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EVOLUTION OF PHASES AT THE BIFURCATION POINT

ЭВОЛЮЦИЯ ФАЗ В ТОЧКЕ БИФУРКАЦИИ

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Abstract *In chemical reactions, the bifurcation points are determined through the triangulation of the system. In the interaction of the components, bifurcation sequence formed and the system evolves along one of them to form a stable compound. The transformations of the components at the bifurcation point are determined basis on the "The Gibbs function normalized to the total number of electrons". All transformations are described through chemical potential, affinity, thermodynamics force. Calculated the production of entropy, the entropy flux and the reaction rate constant, which allowing the system to choose a certain path of evolutionary transformations.*

KEYWORDS: NONEQUILIBRIUM THERMODYNAMICS, TRIANGULATION, THE GIBBS FUNCTION NORMALIZED TO THE TOTAL NUMBER OF ELECTRONS.

1. Introduction

In a chemical reaction at the bifurcation point, the system loses its stability and passes into a nonequilibrium state in which it is possible to acquire a new quality of the evolution of the dynamic system. There is a restructuring of the nature of the movement and structure of the system. When the system moves to the bifurcation point, the chemical potential and the affinity of the system play a significant role. At the bifurcation point, the system begins to produce entropy, the passage of the reaction is characterized by a certain rate constant. It is from these factors that the evolutionary branch depends on the system, passing through the point of bifurcation. In the interaction of chemical reagents in a real system, it is possible to determine all the ways of evolution of the system. Evolutionary processes between two points of bifurcations obey deterministic regularities [1-3].
The processes of evolution in chemical reactions can be described basis on the transformation of the phase composition of the system's compounds as a cause-effect relationship between the phases. This problem can be solve by the teachings of Kurnakov through the triangulation of systems [4]. The composition-property diagram is an exact geometric model of complex function, which reflects the relationship between temperature, volume, concentration and other physical and chemical factors, which can determine the state of the open system. The composition-property diagram linked into one matter of indissoluble chemical transformations and geometric transformations of space.

2. Method of research

For example, considered the system CaO-SiO2-H2O. In this system was established the formation of 86 compounds (table), and the system was triangulated basis on the Kurnakov's teaching [4] (figure) and using the "The Gibbs function normalized to the total number of electrons". The principle of triangulation of systems is given in [5]. Thermodynamic indices of compounds are calculated basis on the method of ion increments and increments of Aldabergenov [5]. The calculations show good consistency with the literature data, the relative error does not exceed 0.87%. The thermodynamic parameters of many compounds were calculated for the first time.

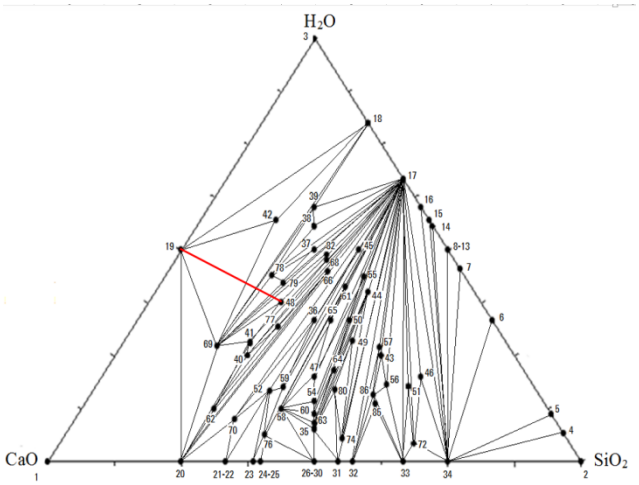

Figure1 *- Triangulation system CaO-SiO_2-H_2O*

Table *- The values of the Gibbs energy of formation (-$\Delta_f G_{298}$) and "The Gibbs function normalized to the total number of electrons" (-$\Delta\bar{G}^o_{298}$) compounds of CaO-SiO_2-H_2O system*

Compounds	-$\Delta_f G_{298}$, kJ/mol		% av.	-$\Delta\bar{G}^o_{298}$, kJ/mol.el
	by increments	[6]		
1	2	3	4	5
1. CaO		603.5		21.55
2. SiO_2		892.6		29.75
3. H_2O		237.2		23.72
4. $H_2Si_{14}O_{29}$	12437.23			28.92
5. $H_2Si_8O_{17}$	7274.17			29.10
6. $H_2Si_2O_5$	2111.11			30.16
7. $H_{10}Si_6O_{17}$	7113.49			30.93
8. H_2SiO_3	1250.60			31.26
9. $H_4Si_2O_6$	2501.19			31.26
10. $H_6Si_3O_9$	3751.79			31.26
11. $H_8Si_4O_{12}$	5002.38			31.26

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1	2	3	4	5
12. $H_{10}Si_5O_{15}$	6252.98			31.26
13. $H_{12}Si_6O_{18}$	7503.58			31.26
14. $H_{10}Si_4O_{13}$	5392.47			31.72
15. $H_8Si_3O_{10}$	4141.87			31.86
16. $H_6Si_2O_7$	2891.28			32.13
17. H_4SiO_4	1640.68			32.81
18. H_8SiO_6	2099.28			29.99
19. $Ca(OH)_2$		897.5		23.62
20. Ca_3SiO_5	2788.84	2785.1	0.13	24.46
21. Ca_2SiO_4	2185.34	2191.3	0.27	25.41
22. $Ca_6Si_3O_{12}$	6460.24			25.04
23. $Ca_8Si_5O_{18}$	9548.14			25.53
24. $Ca_3Si_2O_7$	3724.29	3756.7	0.87	25.86
25. $Ca_6Si_4O_{14}$	7362.80			25.57
26. $CaSiO_3$	1538,95	1543.9	0.32	26.53
27. $Ca_2Si_2O_6$	3077.90			26.53
28. $Ca_3Si_3O_9$	4616.85			26.53
29. $Ca_6Si_6O_{18}$	9233.70			26.53
30. $Ca_7Si_7O_{21}$	10772.65			26.53
31. $Ca_5Si_6O_{17}$	8587.31			26.84
32. $Ca_3Si_4O_{11}$	5509.41			27.01
33. $CaSi_2O_5$	2431.51			27.63
34. $CaSi_3O_7$	3324.07			28.17
35. $CaSiO_3 \cdot 0{,}16H_2O$	1574.15			26.41
36. $CaSiO_3 \cdot H_2O$	1758.95			25.87
37. $CaSiO_3 \cdot 2H_2O$	1978.95			25.37
38. $CaSiO_3 \cdot 2{,}5H_2O$	2088.95			25.17
39. $CaSiO_3 \cdot 3H_2O$	2198.95			24.99
40. $Ca_2SiO_4 \cdot H_2O$	2405.34			25.06
41. $Ca_2SiO_4 \cdot 1{,}17H_2O$	2442.74			25.00
42. $Ca_2SiO_4 \cdot 4H_2O$	3065.34			24.33
43. $CaSi_2O_5 \cdot H_2O$	2651.51			27.06
44. $CaSi_2O_5 \cdot 2H_2O$	2871.51			26.59
45. $CaSi_2O_5 \cdot 3H_2O$	3091.51			26.20
46. $CaSi_3O_6(OH)_2$	3553.37			27.76
47. $Ca_2Si_2O_6 \cdot H_2O$	3297.90			26.17
48. $Ca_3Si_2O_6(OH)_2 \cdot 2H_2O$	4393.59			25.25
49. $Ca_2Si_3O_8 \cdot 2H_2O$	4367.57			26.31
50. $Ca_2Si_3O_8 \cdot 2{,}5H_2O$	4477.57			26.18
51. $Ca_2Si_5O_{12} \cdot 1{,}5H_2O$	6085.58			27.54

1	2	3	4	5
52. $Ca_3Si_2O_7 \cdot H_2O$	3944.29			25.61
53. $Ca_3Si_2O_7 \cdot 3H_2O$	4384.29			25.20
54. $Ca_3Si_3O_9 \cdot H_2O$	4836.85			26.29
55. $Ca_3Si_6O_{15} \cdot 7H_2O$	8834.53			26.45
56. $Ca_3Si_6O_{13}(OH)_4$	7753.13			27.30
57. $3[Ca_3Si_6O_{13}(OH)_4 \cdot] \cdot 4H_2O$	24139.39			27.06
58. $Ca_4Si_3O_{10} \cdot H_2O$	5473.24			25.82
59. $Ca_4Si_3O_{10} \cdot 1{,}5H_2O$	5583.24			25.73
60. $Ca_4Si_4O_{12} \cdot H_2O$	6375.80			26.35
61. $Ca_4Si_6O_{13}(OH)_6 \cdot 4H_2O$	9508.82			26.27
62. $Ca_5Si_2O_9 \cdot H_2O$	5108.40			24.33
63. $Ca_5Si_5O_{15} \cdot H_2O$	7914.75			26.38
64. $Ca_5Si_6O_{17} \cdot 3H_2O$	9247.31			26.42
65. $Ca_5Si_6O_{17} \cdot 5{,}5H_2O$	9797.31			26.13
66. $Ca_5(Si_6O_{18}H_2) \cdot 8H_2O$	10576.61			25.80
67. $Ca_5Si_6O_{17} \cdot 9H_2O$	10567.31			25.77
68. $Ca_5Si_6O_{17} \cdot 10H_2O$	10787.31			25.68
69. $Ca_6[Si_2O_7] \cdot (OH)_6$	6222.69			24.12
70. $Ca_6Si_3O_{12} \cdot H_2O$	6680.24			24.93
71. $Ca_6Si_6O_{18} \cdot H_2O$	9453.70			26.41
72. $Ca_7Si_{16}O_{39} \cdot H_2O$	18768.35			27.36
73. $Ca_8Si_6O_{17}(OH)_6$	11085.71			25.54
74. $Ca_8Si_{10}O_{28} \cdot H_2O$	14316.72			26.81
75. $Ca_8Si_{12}O_{30}(OH)_4 \cdot 6H_2O$	17960.44			27.05
76. $Ca_9Si_6O_{21} \cdot H_2O$	11221.31			25.39
77. $Ca_9Si_6O_{21} \cdot 7H_2O$	12541.31			24.98
78. $Ca_9(Si_3O_9H) \cdot (Si_2O_7H)(OH)_8 \cdot 6H_2O$	12651.03			24.71
79. $Ca_9(Si_6O_{18}H_2) \cdot (OH)_8 \cdot 6H_2O$	13467.81			24.85
80. $2[Ca_{10}Si_{12}O_{31}(OH)_6] \cdot 3H_2O$	36385.04			26.56
81. $Ca_{10}Si_{12}O_{31}(OH)_6 \cdot 8H_2O$	19622.52			26.16
82. $Ca_{10}Si_{12}O_{31}(OH)_6 \cdot 18H_2O$	21822.52			25.67
83. $Ca_6Si_6O_{17}(OH)_2$	9463.00			26.43
84. $Ca_{12}(Si_6O_{17})_2(OH)_4 \cdot 12Ca(OH)_2$	29696.00			25.34
85. $Ca_{14}Si_{24}O_{58}(OH)_8 \cdot 2H_2O$	31828.10			27.16

86. $Ca_{14}Si_{24}O_{61}(OH)_2 \cdot 6H_2O$	32020.20			27.09

In the $CaO-SiO_2-H_2O$ system, the most active and reactive is $Ca(OH)_2$. Therefore, considered the interaction of $Ca(OH)_2$ (compound # 19) with $Ca_3Si_2O_6$ (OH) $_2 \cdot 2H_2O$ (compound # 48) in the exchange reactions. For this purpose, a straight line 19-48 runs between the poles of these compounds, which intersects the stable sections: 42-69; 18-69; 39-69; 69-78; 69-79; 69-17; 69-82 (Figure). The intersection points of the lines are bifurcation points. At this point the system loses stability and new solutions to evolution arise due to branching (bifurcation). The line $Ca(OH)_2$-$Ca_3Si_2O_6$ (OH) $_2 \cdot 2H_2O$ (19-48) shows that in the presence of a small displacement of the original components, the system is capable of jumping between stable states.

3. Results and discussion

To determine the ways of evolution of the system in chemical reactions are used two concepts:
- "The Gibbs function normalized to the total number of electrons" [5,7];
- triangulation of a multicomponent system [4].

The physical meaning of the "The Gibbs function normalized to the total number of electrons" ($\Delta\overline{G}^{o}_{298}$) is to define the chemical bond as a collective effect of electron-nuclear interaction. It is calculated by dividing the Gibbs energy of formation of a compound by the total number of electrons in a given compound, i.e. determines the energy density of the formation of a compound per electron. This function characterizes the accumulation of the Gibbs energy density on molecular bonds. The "The Gibbs function normalized to the total number of electrons" in the formation of bonds adequately reacts to all changes in the structure of the compound. This property allows us to describe many characteristics, like the reactivity of the compound, its stability [7], determine the chemical potential and affinity, calculate the production and flux of entropy, thermodynamic force and flow, the thermodynamic "probability" of interaction, the degree of conversion of components in the course of a chemical reaction, describe the processes of "self-organization" [8], triangulate multicomponent systems and establish mechanisms of reactions. The "The Gibbs function normalized to the total number of electrons" interpreted as the chemical potential of the substance, i.e. $\overline{G^{0}_{298}} = \mu$.

Described the chemical reactions of the interaction of $Ca(OH)_2$ with $Ca_3Si_2O_6$ $(OH)_2 \cdot 2H_2O$ at the points of bifurcations

19 + 48 = 42 + 69

$$15Ca(OH)_2 + 7[Ca_3Si_2O_6(OH)_2 \cdot 2H_2O] = 6[Ca_2SiO_4 \cdot 4H_2O] + 4[Ca_6Si_2O_7(OH)_6] \quad (1)$$

A = -0.42 kJ/mol·el.

19 + 48 = 69 + 18

$$15Ca(OH)_2 + 11[Ca_3Si_2O_6(OH)_2 \cdot 2H_2O] = 8[Ca_6Si_2O_7(OH)_6] + 6H_8SiO_6 \quad (2)$$

A = 5.24 kJ/mol·el.

19 + 48 = 69 + 39

$$9Ca(OH)_2 + 7[Ca_3Si_2O_6(OH)_2 \cdot 2H_2O] = 4[Ca_6Si_2O_7(OH)_6] + 6[CaSiO_3 \cdot 3H_2O] \quad (3)$$

A = 0.24 kJ/mol·el.

19 + 48 = 69 + 78

$$21Ca(OH)_2 + 19[Ca_3Si_2O_6(OH)_2 \cdot 2H_2O] = 4[Ca_6Si_2O_7(OH)_6] + 6[Ca_9(Si_3O_9H)(Si_2O_7H)(OH)_8 \cdot 6H_2O] \quad (4)$$

A = -0.04 kJ/mol·el.

19 + 48 = 69 + 79

$$6Ca(OH)_2 + 11[Ca_3Si_2O_6(OH)_2 \cdot 2H_2O] = 2[Ca_6Si_2O_7(OH)_6] + 3[Ca_9Si_6O_{18}H_2(OH)_8 \cdot 6H_2O] \quad (5)$$

A = 0.1 kJ/mol·el.

19 + 48 = 69 + 17

$$3Ca(OH)_2 + 7[Ca_3Si_2O_6(OH)_2 \cdot 2H_2O] = 4[Ca_6Si_2O_7(OH)_6] + 3H_4SiO_4 \quad (6)$$

A = 8.06 kJ/mol·el.

19 + 48 = 69 + 82

$$9Ca(OH)_2 + 29[Ca_3Si_2O_6(OH)_2 \cdot 2H_2O] = 11[Ca_6Si_2O_7(OH)_6] + 3[Ca_{10}Si_{12}O_{31}(OH)_6 \cdot 18H_2O] \quad (7)$$

A = 0.92 kJ/mol·el.

The affinity (A) (according to T. de Donder [9]) defined for elementary collision acts. If the affinity is positive, then the reaction rate is also positive, i.e. the reaction goes from left to the right. The negative value of the affinity of the reaction indicates the impossibility of the spontaneous flow of this reaction. As can be seen from the reactions (1), (4) spontaneously do not flow, but (2), (3), (5-7) - flow. It is determine that the chemical affinity is the driving force of chemical reactions.
Calculated the temperature of the process of transformation of the initial component into a stable compound, the thermodynamic force, entropy production, the entropy flux, and the conversion rate constant.

4. Conclusion.

The "The Gibbs function normalized to the total number of electrons".and the triangulation of the system make it possible to determine the bifurcation points in the interaction of the components. Appears the bifurcation sequence, the further transition of the system to the evolutionary path with the formation of a stable compound depends on the production of entropy, the entropy flux, and the reaction rate constant.

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