Calculation of standard molar enthalpy and Gibbs free energy of formation anhydrous silicates

Archil SARUKHANISHVILI*
Ekaterine MATSABERIDZE**
Marina KAPANADZE***
Maia MSHVILDADZE****
Tamar LOLADZE*****

Abstract

In the present work a method for calculating the standard molar enthalpy and Gibbs free energy of formation anhydrous silicates is proposed. The method is based on the principles of structural analogy and additivity of properties involving thermodynamics of substances and information on parameters which are considered insufficiently defined. Testing of the proposed method at thermodynamic evaluation of reactions, involving anhydrous silicates, has yielded positive results - chemical equilibrium estimation error does not exceed 1-3%.

Keywords: Thermodynamic parameters, standard molar values, crystallochemical classification, framework, layer, chain, ringed silicates, sorosilicates, nesosilicates, correction and leveling structural components

Introduction

In the last three decades various thermodynamic research methods, including the method of minimizing the Gibbs free energy, were worked out in different areas of science and technology. The basis of these methods are calculations involving assessment and establishment of equilibrium chemical reactions requiring a variety of source data scattered in different reference books. Even under increasing virtual search capabilities it is often time-consuming to calculate a set of reactions. The complexities are aggravated in case of lack of information on the thermodynamic properties of the substances involved in the reactions.

One of the methods proposed by (Matveev, 1957), creates the possibility of calculating $\Delta H^o_{f,298}$ and $\Delta G^o_{f,298}$ for meta- and orthosilicates of II group of the periodic table, and for its application in any binary and ternary silicate systems it is necessary to establish amount of energy introduced by the metal cation and the contribution in the formation of silica framework. Another method (Chao-Hsia Chen. 1975), requires the use of regression analysis, determining the ex-

trapolated values of the independent variable and the mineral; other method by (Hoppe, 1958) requires the knowledge of chloride and oxide data; in the case of method proposed by (Karapetyan, 1954), it is limited by metasilicates (Chao-Hsia Chen, 1975). One more method (Turkdogan & Pearson, 1953) requires data on molecular volumes of related groups of compounds, and one more method (Gvelesiani & Baghdavadze, 2006) involves application of quasi-additive method with the possibility of changing the parameters of ions depending on the charge quantity in the case of ionic crystals, and in the case of double oxides - taking into account the number of oxygen in the compound, stoichiometry factor and constants of so-called central cation. In the case of ternary oxides a series of experiments are recommended.

Unique for a number of solids is, in our opinion, the method proposed by Landia for determining Cp,T. Long before the development of computational chemistry he had proposed an algorithm for defining high temperature heat capacities according to standard entropy (Landya, 1990).

*Prof .Dr. Department of Chemical and Biological Engineering, Georgian Technical University
 E-mail: sarukhanishviliarchil@rambler.ru

**Assist. Prof. Ph. D. Department of Chemical and Biological Engineering, Georgian Technical University
 E-mail: ekaterinematsaberidze@hotmail.com

***Dr. Department of Chemical and Biological Engineering, Georgian Technical University
 E-mail: m.kapanadze@gtu.ge

****Prof. Dr. Department of Chemical and Biological Engineering, Georgian Technical University
 E-mail: maia_mshvildadze@gtu.ge

*****Assoc. Prof. Dr. Department of Metallurgy, Metals Science and Metal Processing, Georgian Technical University. Lecturer at the Faculty of Computer Technologies and Engineering, International Black Sea University
 E-mail: t.loladze@gtu.ge;   tloladze@ibsu.edu.ge

In the case of anhydrous silicates these methods are those for calculation of $\Delta H^o_{f,298}$ and $\Delta G^o_{f,298}$, proposed in the works of different scholars (Matveev, 1957; Chao-Hsia Chen, 1975; Hoppe, 1958; Karapetyan, 1954), and of $S^o_{f,298}$ and Cp=f(T) proposed by other group of scholars (Turkdogan & Pearson, 1953; Landya, 1990; Gvelesiani & Baghdavadze, 2006).

However, each of them is characterized by certain drawbacks limiting the application of the method or hindering fast and easy obtaining of reliable outcomes.

Testing of the proposed method at thermodynamic evaluation of reactions, involving anhydrous silicates, has yielded positive results - chemical equilibrium estimation error does not exceed 1-3%.

Working Methodology

To reduce the time required for establishing the thermodynamic properties of the substances involved in the reactions, the method of calculation of standard molar enthalpy and Gibbs free energy of formation anhydrous silicates is proposed by us.   The method is based on the classification of $[SiO_2]$ –tetrahedra according to their chemical charging, structural analogy and additivity of properties.

Results

All silicates can be classified according to individual groups of compounds having the same type of silicon-oxygen radical by the O/Si ratio. These groups can be presented as it is shown in Figure. 1. (Appen, 1970).

Analysis of the data shown in Table 1 shows that each silicate of any crystallochemical group can be obtained by coupling a compound with less developed silicon-oxygen grid with more developed one or by combination of a compound without this grid (frame) with a compound having the frame. For example, subgroups of olivine silicates can be obtained by the following schemes:

$$MgO + MgSiO_3 \rightarrow Mg_2SiO_4 \text{ (forsterite)}$$

$$MgO + CaSiO_3 \rightarrow CaMgSiO_4 \text{ (monticellite)}$$

$$CaAl_2O_4 + Ca_2SiO_4 , Ca_3AlSiAlO_8$$
(calcium aluminosilicate)

$$CaO + MgO + 2CaSiO_2, Ca_3MgSi_2O_9 \text{ (merwinite)}$$

Sorosilicates can be obtained according to the scheme:

$$MgO + 2(CaO{\cdot}SiO_2) , Ca_2MgSi_2O_7 \text{ (akermanite)}$$

$$CaAl_2O_3 + CaO{\cdot}SiO_2 , Ca_2AlSiAlO_7 \text{ (gehlenite)}$$

$$CaO + 2(Ca_2SiO_3) , Ca_3Si_2O_7 \text{ (rankinite)}$$

In these schemes MgO, CaO, $CaAl_2O_4$ are substances not characterized by silicon-oxygen grid and the rest have the grids respective to the group of silicates with doubled discrete and discrete grid orientation.

As examples of combination of raw materials having different silicon-oxygen-oriented grid may serve ring silicates, which are subdivided into the ring and genuine ring silicates. Ring silicates are obtained according to the schemes:

$$Ca_2SiO_4 + CaSiO_3 + SiO_2 , Ca_3Si_3O_9 \text{ (wollastonite)}$$

$$Mn_2SiO_4 + MnSiO_3 + SiO_2 , Mn_3Si_3O_9 \text{ (rhodonite)}$$
$$2CaSiO_3 + Na_2SiO_3 + SiO_2 , Na_2Ca_2Si_3O_9$$
(Na-Ca silicate)
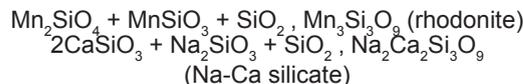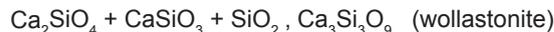
In the first two schemes, there are combined substances of higher ($CaSiO_3$, $MnSiO_3$) and lower (Ca_2SiO_4. Mn_2SiO_4) orientations than those of the desired ones. In the third scheme starting silicates have the orientation corresponding to the distribution of metasilicate in silicon-oxygen grid (SiO_2).

In genuine ring silicates substances without characteristic orientation of silicates, as a rule, are combined with the substance with the highest degree of orientation. The former include aluminates, and the second - silica:

$$2(Mg_2Al_2O_4) + 5SiO_2 , Mg_2Al_3Si_5AlO_{18} \text{ (cordierite)}$$

$$2(MgAl_2O_4) + 5SiO_2 , Fe_2Al_3S_5AlO_{18}) \text{ (Fe –cordierite)}$$

The substances located on the left side of the above schemes are called "structural components".

Analysis of the database of thermodynamic properties of silicates (Babushkin, Matveev & Mchedlov – Petrosyan, 1986; Yokokama Hamumi, 1988), showed that most reliable are standard molar values of those substances (SMV), used as structural components. This made it possible to calculate SMV of most silicates, SMV of which are also considered as reliably established and compare the results of calculations with those in the database.

For example, in Figure 2 and Figure 3 there are given calculations of SMV for nesosilicates and sorosilicates and also the results of comparisons.

Based on the information provided in Figure 2 and Figure 3, it can be concluded that the error in determining the SMV of the silicates with discrete and dual discrete types of silicon-oxygen grid, as well as in other types, does not exceed 1% which is quite acceptable for establishing $\Delta H^o_{f,298}$ and $\Delta G^o_{f,298}$ for those anhydrous silicates SMV of which are not defined. It requires the knowledge of structural components and the values of their $\Delta H^o_{f,298}$ and $\Delta G^o_{f,298}$, affiliation of the test substance to a particular type of silicates and leveling ratio (K_L):

Information about structural components and K_L by types of crystallochemical grids are given in Figure 4.

Conclusion

In conclusion, calculated data for thermodynamically unstudied anhydrous silicates with different orientations of tetrahedra of values $\Delta H^o_{f,298}$ and $\Delta G^o_{f,298}$ were used for the assessment of many thermodynamic reactions for determining confidence limit. There were determined $\Delta G^o_{f,298}$ of these reactions using the Ulih first-order approximation, the method of Gibbs free energy minimization and the first consequence of the Hess law. Comparison of the obtained results permits the conclusion that it is possible to use the method proposed by the authors for an approximate estimation of technological processes – divergence in results obtained does not exceed 1-3%. Values of $S^o_{f,298}$, used in the given calculations, were defined by specific methods (Turkdogan & Pearson, 1953; Gvelesiani & Baghdavadze, 2006).

№	Type of silicon-oxygen tetrahedral unit by O/Si ratio	Designation of the state of tetrahedral unit		Name of the group of silicates
		The first	The second	
1	$[SiO_2]$ Continuous in three dimensions	$-\!Si\!-$	$[SiO_{4/2}]^0$	Tectosilicates (three-dimensional framework of tetrahedral units) $A_m(XO_2)_n$
2	$[SiO_5]$ Continuous in two dimensions	$-\!Si\!-$ (with O below)	$[SiO_{3/2+1/1}]^{1-}$	Layer silicates (tetrahedral layer) $A_m(X_2O_5)_n$
3	$[SiO_3]$ Continuous in one dimension (metasilicates)	$-\!Si\!-$ (with O above and below)	$[SiO_{2/2+2/1}]^{2-}$	Chain silicates (tetrahedral chains) $A_m(XO_3)_n$ Ring silicates (rings of tetrahedra) $A_m(XO_3)_n$; $A_m(S_3O_9)_n$; $A_m(S_4O_{12})_n$ or $A_m(S_{16}O_{18})_n$
4	$[Si_2O_7]_2$ Discrete dual tetrahedron	$-\!Si\!-\!O$ (with O above and below)	$[SiO_{1/2+3/1}]^{3-}$	Sorosilicates (dual sorosilicates) $A_m(X_2O_7)_n$
5	$[SiO_4]$ Discrete tetrahedron (orthosilicates)	$O\!-\!Si\!-\!O$ (with O above and below)	$[SiO_{4/1}]^{4-}$	Nesosilicates (isolated tetrahedra) $A_m(XO_4)_n$

Figure 1. *Classification of silicates according to the charging of [SiO$_2$]- tetrahedral unit*

Compounds	$\Delta H^o_{f,298}$ standard (ST) kkal/mol	Structural components		$\Delta H^o_{f,298}$ intermediate (int) kkal/mol	$K_{cor} = \frac{\Delta H^o_{f,298}(st)}{\Delta H^o_{f,298}(int)}$	K lev	$\Delta H^o_{f,298}$ (cal) kkal/mol	Error		Note
		Compounds	$\Delta H^o_{f,298}$ (st) kkal/mol					$\Delta H^o_{f,298}(st) - \Delta H^o_{f,298}(cal)$ kkal/mol	%	
Forsterite 2MgO·SiO$_2$	520,53	MgO·SiO$_2$ MgO	370,25 143,84	514,09	1,013		521,80	+0,97	0,19	st-standard int-intermediate cor-correction lev-leveling Values of $\Delta H^o_{f,298}(st)$ and $\Delta G^o_{f,298}(st)$ are taken from (Appen A. A. 1970) cal-calculation
Fayalite 2FeO·SiO$_2$	354,83	FeO·SiO$_2$ FeO	285,89 63,44	349,33	1,016		354,57	-0,26	0,07	
Tephroite 2MnO·SiO$_2$	413,55	MnO·SiO$_2$ MnO	315,65 92,00	407,65	1,015		413,76	-0,21	0,05	
Monticellite CaO·MgO·SiO$_2$	540,91	CaO·SiO$_2$ MgO	389,75 143,84	533,59	1,014	0,015	541,59	-0,68	0,13	
Merwinite 3CaO·MgO·2SiO$_2$	1091,67	2(CaO·SiO$_2$) CaO MgO	779,50 151,90 143,84	1075,24	1,015		1091,37	+0,30	0,03	
Larnite β-2 CaO·SiO$_2$	551,74	CaO·SiO$_2$ CaO	389,75 151,90	541,65	1,019		551,94	+0,20	0,04	

Figure 2. *Sequence and the results of calculation of $\Delta H^o_{f,298}$ of some nesosilicates*

Compounds	$-\Delta G^\circ_{f,298}(st)$ kkal/mol	Compounds	$-\Delta G^\circ_{f,298}$ (st) kkal/mol	$-\Delta G^\circ_{f,298}(int)$ kkal/mol	K_{cor}	$K_{lev.}$	$-\Delta G^\circ_{f,298}$ (cal) kkal/mol	Δ kkal/mol	%	Note
Forsterite	492,15	MgO·SiO₂	349,48	485,61	1,013		492,8	0.65	0,13	
		MgO	136,13							
Fayalite	330,75	FeO·SiO₂	267,32	325,72	1,015		330,6	-0,15	0,04	
		FeO	58,40							
Tephroite	389,58	MnO·SiO₂	296,55	383,35	1,016		389,10	-0,48	0,12	Values $\Delta H^\circ_{f,298}$ (st) are taken from (Appen A. A. 1970)
		MnO	86,80							
Monticellite	512,14	CaO·SiO₂	369,75	505,88	1,012	0,015	513,46	1,32	0,25	
		MgO	136,13							
Merwinite	1037,33 1033,59 Average 1035,41	2(CaO·SiO₂)	739,50	1020,03	1,015		1035,60	0,19	0,02	
		CaO	144,4							
		MgO	136,13							
Larnite	524,19	CaO·SiO₂	369,75	514,15	1,019		523,90	-0,29	0,05	
		CaO	144,40							

Figure 3. *Sequence and the results of calculation of $\Delta G^\circ_{f,298}$ of some nesosilicates*

Group of silicates	Structural components	$K_L \Delta H$ ($\Delta H_{f,298}$)	K_L ($\Delta G_{f,298}$)
Nesosilicates	RO+RO·SiO₂	1,015	1,005
	R^{I}O+R^{II}+2 R^{I}O·SiO₂		
	2 RO·SiO₂+RO·R₂O₃		
Sorosilicates	R^{I}O+R^{II}+2(R^{I}O·SiO₂)	1,005	1,008
	RO+2(RO·SiO₂)		
	RO·SiO₂+ RO·R₂O₃		
Ring silicates	2 RO·SiO₂+ RO·SiO₂+ SiO₂	1,007	1,010
	2(RO·SiO₂)+R$^I_2$O·SiO₂		
	2 RO·SiO₂+ RO·SiO₂+2R^{I}O·SiO₂+ R^{I}O·SiO₂+2SiO₂		
	2(2 RO·SiO₂)+ R^{I}O·SiO₂+2 SiO₂		
Genuine ring silicates	2(RO· R$^I_2$O₃)+5SiO₂	0,994	1,026
Chain silicates	2(R₂O·SiO₂)+ 2 RO·SiO₂	1,005	1,007
	R₂O·3SiO₂+ R$^I_2$O₃+SiO₂		
	RO·SiO₂+ R^{I}O·SiO₂		
Layer silicates	R₂O·SiO₂+SiO₂	1,007	1,006
	R₂O·SiO₂+3(RO·SiO₂)+2SiO₂		
	R₂O·SiO₂+RO·SiO₂+3SiO₂		
	R₂O·SiO₂+2(RO·SiO₂)+3SiO₂		
Tectosilicates	R₂O·2SiO₂+ R₂O₃	1,015	1,015
	R₂O·4SiO₂+ R₂O₃		
	RO·SiO₂+ R₂O₃+ SiO₂		
	R₂O·4SiO₂+Al₂O₃+ 2Al₂O₃		
	R₂O·3SiO₂+Al₂O₃+ 3 SiO₂	1,008	1,009

Figure 4. *Structural components and leveling ratios of different groups of anhydrous silicates *

References

Matveev G. M. 1957. An interrelation between the structural and thermodynamic properties of silicates. – Proceedings of MUCTR, Vol. 24, p. p. 233-236.

Chao-Hsia Chen. 1975. A method of estimation of standard free energies of formation of silicate minerals at 298,15K. Amer.J.of Science, 275, 7, p. p. 801-817.

Hoppe R. 1958. Zusammenhande zwischen Bildun gswarmen anorganischer verbindungen. Z. anorg. allg. chem., 296,1-6, p. p. 104-116.

Karapetyan S. Kh.1954. Approximate calculation of the Gibbs energies and heats of formation of various substances. Russian Journal of Physical Chemistry. Vol. 28, №1,p.p.186-187.

Turkdogan E.T. Pearson J. 1953. Entropies of Inorganic substances.J. Appt. chem, 3. p. 495.

Landya N. A. 1990. The calculation of high-temperature heat capacities of solid inorganic substances at the standard entropy. Selected Works, Tbilisi, Metsniereba, p. p. 10-196.

Gvelesiani G. G., Baghdavadze D. I. 2006. Calculating methods of determining the thermodynamic functions of inorganic substances Tbilisi, "Universal", p. 128.

Appen A. A. 1970. Chemistry of glass. L - D.; Chemistry. p. 353.

Babushkin V. I., Matveev G. M., Mchedlov-Petrosyan O. P. 1986. Thermodynamics of silicates. M., Stoyizdat, p. 96.

Yokokama Hamumi. 1988. Tables of thermodynamic properties of Inorganic compounds. J: Nat. Chem. Lab. Ind. v. 83., sp.iss. p. p.27-121.