependence of the heat capacity on the number of atoms in the formula unit is similar to the isochoric heat capacity, and the temperature dependence of the free component is similar to the isobaric heat capacity [6, 7].

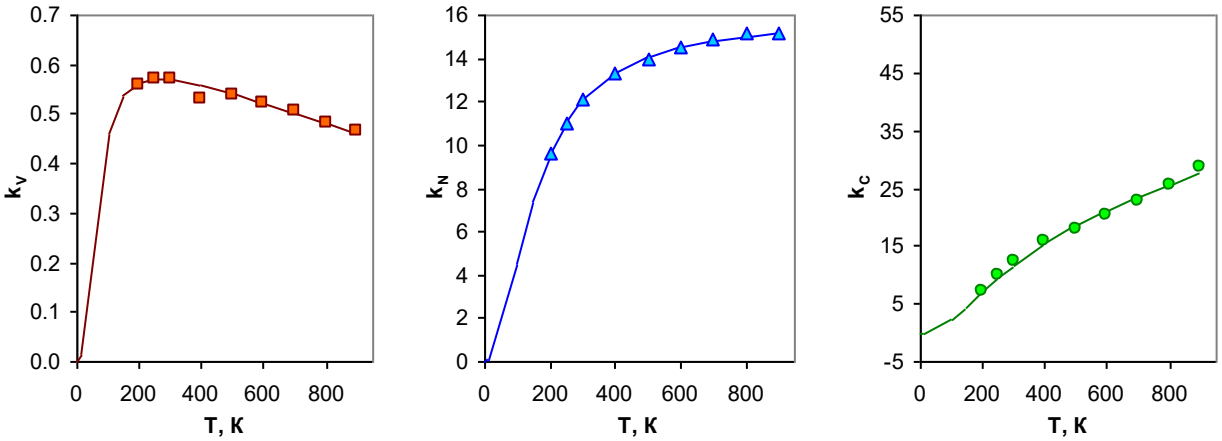

Fig. 2. Dependence of the model coefficients of equation (1) on temperature and their approximation by equations (2)-(4)

Comparison of the experimental data of the average heat capacity for the entire array of data with the model for different values of the average molar volume and the number of atoms in the formula unit of the compound is shown in fig.3. The average values of these parameters for the array of experimental data are N=4 and V=48 (marked by dots).

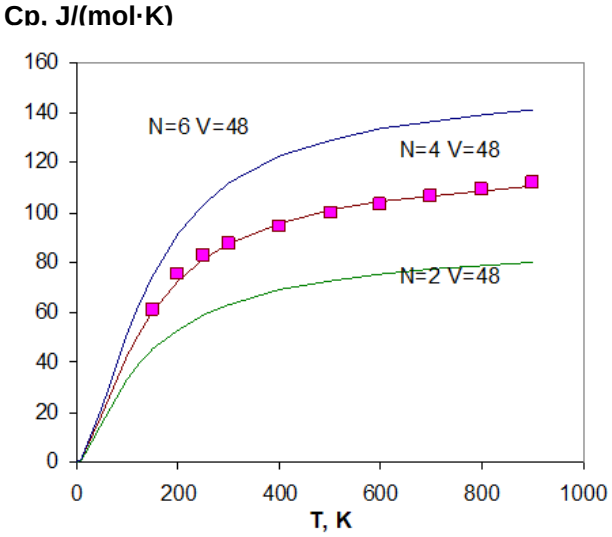

Fig. 3. Calculated entropy values by formulas (5) and (6)

More detailed studies allowed us to obtain the mathematical dependence of the isobaric heat capacity on the average molar volume of chemical compounds and the number of atoms in the formula unit for the condensed state in the widest possible temperature range. It is established that, in contrast to entropy, the influence of the size of the compound (number of atoms of the formula unit) is less than the influence of the average molar volume. It is shown that the proposed mathematical model allows calculating the entropy of a compound with an average accuracy of ±8 J/(mol·K).

REFERENCES

1. L. Glasser, H. D. Jenkins. Volume-Based Thermodynamics: A Prescription for Its Application and Usage in Approximation and Prediction of Thermodynamic Data. J. Chem. Eng. Data 2011, 56, 874–880 / dx.doi.org/10.1021/je100683u

2. P. Ganguly, “Atomic sizes and atomic properties,” J. Phys. B At. Mol. Opt. Phys., vol. 41, no. 10, p. 105002, May 2008

3. Козуб П. А., Мірошніченко Н. М., Лук'янова В. А., Сирова Г. О., Козуб С. М., Мартинюк М. М. Використання середніх мольних об’ємів елементів для розрахунку термодинамічних параметрів // Modern directions of scientific research development. Proceedings of the 16th International scientific and practical conference. BoScience Publisher. Chicago, USA. 2022. Pp. 51-60. URL: https://sci-conf.com.ua/xvi-mizhnarodna-naukovo-praktichna-konferentsiya-modern-directions-of-scientific-research-development-7-9-09-2022-chikago-ssha-arhiv/

4. Kozub P.A., Kozub S.N. (2018) Lognormal distribution as universal function of temperature dependence of heat capacity. // Science and society. Proceedings of the 5th International conference. Accent Graphics Communications & Publishing. Hamilton, Canada. 2018. Pp. 682–692.

5. Козуб П. А., Мірошніченко Н. М., Лук'янова В. А., Сирова Г. О., Козуб С. М., Мартинюк М. М. Математична модель ентропії конденсованих речовин з використанням середніх мольних об’ємів елементів // Modern science: innovations and prospects. Proceedings of the 13th International scientific and

practical conference. SSPG Publish. Stockholm, Sweden. 2022. Pp. 56-60. URL: https://sci-conf.com.ua/xiii-mizhnarodna-naukovo-praktichna-konferentsiya-modern-science-innovations-and-prospects-18-20-09-2022-stokgolm-shvetsiya-arhiv/.

6. Kozub P.A. Universal dependence for the approximation of isobaric specific heat of solids/ P.A.Kozub, S.N. Kozub // Science and society. Proceedings of the 11th International conference. Accent Graphics Communications & Publishing. Hamilton, Canada. 2019, Pp. 151-155.

7. Kozub P.A. Set of functions for calculation of specific heat of solids / P.A.Kozub, S.N. Kozub // Perspectives of science and education. Proceedings of the 10th International youth conference. SLOVO\WORD, New York, USA. 2019, Pp. 394-397.