International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.

https://ijpsat.org/
Vol. 46 No. 1 August 2024, pp. 15-23

The Essence of the Structural Ingredient Additivity Method and the Analysis of the Obtained Results

V.Gordeladze, T. Kentchoshvili

Georgian Technical University

Corresponding Author: V.Gordeladze

Abstract – The paper proposes the main essence of the "Method of Additivity of Structural Ingredients" aimed at determining the thermal constants of solid silicates and a brief analysis of the results obtained by the implementation of this method.
It is shown that unlike the existing calculation methods of the thermal constants of these compounds, the realization of the proposed method is mainly based on the data in the core of thermodynamics itself.
It is noted that this method is based on information in silicates and physical chemistry in general. It is subject to the principle according to which the degree of structural organization of each new solid body is determined by combining elements with a lower and higher degree of structural arrangement, expressed in energy units.
The essence of the concepts used in the proposed method, the calculation method and the evaluation of the obtained results are given. The opinion is expressed that this method belongs to the so-called to the number of "relatives". Using it, it is possible to determine unknown experimental data to evaluate this or that solid, anhydrous substance (reaction).

keywords: thermodynamics, structural ingredient, thermal constant, Additivity, silicate, crystallochemistry.

I. INTRODUCTION

Based on research conducted by theoreticians and practitioners of many countries of the world, it was generally recognized that without thermodynamic studies it is impossible to solve many theoretical or technical problems. Thermodynamic research methods occupy an important place in many fields of science and technology, including silicate chemistry and practice. Nevertheless, a number of delays in process (event) forecasting are not so rare. .

The results obtained by thermodynamic analysis should be characterized by high degree of reliability, that is why certain requirements should be taken into account in the thermodynamic explanation of the process (event). Including:

- High degree of reliability of normal and/or standard molar thermodynamic parameters (normal and/or standard molar values) of all components included in the research system;
- Selection of the appropriate thermodynamic model of the research system;

II. MAIN PART

In the theory and practice of silicates, the thermodynamic method based on the Gibbs free energy minimization method is mostly used. Therefore, the standard molar thermodynamic parameters (thermochemical constants) of the reactants included in the system and the products obtained by their interaction are used in the calculation [1].

As we mentioned above, the thermochemical constant of any substance determined by experiment should be characterized by a high degree of reliability. Due to their direct (experimental) determination, more and more effective means, the

International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.

https://ijpsat.org/
Vol. 46 No. 1 August 2024, pp. 15-23

volume of databases of constants is continuously "filled", but the rate of growth of these databases is significantly lower than the demand for their increase, which is caused by the creation of innovative technologies.

The inconsistency of these two factors led to the creation of methods in which the experiment is either not used, or its use is minimized. Most of such methods are subject to a regular analogy of the thermodynamic properties of compounds. Calculation methods are considered as "approximates", which are "capable" of determining the thermal constants of substances that are not in the databases. Later, as a result of multiple checks of a particular method, the calculations obtained by the approximate method can take an appropriate place in the databases.

In the chemistry and practice of silicates, more than a dozen calculation methods are used, there is a rather extensive literature about them. We highlight [2] among them. It contains the calculation methods created and positively tested in 1986, researches in this direction were not stopped in the following years, as evidenced by the works published by the metallurgical scientists of Georgia [3-5]. In all of them, it is stated that in order to determine the thermal constants of compounds, it is necessary to search for chemical and structural compounds of the same type for silicates, a number of properties from other fields of science, different constants for individual compounds, the inclusion of experiments on energy indicators and the use of many other measures, which cannot ensure the achievement of the set goal in a short time.

We certainly do not deny the importance of the methods for determining the thermal constants of substances listed above and in other sources, but we believe that the information in the core of thermodynamics is not properly used in them. This opinion is based on the principles of modern crystal classification of silicates [6,7], views on solid-phase reactions, information on near and distant forces acting in solid bodies [8,9] and the nature of additivity of physical-chemical properties of these bodies [10,11], as well as Data given in databases (standard tables) of thermal constants of solid bodies [2,12-17].

Based on the information in [18-23], the following postulate was proposed:

- Each new state of silicates is the result of the combination of its previous and subsequent states, expressed in energy units.

The postulate can be expressed by the following equation:

$$E_1 + E_2 = E_3 \pm E_4 \quad (1)$$

Where, E_1 is, the energy of a silicate with less structural arrangement than the searcher (new) silicate, E_2 - the energy of a silicate with a more structural arrangement than the searcher, E_3- Energetics of structural arrangement of silicate, and as for E_4 - it is released (absorbed) energy, which is created as a result of interaction of silicates E_1 and E_2.

If we take into account the crystal-chemical classification of silicates equation (1) is transformed, for its various subclasses of silicate (silicates), equation (1) is transformed into a somewhat different equation. However, in accordance with the above principle.

- For island silicates, equation (1) will have the following form::

$$R_1 + R_2 = Pd \pm E_4 \quad (2)$$

Where, R_1 - the reagent is a substance that is not characterized by silicate arrangement; R_2-substance, the structural arrangement of which is higher than the structural arrangement of the product (Pd). R_1 can be any oxide except SiO_2, or an inorganic substance having no silicate structure. R_2 reagents include silicates with group, ring and isolated groups;

- In the case of group silicates, the expression (2) remains valid. The difference is that the role of R_1 can be an island silicate, which has a lower degree of structural arrangement than the product - a group compound;
- For ring silicates, two reagents can act as R_1, and a silicate with a structural organization greater than Pd (chain, layered, framework) will play the role of R_2.;

International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.

https://ijpsat.org/
Vol. 46 No. 1 August 2024, pp. 15-23

With this logic, the model of receiving silicates of the rest of the subclasses of the crystal chemical classification of silicates is understood.

Based on these considerations, the method of determining the thermal constants of solid anhydrous silicates was called the method of additivity of structural ingredients.

The method of additivity of structural ingredients operates with the following definitions and concepts.:

- **Etalon** (Et) is a silicate (silicates) of any subclass of the crystal-chemical classification of silicates, whose thermal constants are distinguished by a high degree of reliability. It is denoted by the symbol Pd in equation (2), symbols are used to indicate its energy - E_{Et} or A.
- **Structural Ingredient** (SI) It is a simple chemical compound with the same demand as Et. SI participates in the formation of each research substance (silicate). It corresponds to the symbols marked R_1 and R_2 in image (2). E_{SI} symbol is used in The method of additivity of structural ingredients to denote its energy. SI energy sum (ΣE_{SI}) is denoted by A′. In the ideal case ($\Sigma E_{SI}=E_{Et}(A)$= A′, but in most cases the formula is as follows: $A/A' \neq 1$.
- **Relevance coefficient** (K_{acc}) is the A/A′ ratio of the energy ratio of each etalon of a specific subclass of the crystal-chemical classification of silicates with ΣE_{Si}: if several silicates in a certain subclass are to be searched, then the K_{acc} (ΣK_{acc}) of each of them is determined.
- **Leveling coefficient** (K_{niv}) represents the ratio of ΣK_{acc} to the number of standards ($K_{niv}=\Sigma K_{acc}/n$). The obtained value is a multiplier of the image of determining the thermal constant of compounds of any subclass of the crystal-chemical classification of silicates.

$$B=K_{niv} \cdot A'$$

- **Error rate** (Δ) represents the difference between the thermal constants of each subclass compound standard and the same compound obtained by The method of additivity of structural ingredients (Δ=A-B). It is expressed in energy units and/or percentages.

For example, in Table 1, the sequence of determination of thermal constants of three ring silicates by The method of additivity of structural ingredients and the obtained results are presented..

According to the information presented in the table, the thermal constants determined by The method of additivity of structural ingredients are not significantly different from those specified in the databases: - in the case of $\Delta H^0_{f.298}$-, the difference does not exceed 1.6 kcal/mol, - in the case of $\Delta G^0_{f.298}$ - 1.9 kcal/mol, in the case of S^0_{298}- 0.4 cal/(mol • K), and in the case of $C^0_{p.298}$-– 0.7 cal/(mol • K).

Practice has shown us that The method of additivity of structural ingredients. It provides determination of thermal constants of most of the compounds of the subclasses included in the crystal-chemical classification of silicates. with sufficient accuracy, but the number of compounds inconsistency of which between the results obtained by The method of additivity of structural ingredients and the values entered in the databases was determined is not so small. In our opinion, there are two main reasons for this discrepancy:

The first of them is related to the unreliability of the values of the thermal constants of a number of substances in the databases - the confusion of the values of the constant of the same substance in different sources is much higher than allowed for standards.

The second reason is caused by the fact that the crystal-chemical classification of silicates. Contains such subclasses in which there are compounds with different structural features. However, the principles of construction of the crystal-chemical classification of silicates are not violated. This may explain the separation of a number of compounds in a specific subclass into a group of subclasses of compounds and into individual substances.

International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.

https://ijpsat.org/
Vol. 46 No. 1 August 2024, pp. 15-23

Based on the peculiarities of the structure and, accordingly, the energy of the substances. Eliminating both causes requires time and continued research.

Up to 120 simple and complex anhydrous solid silicate thermal constants of all subclasses included in the crystal-chemical classification of silicates are calculated by The method of additivity of structural ingredients, including up to 40 "thermodynamically unknown" ones. The obtained results have been used in the thermodynamic analysis of up to 100 reactions with satisfactory accuracy. This circumstance allows us to assign the proposed method to the number of methods known as "approach" for use in the fields of science and technology, which are engaged in the thermodynamic analysis of processes involving silicates.

International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.

https://ijpsat.org/
Vol. 46 No. 1 August 2024, pp. 15-23

Table 1. Report and results of thermal constants of three ring silicates by The method of additivity of structural ingredients

Compound formula and symbol	E_t-Formula (A)	SI formulas and their thermal constant			Relevance constanta (K_c)	Leveling constant (K_{niv})	The value of the thermodynamic parameter obtained by MASI - $B=K_{niv}\cdot A_{\cdot}$	Error rate	
		SI-formula	Thermal constant of SI	ΣSI Thermal constant ($A_{\cdot}$)				A-B=Δ	%-
1	2	3	4	5	6	7	8	9	10
$-\Delta H^0_{f.298}$-calculation in kcal/mol									
Wollastonite (Woll) $3(CaO\cdot SiO_2)$ C_3S_3	1170.81	$2CaO\cdot SiO_2(C_2S)$ $CaO\cdot SiO_2(CS)$ $SiO_2(Q)$	551.48 390.27 217.73	1159.48	1.0098	1.0111	1172.35	1.54	0.13
Sodium dicalcium trisilicate $Na_2O\cdot 2CaO\cdot 3SiO_2$ NC_2S_3	1167.20	$2(CaO\cdot SiO_2)(C_2S_2)$ $Na_2O\cdot SiO_2)(NS)$	780.54 372.46	1153.00	1.0123	1.0111	1165.80	-1.40	0.12
Strontium metasilicate $3(SrO\cdot SiO_2)$ S'_3S_3	1170.99	$2SrO\cdot SiO_2(S'_2S)$ $SrO\cdot SiO_2(S'S)$ $SiO_2(Q)$	551.16 390.15 217.73	1159.04	1.0112	1.0111	1171.91	-0.92	0.01
$-\Delta G^0_{f.298}$-calculation in kcal/mol									

International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.

https://ijpsat.org/
Vol. 46 No. 1 August 2024, pp. 15-23

C_3S_3	1110.03	C_2S CS Q	524.04 370.01 204.75	1098.80	1.0102	1.0102	1110.00	-0.03	0
NC_2S_3	1103.80	C_2S_2 NS	700.02 390.76	1090.78	1.0119	1.0102	1101.90	-1.90	0.18
S'_3S_3	1113.30	S'_2S S′S Q	528.08 371.09 204.75	1103.92	1.0085	1.0102	1115.18	1.88	0.20
$C^0_{p.298}$-calculation in kcal/mol									
C_3S_3	62.85	C_2S CS Q	30.74 20.67 10.64	62.05	1.0129	1.0030	62.24	-0.61	0.97
NC_2S_3	68.75	C_2S_2 NS	41.30 26.77	68.07	1.0012	1.0030	68.27	0.48	0.17
S'_3S_3	61.47	S'_2S S′S Q	30.34 20.81 10.64	61.79	0.9948	1.0030	61.98	0.51	0.16
S^0_{298}-calculation in kcal/mol									

International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.

https://ijpsat.org/
Vol. 46 No. 1 August 2024, pp. 15-23

C_3S_3	59.76	C_2S CS Q	30.50 19.92 10.33	60.75	0.9889	0.9900	60.14	0.38	0.12
NC_2S_3	66.40	C_2S_2 NS	39.84 27.20	67.04	0.9905	0.9900	66.37	-0.03	0.05
S'_3S_3	68.67	S'_2S S′S Q	36.43 22.89 10.00	69.32	0.9906	0.9900	68.63	-0.04	0.06

Indications: C_3S_3 – $3(CaO{\cdot}SiO_2)$; NC_2S_3 – $Na_2O{\cdot}2CaO{\cdot}3SiO_2$; S'_3S_3 – $3(SrO{\cdot}SiO_2)$; C_2S -$2CaO{\cdot}SiO_2$; CS - $CaO{\cdot}SiO_2$; C_2S_2 – $2(CaO{\cdot}SiO_2)$; NS($Na_2O{\cdot}SiO_2$); S'_2S – $2SrO{\cdot}SiO_2$; S′S – $SrO{\cdot}SiO_2$; Q – SiO_2

REFERENCES

[1]. A. Sarukhanishvili, A. Gogishvili, V. Gordeladze, D. Eristavi. Gibbs free energy minimization method. Tbilisi, Publishing House "Technical University", 2007.-81 p.

[2]. Babushkin V.I., Matveev G.M., Muedlov-Petrosyan O.P. Thermodynamics of silicates. M.: Stroyzdat, 1986. -406 p.

[3]. Nadiradze N.R., Dzhaoshvili K.R., Tsagareishvili D.Sh. // Ed. AN GSSR, ser. chem. vol. 16, no. 4, 1990. -277-281 p.

[4]. Bagdavadze D.I., Tsagareishvili et al. // Ed. AN GSSR, ser. Chemistry, vol. 14, no. 3, 1988.-199-206 p.

[5]. Gvelesiani G.G., Bagdavadze D.I. Calculation methods for determining the thermodynamic functions of inorganic substances and their application in a complete thermodynamic analysis of metallurgical processes. Tb.: Universal, 2006.-128 p.

[6]. F. Liebau. Structural chemistry of silicates. Moscow, Mir, 1998.-410 p.

[7]. Berrill L., Meison B., Dietrich R. Mineralogy. M., Mir, 1987.–592 p.

[8]. West A. Solid State Chemistry. vol.1., vol.2., Transl. from English M., Mir, 1988. - 555 s (I vol t), -334 s. (II vol).

[9]. P.P. Budnikov, A.M. Ginstlich. Reactions in mixtures of solids. Moscow, Stroizdat, 1965. -474 p.

[10]. Muller R.L. Solid state chemistry and glassy state. In the book. Solid State Chemistry. L.: LU, 1965.-9-63 p.

[11]. M.M. Shultz, O.V. Mazurin. Modern ideas about the structure of glasses and their properties. SCIENCE, Leningrad branch, 1988. -198 p.

[12]. Yakakova Hazumi. Tables of Thermodynamic properties of inorganic compounds. Nat. Chem. Lab. Japan, 83, 1988. -121p.

[13]. Thermal constants of substances P/r. V.P. Glushko. Vol. I–x, M., USSR Academy of Sciences, VINTI, 1961-1981.

[14]. Kireev V.A. Methods of practical calculations in the thermodynamics of chemical reactions. M., “Chemistry”, 1975. -357-371 p.

[15]. Saxena S.K. at al. Thermodynamic Data on Oxides and Silikates. New York, Berlin Haidenberg, Springer-Vertag, 1993.-428 p.

[16]. Bulakh A.G. Methods of thermodynamics in mineralogy. L., “Nedra”, 1974. -155-169 p.

[17]. Karpov I.K. and others. Constants of substances for thermodynamic calculations in geochemistry and mineralogy. M., “Science”, 2968. -10-65 p.

[18]. Sarukhanishvili A.V., Mshvildadze M.J. and others. Calculation of standard molar values of the enthalgy of formation of minerals. groups of slitheen. Sat. Chem. Journ. G. 9, #4. 2009.- 324–328 p.

[19]. Sarukhanishvili A.V., Matsaberidze E.L. and others. On the issue of calculating $-\Delta H^0_{f.298}$, $\Delta G^0_{f.298}$ and S^0_{298} -silicate compounds. Sat. Chem. Journ. G. 10, #1. 2010.- 82–86 p.

[20]. Sarukhanishvili A.V., Matsaberidze E.L. Additive system of ingredient structures for calculating standard molar values of thermodynamic anhydrous silicates. Proceedings of Stu, #4(478), 2010.-29–33 p.

[21]. Sarukhanishvili A.V., Matsaberidze E.L. Method for calculating standard molar values of the thermodynamic properties of anhydrous silicates. Sat. mat. II Int. conference on chemistry and chemistry. tech. Armenia, Yerevan, 2010. -29-33 p.

[22]. Ekaterine Matsaberidze. Creation of a thermodynamic database for evaluating silicate and glass formation in multimineral systems. Dissertation submitted for the academic degree of Doctor. Tbilisi. Stu. 2011. -112 p.

[23]. Sarukhanishvili A.V.,Gordeladze V.G.,Kentchoshvili T.L.Calculation of thermal constants of garnet group minerals using the method of additivity of structural ingredients. Journal of the Association of Ceramists of Georgia. T.20. No. 2(40). 2018.- 25-30p.

THE ESSENCE ON ADDITIVE METHOD OF STRUCTURAL INGREDIENTS AND THE ANALISIS OF THE RESULTS OBTAINED

Gordeladze V., Kentchoshvili T.

Georgian Technical University

Summary

In order to determine thermal constants of hard silicates, the paper suggests the basic essence on additive method of structural ingredients" and the short analysis of results obtained from the realization of this method.

It is shown that, unlike the existing calculation methods of thermal constants of these compounds, the proposed method is based on the data in thermodynamic basins itself.

It is noted, that this method of silicates is based on the information existed in physical chemistry. It is subject to the principle that the quality of each new body structural organization is determined by combining elements with a lower and higher structural arrangement of quality in the energy units.

The essence of the concepts used in the proposed method, the calculation and the assessment of the received assignments are given. The idea is that this method belongs to the so-called " the number of "approximations." It is possible to estimate obscure experimental data for assessing a solid, anhydrous substance (reaction).