საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 4, № 2, 2010
BULLETIN OF THE GEORGIAN NATIONAL ACADEMY OF SCIENCES, vol. 4, no. 2, 2010

Physical Chemistry

Thermodynamic Probability of Obtaining Boron, Carbide and Boron Nitride from Potassium Tetrafluoboron and Boron Oxide at Self-Propagating High-Temperature Synthesis

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ABSTRACT. A thermodynamic analysis of the reaction for obtaining boron, carbide and boron nitride upon the basis of KBF_4 and B_2O_3 at self-propagating high-temperature synthesis was conducted. It is suggested that most acceptable results are expected at magnesium-thermal reduction of KBF_4. *© 2010 Bull. Georg. Natl. Acad. Sci.*

Key words: *SHS, boron, thermodynamic analysis, Gibbs free energy, reaction.*

The issues related to development of techniques for obtaining boron and refractory compounds upon its basis are of high importance for modern technology [1].

In the present work the problem is posed of establishing the thermodynamic probability of obtaining elementary boron, refractory compounds – B_4C and BN on the basis of potassium tetrafluoboron (KBF_4) and boron oxide (B_2O_3) at self-propagating high-temperature synthesis (SHS) with previous metal-thermal reduction. To this end, the method of trinomial equation was applied:

$$\Delta G_T^\circ = A + BT\lg T + CT \qquad (1)$$

of temperature variation of Gibbs free energy (ΔG_T°) developed in [2], the concrete scheme of carrying out calculations is similar to the one presented in [3].

All data necessary for thermodynamic analysis [4-6] are presented in Table 1, which also comprises the values of high-temperature heat capacity of some components defined through [7, 8] and those missing for calculations.

Upon the basis of the analysis of original data in the systems concerned within corresponding temperature ranges, the following reactions are expected to take place:

- Synthesis of carbide and boron nitride at direct interaction of boron with carbon and nitrogen

1. $B + \frac{1}{4}C = \frac{1}{4}B_4C$
2. $B + \frac{1}{2}N_2 = BN$

- Metal-thermal reduction of potassium tetrafluoboron with magnesium and aluminum

3. $KBF_4 + 1\frac{1}{2}Mg = B + KF + 1\frac{1}{2}MgF_2$
4. $KBF_4 + Al = B + KF + AlF_3$

- Synthesis of B_4C and BN upon the basis of KBF_4 at SHS process preceded by metal-thermal reduction

5. $KBF_4 + 1\frac{1}{2}Mg + \frac{1}{4}C = \frac{1}{4}B_4C + KF + 1\frac{1}{2}MgF_2$
6. $KBF_4 + Al + \frac{1}{4}C = \frac{1}{4}B_4C + KF + AlF_3$
7. $KBF_4 + 1\frac{1}{2}Mg + \frac{1}{2}N_2 = BN + KF + 1\frac{1}{2}MgF_2$
8. $KBF_4 + Al + \frac{1}{2}N_2 = BN + KF + AlF_3$

- Metal-thermal reduction of boron oxide by magnesium and aluminum

9. $\frac{1}{2}B_2O_3 + 1\frac{1}{2}Mg = B + 1\frac{1}{2}MgO$
10. $\frac{1}{2}B_2O_3 + Al = B + \frac{1}{2}Al_2O_3$

- Synthesis of carbide and boron nitride upon the basis of B_2O_3 at SHS with previous metal-thermal

Table 1

Original data for conducting thermodynamic analysis of the processes expected during obtaining elementary boron, carbide and boron nitride by the method of self-propagating high-temperature synthesis (1 kal=4. 184j)

Element, compound	$-\Delta H^\circ_{298}$, kkal/mole^{-1}	S°_{298}, kal/mole$^{-1}\cdot K^{-1}$	T_{tr}	T_m	T_b	λ_m	λ_{tr}	λ_b	Coefficients of equation $Cp=A+BT+CT^{-2}$ (kal/mole$^{-1}\cdot K^{-1}$)			Temperature range of the equation Cp=f (T) K	Cp(L)	Cp(g)
			K			kkal/mole^{-1}			A	$B\cdot 10^3$	$-C\cdot 10^{-5}$		kal/mole$^{-1}\cdot K^{-1}$	
O_2	-	49.005±0.008	-	-	-	-	-	-	7.16	1.00	0.40	298-3000	-	-
F_2	-	48.45±0.06	-	-	-	-	-	-	8.29	0.44	0.80	298-2000	-	-
N_2	-	45.769±0.013	-	-	-	-	-	-	6.66	1.02	-	298-2500	-	-
C	-	1.372±0.015	-	-	-	-	-	-	5.841	0.104	7.559	298-4000	-	-
K	-	15.46±0.05	-	336.66	1040	-	0.558±0.05	19.0±0.2	6.04	3.12	-	298- T_m	7.09*	4.97
Mg	-	7.81±0.02	-	923	1368	-	2.03±0.05	30.55±0.25	5.33	2.45	0.103	298- T_m	8.11*	4.98
Al	-	6.775±0.02	-	933.5	-	-	2.58±0.03	-	4.94	2.96	-	298- T_m	7.6	-
B	-	1.40±0.02	-	2348	-	-	5.4±1.0	-	4.735	1.38	2.20	298-1700	-	-
KF	135.3±0.3	15.90±0.05	-	131.1	1780±10	-	7.02±0.1	41.0±1.0	11.02	3.12	-	298- T_m	16.1*	-
MgF_2	268.7±0.3	13.72±0.05	-	1536.0	2545	-	13.9±0.2	65.4±2.0	16.93	2.52	2.20	298- T_m	22.6	
AlF_3	361.0±0.3	15.89±0.08	727±1	-	1552±20	0.136	-	65.1±0.2	17.27 20.93	10.96 3.0	2.3 -	298-727(α) 727-1400 (β)		
KBF_4	450.3±0.4	32.0±4.0	556	843	-	3.3±0.1	4.3±0.1	-	27.96 38.66 39.94	18.27 - -	2.88 - -	298-556 556-843 >843		
MgO	143.76±0.07	6.47±0.05	-	30.98	-	-	18.5±1.5	-	11.71	0.75	2.80	298-3095		
Al_2O_3	400.5±0.3	12.17±0.02	-	2326	-	-	27.0±2.0	-	25.48	4.25	6.82	298-1800		
B_2O_3	304.23±0.29	12.90±0.07	-	723	-	-	5.87±0.02	-	13.63	17.45	3.36	298- T_m	30.50 (T_m-1800)	
B_4C	17.1±2.8	6.48±0.03	-	2623					26.8	1.75	12.5	298-2623**		
BN	60.38±0.43	3.54±0.04	-	3240±20					11.08	0.67	4.23	298-1700**		

* Calculated according to the method proposed in [7]; ** Coefficients of the equation Cp=f (T) calculated according to the method proposed in [8]

reduction

11. ½ B_2O_3+ 1½ Mg + ¼C = ¼B_4C+1½ MgO
12. ½ B_2O_3+ Al + ¼C = ¼B_4C+ ½ Al_2O_3
13. ½ B_2O_3+ 1½ Mg + ½ N_2 = BN+1½ MgO
14. ½ B_2O_3+ Al + ½ N_2 = BN+ ½ Al_2O_3

For a comparative assessment of the obtained results all the reactions are composed counting upon one mole of boron. Considering the aforementioned situation for reactions 1-14 within corresponding temperature ranges, equations of temperature dependence of Gibbs free energy were formed; the numerical values of coefficients of these equations are presented in Table 2.

Table 2

Coefficients of the equation of temperature dependence of Gibbs free energy of the reactions expected during reduction of boron from potassium tetra fluoboron (KBF_4) and boron oxide as well as of the synthesis of carbide and boron nitride by a direct method and SHS (1 kal =4.184j)

Reaction	Coefficients of the equation ΔG_T° = A+BTlgT+CT			Temperature range K
	-A	B	C	
1	2	3	4	5
1 $B_{(S)}$+ ¼$C_{(S)}$= ¼ $B_4C_{(S)}$	4050 (±700)	0.45	-1.74 (±0.1)	298-1700
2 $B_{(S)}$+ ½ $N_{2\,(g)}$= $BN_{(S)}$	60890 (±430)	-3.55	32.24 (±0.07)	298-1700
3 $KBF_{4(S)}'$+1½$Mg_{(S)}$=$B_{(S)}$+ $KF_{(S)}$ +1½$MgF_{2(S)}$	88160 (±400)	4.42	-5.78 (±0.40)	298-337
$KBF_{4(S)}'$+1½$Mg_{(S)}$=$B_{(S)}$+ $KF_{(S)}$ +1½$MgF_{2(S)}$	94790 (±450)	7.13	-0.21 (±0.39)	337-556
$KBF_{4(S)}''$ +1½$Mg_{(S)}$=$B_{(S)}$+ $KF_{(S)}$ +1½$MgF_{2(S)}$	90180 (±450)	12.9	-25.71 (±0.6)	556-843
$KBF_{4(L)}$ +1½$Mg_{(S)}$=$B_{(S)}$+ $KF_{(S)}$ +1½$MgF_{2(S)}$	94340 (±480)	13.34	-20.85 (±0.6)	843-923
$KBF_{4(L)}$ +1½$Mg_{(L)}$=$B_{(S)}$+ $KF_{(S)}$ +1½$MgF_{2(S)}$	95780 (±750)	12.78	-19.67 (±0.93)	923-1040
$KBF_{4(L)}$ +1½$Mg_{(L)}$=$B_{(S)}$+ $KF_{(S)}$ +1½$MgF_{2(S)}$	98130 (±800)	7.28	-0.87 (±1.06)	1040-1131
$KBF_{4(L)}$ +1½$Mg_{(L)}$=$B_{(S)}$+ $KF_{(S)}$ +1½$MgF_{2(S)}$	93100 (±860)	3.6	5.96 (±1.1)	1131-1368
$KBF_{4(L)}$ +1½$Mg_{(g)}$=$B_{(S)}$+ $KF_{(L)}$ +1½$MgF_{2(S)}$	150160 (±1060)	-12.91	99.29 (±1.53)	1368-1536
$KBF_{4(L)}$ +1½$Mg_{(g)}$=$B_{(S)}$+ $KF_{(L)}$ +1½$MgF_{2(L)}$	132240 (±1200)	-20.0	110.08 (±1.66)	1536-1700
4 $KBF_{4(S)}'$+ $Al_{(S)}$= $B_{(S)}$+ $KF_{(S)}$ + $AlF_{3(\alpha)}$	45740 (±500)	3.05	-4.83 (±0.46)	298-337
$KBF_{4(S)}'$+ $Al_{(S)}$= $B_{(S)}$+ $KF_{(S)}$ + $AlF_{3(\alpha)}$	52370 (±550)	3.76	0.74 (±0.55)	337-556
$KBF_{4(S)}''$ + $Al_{(S)}$= $B_{(S)}$+ $KF_{(S)}$ + $AlF_{3(\alpha)}$	46760 (±600)	11.53	-24.76 (±0.81)	556-727
$KBF_{4(S)}''$ + $Al_{(S)}$= $B_{(S)}$+ $KF_{(S)}$ + $AlF_3(\beta)$	46550 (±600)	11.32	-24.45 (±0.81)	727-843
$KBF_{4(L)}$ + $Al_{(S)}$= $B_{(S)}$+ $KF_{(S)}$ + $AlF_3(\beta)$	51710 (±650)	11.76	-18.59 (±0.86)	843-934
$KBF_{4(L)}$ + $Al_{(L)}$= $B_{(S)}$+ $KF_{(S)}$ + $AlF_3(\beta)$	53930 (±670)	14.56	-25.23 (±0.9)	934-1040
$KBF_{4(L)}$ + $Al_{(L)}$= $B_{(S)}$+ $KF_{(S)}$ + $AlF_3(\beta)$	56280 (±730)	9.06	-6.43 (±1.05)	1040-1131
$KBF_{4(L)}$ + $Al_{(L)}$= $B_{(S)}$+ $KF_{(L)}$ + $AlF_3(\beta)$	51250 (±780)	5.37	0.4 (±1.1)	1131-1552

Table 2 continue

1	2	3	4	5
5				
$KBF_{4(S)}' + 1\tfrac{1}{2}Mg_{(S)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + \tfrac{1}{2}MgF_{2(S)}$	92210 (±600)	4.87	-7.52 (±0.40)	298-337
$KBF_{4(S)}' + 1\tfrac{1}{2}Mg_{(S)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + \tfrac{1}{2}MgF_{2(S)}$	98840 (±650)	7.58	-1.98 (±0.42)	337-556
$KBF_{4(S)}'' + 1\tfrac{1}{2}Mg_{(S)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + \tfrac{1}{2}MgF_{2(S)}$	93230 (±680)	13.35	-27.45 (±0.60)	556-843
$KBF_{4(L)} + 1\tfrac{1}{2}Mg_{(S)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + \tfrac{1}{2}MgF_{2(S)}$	98390 (±720)	13.79	-22.59 (±0.63)	843-923
$KBF_{4(L)} + 1\tfrac{1}{2}Mg_{(S)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + \tfrac{1}{2}MgF_{2(S)}$	99830 (±750)	13.23	-21.41 (±0.65)	923-1040
$KBF_{4(L)} + 1\tfrac{1}{2}Mg_{(L)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + \tfrac{1}{2}MgF_{2(S)}$	101880 (±780)	7.73	-2.61 (±0.74)	1040-1131
$KBF_{4(L)} + 1\tfrac{1}{2}Mg_{(L)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(L)} + \tfrac{1}{2}MgF_{2(S)}$	97150 (±800)	4.04	4.22 (±0.76)	1131-1368
$KBF_{4(L)} + 1\tfrac{1}{2}Mg_{(g)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(L)} + \tfrac{1}{2}MgF_{2(S)}$	154210 (±940)	-12.46	97.55 (±1.05)	1368-1536
$KBF_{4(L)} + 1\tfrac{1}{2}Mg_{(g)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(L)} + \tfrac{1}{2}MgF_{2(S)}$	136290 (±1040)	-19.51	108.34 (±1.14)	1536-1700
6				
$KBF_{4(S)} + Al_{(S)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + AlF_3(\alpha)$	50060 (±560)	3.50	-6.57 (±0.34)	298-337
$KBF_{4(S)}' + Al_{(S)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + AlF_3(\alpha)$	56420 (±600)	6.21	1.00 (±0.4)	337-556
$KBF_{4(S)}'' + Al_{(S)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + AlF_3(\alpha)$	50810 (±630)	11.98	-26.5 (±0.54)	556-727
$KBF_{4(S)}'' + Al_{(S)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + AlF_3(\beta)$	50500 (±630)	11.77	-26.19 (±0.56)	727-843
$KBF_{4(L)} + Al_{(S)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + AlF_3(\beta)$	55760 (±670)	12.21	-21.33 (±0.61)	843-934
$KBF_{4(L)} + Al_{(L)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + AlF_3(\beta)$	57980 (±680)	15.01	-26.97 (±0.63)	934-1040
$KBF_{4(L)} + Al_{(L)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + AlF_3(\beta)$	60330 (±720)	9.51	-8.17 (±0.73)	1040-1131
$KBF_{4(L)} + Al_{(L)} + \tfrac{1}{4}C_{(S)} = \tfrac{1}{4}B_4C_{(S)} + KF_{(S)} + AlF_3(\beta)$	55300 (±750)	5.82	1.35 (±0.76)	1131-1552
7				
$KBF_{4(S)}' + 1\tfrac{1}{2}Mg_{(S)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + 1\tfrac{1}{2}MgF_{2(S)}$	149500 (±530)	-0.87	26.46 (±0.30)	297-337
$KBF_{4(S)}' + 1\tfrac{1}{2}Mg_{(S)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + 1\tfrac{1}{2}MgF_{2(S)}$	156040 (±560)	3.58	32.03 (±0.31)	337-556
$KBF_{4(S)}'' + 1\tfrac{1}{2}Mg_{(S)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + 1\tfrac{1}{2}MgF_{2(S)}$	150430 (±570)	9.35	6.52 (±0.42)	556-843
$KBF_{4(L)} + 1\tfrac{1}{2}Mg_{(S)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + 1\tfrac{1}{2}MgF_{2(S)}$	155590 (±630)	9.79	11.39 (±0.49)	843-923
$KBF_{4(L)} + 1\tfrac{1}{2}Mg_{(L)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + 1\tfrac{1}{2}MgF_{2(S)}$	157030 (±640)	9.23	12.57 (±0.48)	923-1040
$KBF_{4(L)} + 1\tfrac{1}{2}Mg_{(L)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + 1\tfrac{1}{2}MgF_{2(S)}$	159020 (±690)	3.73	31.37 (±0.54)	1040-1131
$KBF_{4(L)} + 1\tfrac{1}{2}Mg_{(L)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + 1\tfrac{1}{2}MgF_{2(S)}$	153990 (±720)	0.04	38.20 (±0.57)	1131-1368
8				
$KBF_{4(S)}' + Al_{(S)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + AlF_3(\alpha)$	105630 (±480)	-0.50	27.41 (±0.26)	298-337
$KBF_{4(S)}' + Al_{(S)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + AlF_3(\alpha)$	113260 (±510)	2.21	32.98 (±0.29)	337-556
$KBF_{4(S)}'' + Al_{(S)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + AlF_3(\alpha)$	107650 (±540)	7.98	7.48 (±0.42)	556-727
$KBF_{4(S)}'' + Al_{(S)} + \tfrac{1}{2}N_{2(g)} = BN_{(S)} + KF_{(S)} + AlF_3(\beta)$	107440 (±540)	7.77	7.79 (±0.48)	727-843

Table 2 continue

1	2	3	4	5
$KBF_{4(L)} + Al_{(S)} + ½ N_{2(g)} = BN_{(S)} + KF_{(S)} + AlF_3(\beta)$	112500 (±580)	8.21	12.65 (±0.45)	843-934
$KBF_{4(L)} + Al_{(L)} + ½ N_{2(g)} = BN_{(S)} + KF_{(S)} + AlF_3(\beta)$	114820 (±590)	11.01	7.01 (±0.46)	934-1040
$KBF_{4(L)} + Al_{(L)} + ½ N_{2(g)} = BN_{(S)} + KF_{(S)} + AlF_3(\beta)$	117170 (±630)	5.51	25.81 (±0.54)	1040-1131
$KBF_{4(L)} + Al_{(L)} + ½ N_{2(g)} = BN_{(S)} + KF_{(S)} + AlF_3(\beta)$	112140 (±660)	1.82	32.64 (±0.57)	1131-1552
9				
$½ B_2O_{3(S)} + 1½ Mg_{(S)} = B_{(S)} + 1½ MgO_{(S)}$	64830 (±130)	-6.99	28.8 (±0.57)	298-723
$½ B_2O_{3(L)} + 1½ Mg_{(S)} = B_{(S)} + 1½ MgO_{(S)}$	65240 (±140)	4.02	-4.1 (±0.5)	723-923
$½ B_2O_{3(L)} + 1½ Mg_{(L)} = B_{(S)} + 1½ MgO_{(S)}$	76530 (±180)	5.91	-5.11 (±0.38)	923-1368
$½ B_2O_{3(L)} + 1½ Mg_{(g)} = B_{(S)} + 1½ MgO_{(S)}$	120300 (±180)	-5.74	70.0 (±0.27)	1368-1800
10				
$½ B_2O_{3(S)} + Al_{(S)} = B_{(S)} + ½ Al_2O_{3(S)}$	49070 (±150)	-5.44	23.28 (±0.3)	298-723
$½ B_2O_{3(L)} + Al_{(S)} = B_{(S)} + ½ Al_2O_{3(S)}$	49480 (±170)	5.27	-7.62 (±0.23)	723-934
$½ B_2O_{3(L)} + Al_{(L)} = B_{(S)} + ½ Al_2O_{3(S)}$	54420 (±180)	2.93	5.51 (±0.26)	934-1800
11				
$½ B_2O_{3(S)} + ½ Mg_{(S)} + ¼ C_{(S)} = ¼ B_4C + 1½ MgO_{(S)}$	68880 (±480)	-6.24	27.66 (±0.62)	298-723
$½ B_2O_{3(L)} + ½ Mg_{(S)} + ¼ C_{(S)} = ¼ B_4C + 1½ MgO_{(S)}$	69290 (±490)	4.25	-3.84 (±0.54)	723-923
$½ B_2O_{3(L)} + ½ Mg_{(L)} + ¼ C_{(S)} = 1/4 B_4C + 1½ MgO_{(S)}$	71580 (±530)	6.36	-6.85 (±0.43)	923-1368
$½ B_2O_{3(L)} + ½ Mg_{(g)} + ¼ C_{(S)} = 1/4 B_4C + 1½ MgO_{(S)}$	124350 (±530)	-5.29	68.25 (±0.32)	1368-1700
12				
$½ B_2O_{3(S)} + Al_{(S)} + ¼ C_{(S)} = ¼ B_4C_{(S)} + ½ Al_2O_{3(S)}$	53120 (±500)	-4.99	21.14 (±0.35)	298-723
$½ B_2O_{3(L)} + Al_{(S)} + ¼ C_{(S)} = ¼ B_4C_{(S)} + ½ Al_2O_{3(S)}$	53530 (±520)	5.72	-9.36 (±0.27)	723-934
$½ B_2O_{3(L)} + Al_{(L)} + ¼ C_{(S)} = ¼ B_4C_{(S)} + ½ Al_2O_{3(S)}$	58470 (±530)	3.38	3.77 (±0.18)	934-1700
13				
$½ B_2O_{3(S)} + ½ Mg_{(S)} + ½ N_{2(g)} = BN_{(S)} + 1½ MgO_{(S)}$	125720 (±230)	-10.54	61.04 (±0.4)	298-723
$½ B_2O_{3(L)} + ½ Mg_{(S)} + ½ N_{2(g)} = BN_{(S)} + 1½ MgO_{(S)}$	126130 (±240)	0.47	30.14 (±0.35)	723-923
$½ B_2O_{3(L)} + ½ Mg_{(L)} + ½ N_{2(g)} = BN_{(S)} + 1½ MgO_{(S)}$	128420 (±260)	2.30	27.13 (±0.28)	923-1368
$½ B_2O_{3(L)} + ½ Mg_{(g)} + ½ N_{2(g)} = BN_{(S)} + 1½ MgO_{(S)}$	181190 (±260)	-9.29	102.23 (±0.2)	1368-1700
14				
$½ B_2O_{3(S)} + Al_{(S)} + ½ N_{2(g)} = BN_{(S)} + ½ Al_2O_{3(S)}$	109960 (±240)	-9.29	55.52 (±0.22)	298-723
$½ B_2O_{3(L)} + Al_{(S)} + ½ N_{2(g)} = BN_{(S)} + ½ Al_2O_{3(S)}$	110370 (±250)	1.72	24.62 (±0.17)	723-934
$½ B_2O_{3(L)} + Al_{(L)} + ½ N_{2(g)} = BN_{(S)} + ½ Al_2O_{3(S)}$	115310 (±260)	-0.62	37.75 (±0.11)	934-1700

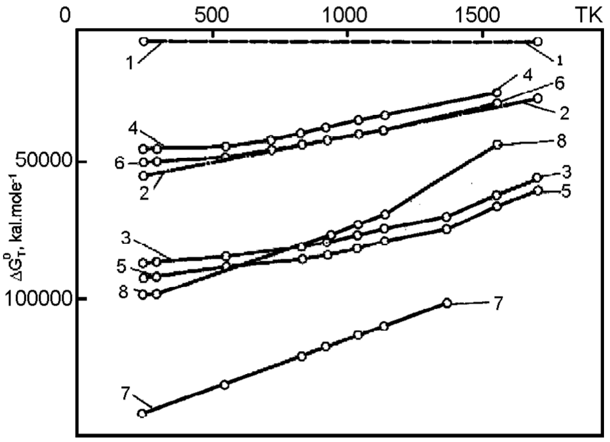

Fig. 1. Dependence of ΔG_T° reactions 1-8 on temperature

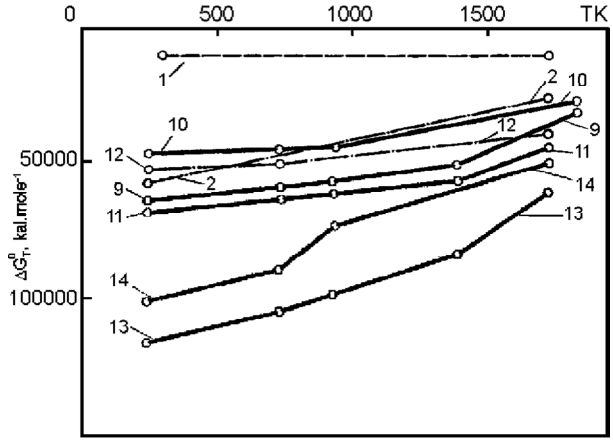

Fig. 2. Dependence of ΔG_T° reactions 1,2,9-14 on temperature

Upon the basis of Table 2 data, a diagram of dependence of Gibbs free energy (ΔG_T°) versus the temperature for the reactions 1-14 was constructed. Fig. 1 presents ΔG_T° for the reactions (3-8), proceeding on the basis of potassium tetra fluoboron KBF_4 and for comparison - ΔG_T° reactions of a direct synthesis of B_4C and BN from the elements (curves 1, 2), while in Fig.2 - ΔG_T° for the reactions (9-14) proceeding on the basis of boron oxide - B_2O_3, as well as similarly – to the previous case - ΔG_T° of the reactions 1 and 2.

From the cited diagrams (Fig. 1, 2) there follows that in the considered temperature range, the probability of a direct synthesis of B_4C, according to reaction 1 is too low; on the other hand, the probability of nitration of boron at rather moderate temperatures - within 1000K is not excluded. The data in Fig. 1 confirm that metal-thermal reduction of KBF_4 by magnesium (curve 3 - Fig. 1) is energy-wise more profitable than aluminothermics (curve 4 - Fig.1). Analogously, the SHS process with the preceding thermomagnesium reduction (curves 5, 7 - Fig.1) as compared to aluminothermics (curves 6-8 – Fig. 1), provides more acceptable energy-wise results.

A similar result is provided while using B_2O_3 as raw material (Fig. 2); however, the curves ΔG_T° are moved to less energy-negative values, therefore, the probability of obtaining the desired product - B, B_4C and BN, upon the basis of B_2O_3 is energy-wise lower than while using KBF_4. Besides, an additional barrier is the difficulty with separation of the obtained product. While using KBF_4, such product as KF, MgF_2 and AlF_3, due to volatility, is easily removable from the reaction zone, while in the case of B_2O_3 removal of such product as MgO and Al_2O_3 is a rather complicated problem.

An analysis of the data in Fig. 1 and 2 allows to conclude that in the sphere of melting of original materials KBF_4 (843 K), B_2O_3 (723 K), magnesium (923 K) and aluminum (934 K) favorable kinetic conditions will be provided for implementing the aforementioned reactions, which will have to attain high rates within the temperature range 1100-1300 K.

ფიზიკური ქიმია

ბორის, ბორის კარბიდისა და ნიტრიდის მიღების პროცესის თერმოდინამიკური ალბათობა თვითგავრცელებადი მაღალტემპერატურული სინთეზის დროს

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თვითგავრცელებადი მაღალტემპერატურული სინთეზის (თმს) დროს კალიუმის ტეტრაბორფტორატისა და ბორის ოქსიდის ბაზაზე ბორის, მისი კარბიდისა და ნიტრიდის მიღებისას შესაძლებელ რეაქციათა განხორციელების ალბათობის დადგენისათვის შედგენილ იქნა გამოსაკვლევ რეაქციათა (სულ 14 რეაქცია) გიბსის თავისუფალი ენერგიის (ΔG_T°) ტემპერატურული ცვალებადობის განტოლებები. მიღებული განტოლებების ანალიზის საფუძველზე შეიძლება დავადგინოთ, რომ თმს წინმსწრები მაგნითერმიით ენერგეტიკულად უფრო ხელსაყრელია ვიდრე ალუმოთერმია. ბორის ნიტრიდი შესაძლებელია მივიღოთ აგრეთვე ბორის პირდაპირი აზოტირებითაც. კინეტიკური კანონზომიერებიდან გამომდინარე საწყის მასალად კალიუმის ტეტრაბორფტორატის გამოყენება უზრუნველყოფს სუფთა ინდივიდუალური პროდუქტების მიღებას.

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Received December, 2009