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Regarding the Possibility of Calculating the Series of Silicides S^0_{298} Based on the Principle of Additivity

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Abstract – The paper demonstrates the possibility of using the method of additivity of structural ingredients in determining the standard molar values of thermodynamic parameters. Using this method, the probability of determining silicides S^0_{298} reaches up to one entropic unit.

Keywords – Entropy, thermodynamics, additivity, ingredient, molar, silicide, standard, structural.

Introduction

In the production of silicides, the primary reason for the low application of predictive methods and the creation of certain materials is the complexity of the physicochemical processes possible during synthesis. This circumstance may explain the increase in the duration of research work, as well as the material and energy intensity involved in seeking innovative solutions for silicide production.

Main Part

Chemical thermodynamics can provide invaluable assistance in reducing the amount of experimental work, as has been proven multiple times in solving highly complex scientific and practical problems. However, the full utilization of thermodynamic capabilities is often hindered by the lack of initial data necessary for analysis—specifically, the standard molar values of the thermodynamic parameters of silicides. According to our information, over 80 silicides currently lack such data. In most cases, they are characterized by incomplete data required for thermodynamic analysis and significant variability in parameter values. For instance, Table 1 contains information regarding $\Delta H^0_{f,298}$ და S^0_{298}, which is given in [1-3].

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Table 1. Data of several silicides - $\Delta H^0_{f,298}$ and S^0_{298}

Silicides	$\Delta H^0_{f,298}$ and S^0_{298}					
	- $\Delta H^0_{f,298}$, kcal/mol			S^0_{298} kcal/mol-·K)		
	[1]	[2]	[3]	[1]	[2]	[3]
CaSi	-	36,09	36,0	-	10,80	-
Ca_2Si	50,0	49,95	50,0	-	19,04	-
$CaSi_2$	-	36,09	36,0	-	12,09	-
CoSi	-	24,00	22,7	-	10,30	10,20
Co_2Si	27,6	-	28,0	-	-	-
$CoSi_2$	-	24,59	23,6	-	15,32	15,30
Cr_3Si	-	30,11	22,0	-	20,96	20,6
CrSi	-	15,06	12,7	-	10,79	10,50
$CrSi_2$	-	22,94		-	13,97	14,0
Cr_5Si_3	-	64,05	50,50		43,44	40,40
Fe_3Si	-	22,39	-	-	24,81	-
$FeSi_2$	18,20	19,41	-	13,29	15,33	-
Fe_2Si	20,0	-	-	24,7	-	-
Fe_5Si	46,0	-	-	50,0	-	-
Mg_2Si	18,95	18,59	16,23	18,11	17,93	15,25
MnSi	18,60	14,48	14,50	11,25	11,10	11,10
Mn_3Si	26,50	19,02	19,0	24,95	24,97	24,80
Mn_5Si_3	-	47,99	48,0	-	57,11	57,0
Mn_2Si_7	20,0	18,07	-	13,26	13,40	-
Mo_3Si	24,3	22,94	27,80	25,4	24,69	25,45
$MoSi_2$	28,40	27,96	31,50	-	15,54	15,55
Mo_5Si_3	-	20,60	21,40	-	11,21	10,60
NiSi	-	20,6	21,40	-	11,21	10,60

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$NiSi_2$	-	-	22,50	-	-	15,60
Ni_2Si	33,6	33,6	34,10	-	18,31	-
Ni_3Si_2	-	-	55,5	-	-	-
TiSi	31,00	31,07	31,00	-	11,71	11,70
$TiSi_2$	32,00	32,03	32,1	-	14,60	14,60
Ti_5Si_3	139,0	-	138,0	-	-	52,10
ZrSi	35,0	37,05	35,5	-	13,91	-
$ZrSi_2$	36,0	38,0	-	-	17,09	-
Zr_3Si_2	92,0	-	-	-	-	-
Zr_2Si	50,0	49,95	81,0	-	23,90	-
Zr_4Si	51,0	-	-	-	-	-
Zr_5Si_3	203,0	-	203,0	-	-	-
SrSi	45,0	-	-	-	-	-
Sr_2Si	60,0	-	-	-	-	-
$SrSi_2$	45	-	-	-	-	-
V_3Si	25,0	41,20	-	27,0	23,47	-
VSi_2	36,0	29,18	-	14,10	14,13	-
V_2Si	37,0	-	-	-	-	-
V_5Si_3	112,0	-	-	-	-	-
W_5Si_3	-	32,31	-	-	54,99	-
WSi_2	-	21,99	-	-	15,30	-

In studying the processes occurring at the "glass coating – copper" interface, attention was drawn to the fact that during the firing of "raw" coatings, an intermediate layer may form on the surface of the copper, which could promote (or improve) the adhesion of the glass coating to the copper. To confirm this possibility, it was decided to thermodynamically evaluate various potential physicochemical processes, one of the products of which included silicides of different compositions. A major obstacle to realizing this sequence of processes was the lack of, or variability in, the values of the aforementioned thermodynamic parameters, particularly those of component S^0_{298}. This prompted the search for calculation methods, which led us to the work of Georgian metallurgists [4]. The study [4] proposes a method for calculating the entropies of silicides (S^0_{298}), and by using this method, in some cases, we obtained fairly acceptable results—the error (probable deviation) did not exceed 2-3 entropic units.

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A subsequent attempt involved applying the method of additivity of structural ingredients, which had previously been used for calculating the standard molar thermodynamic parameters of silicates and borates [5-9], with appropriate modifications based on the nature of the research objects. The calculations were based on classifying the silicides according to bond type, and instead of "structural ingredients," the atoms constituting the silicide were used. The calculation process and the results for iono-covalent bond silicides and certain metallic-like silicides are presented in Tables 2 and 3.

Table 2. S^0_{298} calculation procedure of ionic-covalent silicides and calculation results

Silicides	Standard values [1-3] $S^0_{298\ (standard)}$ kcal/mol •K	Calculation values S^0_{298} $(_{calculation})$ kcal/mol •K	S^0_{298} (standard)/ S^0_{298} (calculation) = $K(_c)$	Leveling coefficient -K_l	S^0_{298} $_{(calculation)}\times$ K_l= S^0_{298}(basic) kcal/mol •K	Δ= S^0_{298} (standard)- S^0_{298} (basic) kcal/mol •K
1	2	3	4	5	6	7
Ca_2Si	19,04	24,30	0,7835		19,95	-0,91
Mg_2Si	17,10	20,12	0,8499		16,43	0,67
Sr_2Si	-	29,50	-	0,8167	24,09	-
Ba_2Si	-	34,52	-	0,8167	28,19	-
Silicides with Si chains (RSi)						
CaSi	10,8	14,40	0,7500	0,7500	10,8	0
Sr_2Si	-	17,00	-	0,7500	12,75	-
Ba_2Si	-	19,51	-	0,7500	14,63	-
Silicides with corrugated layers (RSi_2)						
$CaSi_2$	12,09	18,90	0,6397	0,6397	12,09	
$SrSi_2$	-	21,50	-	0,6397	13,75	-
$BaSi_2$	-	24,01	-	0,6397	15,36	-

Note: In the case of RSi and RSi_2, the calculation was made using a single "standard", so errors are possible.

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Table 3. Procedure for calculation of metal-like silicides S^0_{298} and results of this calculation

Silicides	Standard values [1-3] $S^0_{298\ (standard)}$ kcal/mol •K	Calculation values $S^0_{298\ (calculation)}$ kcal/mol •K	S^0_{298} (standard)/ S^0_{298} (calculation)= K(c)	Leveling coefficient - K_l	$S^0_{298\ (calculation)}\times K_l = S^0_{298}$ (basic) kcal/mol •K	$\Delta = S^0_{298}$ (standard)- S^0_{298} (basic) kcal/mol •K
1	2	3	4	5	6	7
TiSi	11,71	11,82	0,9907		11,21	0,5
MnSi	11,10	12,15	0,9114		11,53	-0,43
FeSi	10,99	11,02	0,9973		10,45	0,54
CoSi	10,30	11,68	0,8818		11,08	-0,78
NiSi	11,21	11,65	0,9622		11,05	0,16
CuSi	-	12,42	-	0,9487	11,78	-
ZnSi	-	14,45	-	0,9487	13,71	-
VSi	-	11,41	-	0,9487	10,82	
CrSi	(10,47)	10,18	-	0,9487	9,66	-
RSi_2 types of silicides						
$TiSi_2$	14,6	16,32	0,8952		15,44	-0,84
$CrSi_2$	13,97	14,18	0,9852		13,41	0,83
$CoSi_2$	15,32	16,18	0,9468		15,89	-0,57
$NiSi_2$	15,60	16,14	0,9559		15,26	0,34
$MnSi_2$	-	16,65	-	0,9458	15,25	
$FeSi_2$	(13,29)	15,52	-	0,9458	14,68	-
VSi_2	-	15,91	-	0,9458	15,05	-
$ZrSi_2$	-	18,95	-	0,9458	17,92	-
$CuSi_2$	-	16,92	-	0,9458	16,00	-

Note: In our opinion, $S^0_{298,Cr,Si}$ S^0_{298,Fe,Si_2} values need to be revised. Therefore, these silicides are excluded from the number of "standards".

Conclusion

As it follows from the data presented in Tables 2 and 3, the used method makes it possible to obtain S^0_{298} values that differ from the standards by no more than 1 kcal/mol •K. Verification of the admissibility of S^0_{298} values of the silicides determined by this method for the thermodynamic analysis of the possible processes at the separation surface of the glass coating with copper showed a satisfactory agreement between the results of this analysis and the experimentally obtained ones.

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