STUDIES ON REACTION BETWEEN GAS AND SOLID. VI. AZOTATION OF CALCIUM CARBIDE AND THE EFFECT OF CATALYSERS ON ITS VELOCITY.[1]

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It has been known that the most effective and technically important catalysers for the reaction of calcium carbide with nitrogen to form calcium cyanamide are chloride and fluoride of calcium.[2] In the present work the effects of catalysers of various kinds in various quantities upon some kinds of technical carbide have been experimentally studied.

Experimental.

1. Calcium Fluoride. The samples of carbide (powdered) and the method employed were similar to those of the former experiments for the determination of the effect of temperature upon the same reaction. The results are shown in Table 1 and Figs. 1 and 2. The temperature was kept at 1000°C. The samples of carbide of Exp. No. 362, 375, 391, 392, 393, 394 were the same, while that of No. 425 was taken from another source. Fig. 2 was obtained from Fig. 1 by integrating the velocity graphically and comparing the final values with the results of analyses of the products.

Similar results were obtained with "granular carbide," which was prepared by K. Hibi's method in a spherical grain of about 1–2 mm. in diameter. The temperature was kept at 1140°C. (Tables 2, 3 and Fig. 3). Taking the quantity of calcium fluoride added to the carbide as abscissa, and the time (in min.) required to reach definite degrees of azotation as ordinate, we have Fig. 4.

From these experimental results we see that there is an optimum quantity of fluoride to be added to the carbide, as was reported by F. Foerster and H. Jacoby.[3] The optimum quantity is a function of reaction temperature and kinds of carbides; for instance, no effect being perceived by adding CaF_2 at 870°C.

It is also interesting that the point of the maximum velocity is also a function of the quantities of CaF_2 added, the larger the quantity, the later comes the point (Table 4).

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(1) Read before the meeting of the Chemical Society of Japan in Dec. 1931.
(2) F. Foerster and H. Jacoby, *Z. Elektrochem.* **12** (1907), 101. G. Bredig, W. Fraenkel and E. Wilke, ibid. **13** (1907), 605. Polzeniuss, D. R. P. Nr. 163320, Kl. 12k (1901).
(3) F. Foerster and H. Jacoby, *Z. Elektrochem.* **12** (1907), 101.

Table 1.

Azotation velocity of powdered carbide with various quantities of calcium fluoride at const. temp. of 1000°C.

Exp. No.	375		391		392		393		394		425	
$+CaF_2$	6 *u**		11 *u*		4 *u*		2.5 *u*		1 *u*		0 *u*	
CaC_2 %	66.8		64.2		68.5		69.5		70.6		74.4	
Sample, gr.	3.0012		3.3011		3.0929		3.0011		3.0012		3.0135	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1		0.02	0.07	0.14	0.07	0.14	0.09	0.16	0.09	0.19	0.175	0.29
2		0.07	0.08	0.29	0.08	0.30	0.13	0.39	0.14	0.40	0.24	
3	0.068	0.18	0.09	0.46	0.11	0.49	0.20	0.72	0.24	0.76	0.30	0.87
4	0.10	0.35	0.11		0.14	0.75	0.29	1.21	0.40	1.41	0.33	1.51
5	0.15	0.57	0.14	0.94	0.18		0.40	1.89	0.73	2.62	0.33	2.19
6	0.18	0.83	0.17		0.22	1.51	0.53	2.81	1.21	4.54	0.325	
7	0.21	1.23	0.20	1.65	0.26	2.03	0.72	4.06		7.55	0.315	3.53
8	0.31	1.72	0.23		0.33	2.64	1.05	5.91	1.92	11.50	0.303	
9	0.38	2.36	0.26	2.62	0.43	3.44	1.60	8.83	1.61	15.29	0.294	
10	0.47	3.11	0.30	3.22	0.57	4.50	2.85	13.44	1.28	18.34	0.283	5.39
12	0.80	5.33	0.43	4.78	1.04	7.87	3.76	27.85	1.07	23.36	0.26	
14	1.25	9.01	0.63	7.01	2.22	14.54	2.50	41.08	0.93	27.63	0.24	
16	2.015	15.22	0.90	10·23	2.50	24.62	1.46	48.95	0.81	31.36	0.22	
18	2.02	22.75	1.19	14.56	1.67	33.83	0.88	53.70	0.69	34.55	0.203	
20	1.84	29.96	1.43	20.10	1.15	39.54	0.71	56.90	0.58	37.21	0.185	10.14
25	1.08		1.14	34.90	0.80		0.52	62.90	0.51	43.10	0.160	
30	0.82	50.97	0.96	45.86	0.56	56.59	0.38	67.45	0.44	48.25	0.155	13.54
35	0.63		0.73	54.82	0.41		0.35	71.00	0.39		0.146	15.08
40	0.53	62.95	0.55	61.55	0.35	65.90	0.30	74.50	0.37	56.60	0.135	16.56
45	0.43		0.45		0.31	69.40	0.22	77.10	0.35	60.40	0.128	17.92
50	0.32	70.72	0.37	71.10	0.23	72.20	0.17	79.10	0.31	63.90	0.12	19.21
60	0.21	75.60	0.19	77.00	0.17	76.35	0.11	81.85	0.245	69.85	0.104	21.53
70	0.13	78.35	0.10		0.11	79.35	0.07	83.60	0.19	74.45	0.10	23.60
80	0.09	80.00	0.06	80.95	0.08	81.35	0.045	84.75	0.145	78.05	0.095	25.56
90	0.06	81.30	0.03	82.45	0.06	82.75	0.025	85.55	0.095	80.40	0.088	27.50
100	0.05	82.20	0.025	83.10	0.04	83.90	0.020	85.95	0.07	82.15	0.080	29.20
120	0.02	83.15	0.013	83.80	0.024	85.10	0.008	86.50	0.036	84.25	0.077	32.45
140			0.007	84.20	0.014	85.80	0.003	86.65	0.018	85.45	0.074	35.56
160					0.007	86.10			0.011	85.85	0.068	38.48
180					0.004	86.15			0.006	86.20	0.065	41.25
200					0.003	86.20						

* To the author's regret, the unit "*u*" cannot be explained here.

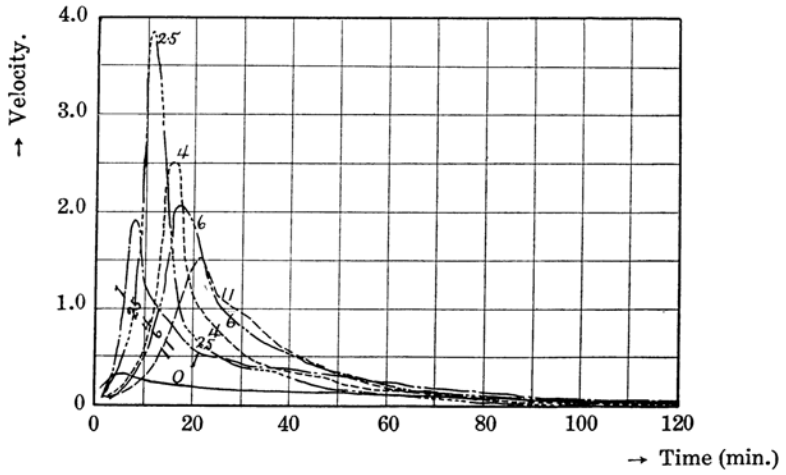

Fig. 1. Azotation velocity of powdered carbide at 1000°C., the numbers on the curves indicating the quantity of CaF_2 added. (in unit "u").

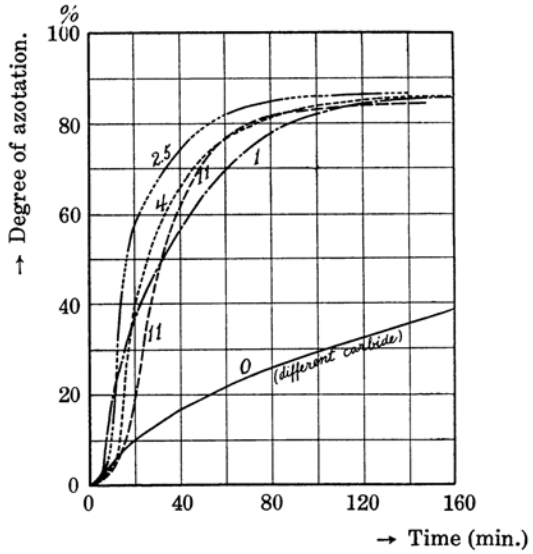

Fig. 2. Effect of CaF_2 upon the azotation of powdered carbide at 1000°C. The numbers on the curves indicate the quantity of CaF_2 added (in unit "u").

Table 2.

Azotation velocity of "granular carbide" with calcium fluoride at constant temp. of 1140°C. Using reaction tube A.

Exp. No.	376		378		379	
$+CaF_2$	0		0		3 *u*	
Carbide %	62.9		72.1		69.2	
Sample gr.	3.0036		3.0043		3.0004	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	1.11	1.70	0.68?	1.06		(0.54)
2	1.30	4.08	0.833	3.39	0.588	1.99
3	1.35	6.61	0.82	5.90	0.908	4.33
4	1.36	9.19	0.78	8.33	1.176	7.75
5	1.35	11.75	0.73	10.59	1.25	11.72
6	1.33	14.28	0.68	12.73	1.00	15.32
7	1.32	16.78	0.66	14.71		18.32
8	1.29	19·25	0.63	16.66	0.80	21.00
9	1·27	21.68	0.61	18.55	0.715	
10	1.24	24.05	0.60	20.40	0.715	25.70
12	1.18	28.63	0.58	23.94	0.55	29.73
14	1.12	33.02	0.55	27.36	0.53	33.34
16	1.06	37.40	0.51	30.65	0.48	36.58
18	0.995	41.10	0.50	33.78	0.46	39.68
20	0.939	44.75	0.49	36.78	0.44	42.58
25			0.44		0.40	49.65
30	0.701	60.02	0.415	50.40	0.37	55.75
35			0.38		0.33	61.40
40	0.464	71.10	0.35	61.95	0.28	66.35
45					0.24	
50	0.192	77.0	0.26	71.10	0.19	75.60
60	0.064	79.2	0.175	77.55	0.09	80.00
70	0.025	79.9	0.080	81.25	0.02	81.55
80	0.000	80.0	0.025	82.70	0.00	81.70
90			0.000	82.90		

Table 3.

Azotation velocity of "granular carbide" with calcium fluoride at constant temp. of 1140°C. Using reaction tube B.

Exp. No.	390		382		383		384		385	
$+CaF_2$	0		6 *u*		10 *u*		2 *u*		4 *u*	
Carbide %	72.3		68.1		65.2		70.3		69.3	
Sample, gr.	3.0008		3.0029		3.0029		3.0030		3.0010	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	1.07	1.05		(0.09)	0.167	0.22	0.213	0.33	0.541	0.68
2	1.25	3.48	0.133	0.38	0.220	0.68	1.00	1.55	0.788	2.13
3	1.25	6.10	0.290	1.04	0.267		1.92	5.20	1.30	4.51
4	1.19	8.65	0.371	2.04	0.303	1.94	1.50	9.11	1.37	7.75
5	1.07	10.98	0.425	3.29	0.353		1.40	12.48	1.37	10.92
6	1.04	13.17	0.500	4.73	0.395	3.60	1.25	15.50	1.25	
7	1.00		0.565	6.36	0.423		1.15	18.10	1.15	16.58
8	1.00	17.36	0.588	8.12	0.447	5.64	0.97	20.35	1.07	
9	0.909		0.605	9.94	0.470		0.88	22.35	0.92	21.25
10	0.909	21.29	0.590	11.75	0.490	7.88	0.84	24.25	0.84	23.25
12	0.862		0.545	14.88	0.510	10.28	0.76	27.82	0.788	26.90
14	0.838		0.513	18.42	0.522	12.77	0.74	31.12	0.730	
16	0.769		0.485	21.45	0.525	15.30	0.70	34.25	0.705	33.62
18	0.685		0.460	24.32	0.520	17.84	0.67	37.20	0.667	
20	0.699	37.92	0.445	27.06	0.510	20.29	0.62	40.00	0.640	39.70
25	0.614	44.73	0.405		0.485		0.55		0.59	
30	0.570	50.90	0.390	39.68	0.460	31.82	0.51	52.30	0·55	53.07
35			0.375		0.440		0.46		0.49	
40	0.440	61.50	0.350	51.10	0,415	42.48	0.415	62.80	0.42	64.10
45	0.377			56.25	0.393		0.365		0.375	
50	0.350	69.65	0.300	61.00	0.370	51.90	0.310	70.90	0.31	72.35
60	0.220	75.30	0.210	69.35	0.320	60.20	0.204	76.60	0.17	77.70
70	0.110	78.90	0.150	74.90	0.270	67.30	0.105	79.90	0.08	80.40
80	0.047	80.40	0.080	78.30	0.200	73.00	0.095	81.45	0.025	
90	0.023	81.10	0.040	80.00	0.135	77.10	0.020	82.10	0.000	81.70
100	0.000	81.35	0.021	80.55	0.075	79.50	0.000	83.13		
120			0.000	80.75	0.010	81.15				

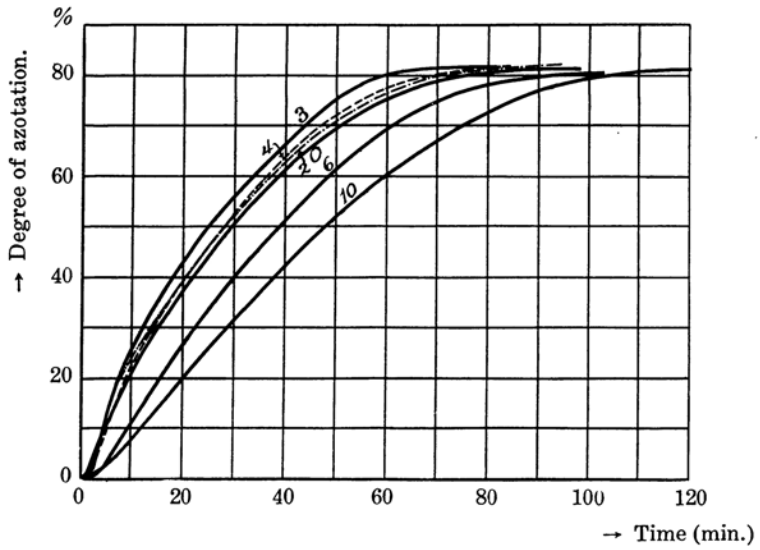

Fig. 3. Effect of CaF_2 upon the azotation of "granular carbide" of 71.0% purity at 1140°C. The numbers on the curves indicate the quantity of CaF_2 added. (in unit "u").

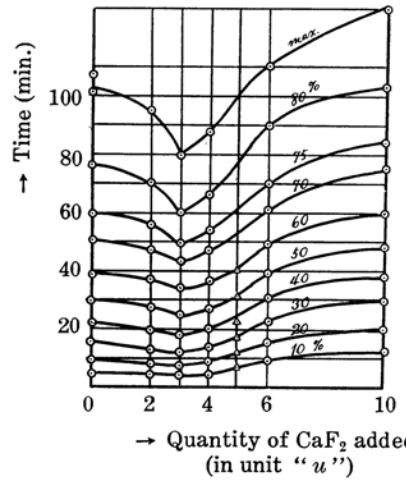

Fig. 4. Time (min.) required to attain to the equal degrees of azotation and the effect of CaF_2 added to the granular carbide of 1 ~ 2 mm. dia. ($CaC_2 = 71.0\%$)

Table 4.

Effect of CaF_2 upon the time of the velocity maximum.

a) Powdered carbide at 1000°C.

Exp. No.	425	394	393	392	375	391
$+CaF_2$	0 *u*	1 *u*	2.5 *u*	4 *u*	6 *u*	11 *u*
Time of vel. max. (min.)	4.5	8.0	11.3	15.–16.5	17–18.5	21.5

b) "Granular carbide" at 1140°C.

Exp. No.	378	384	379	385	382	383
$+CaF_2$	0 *u*	2 *u*	3 *u*	4 *u*	6 *u*	10 *u*
Time of max. vel. (min.)	2.0–2.5	2.5	4.5–5.0	3.2	9.0	15.0–19.0

2. The Slag of a Phosphorus Furnace. This material was prepared from the slag produced by the reaction of phosphate rock and carbon to prepare phosphorus in an electric furnace. The analysis of the slag is as follows (the components are calculated provisionally as oxides):

P_2O_5	SiO_2	Fe_2O_3	Al_2O_3	Total CaO
1.29	18.36	1.75	16.55	49.40%

The effect upon the azotation velocity of calcium carbide is seen in Table 5.

It is very interesting that the slag has not only the accelerating effect, but it also diminishes the time to maximum velocity; the velocity decreases soon after less than two minutes from the beginning, and it is rather uncertain whether the maximum point really exists or not.

Table 5.

Effect of a phosphorus slag added 3% to the powdered carbide (CaC_2 = 74.4%) at 1000°C.

Exp. No.	421		425	
Slag %	3		0	
Sample, gr.	3.0037		3.0135	
Time	vel.	fix. %	vel.	fix. %
1		(2.57)	0.175	0.29
2	1.21	5.15	0.24	
3	1.08		0.30	0.87
4	0.855	10.45	0.33	1.51
5	(0.730)		0.33	2.19
6	0.625	13.63	0.325	
7	0.590		0.315	3.53
8	0.555	16.18	0.303	
9	0.529		0.294	
10	0.500	18.38	0.283	5.39
20	0.332	26.80	0.185	10.14
30	0.262	33.10	0.155	13.54
40	0.228	38.35	0.135	16.56
60	0.173	46.90	0.104	21.53
80	0.150	53.85	0.095	25.56
100	0.133	59.90	0.080	29.20
120	0.118	65.25	0.077	32.45

3. Calcium Chloride. The action of calcium chloride is eminent even at lower temperatures. There is a point of maximum velocity also in this case; the details will be given later with others.

4. Effect of Carbon and Carbon-containing Substances. In the previous paper[1] the author expressed his opinion that the nascent carbon liberated by the reaction, $CaC_2+N_2 = CaCN_2+C$, will be acting as an eminent catalyser for this reaction. To ascertain this problem, the following experiments were carried out, using the same apparatus and the same method hitherto employed. To the carbide powder of 900-mesh fineness and 71.3%

(1) T. Aono, This bulletin, **7** (1932), 247.

purity, a definite quantity of each "Darco carbon" (an active carbon), technical calcium cyanamide (21.68% N and 13.3% C) and calcium chloride (previously ignited and dehydrated) was added respectively and subjected to nitrogen at the same temperature (870°C.) and pressure (1 atm.) and the velocity of azotation was compared with the carbide without any added substance. The results are shown in Table 6, Figs. 5 and 6.

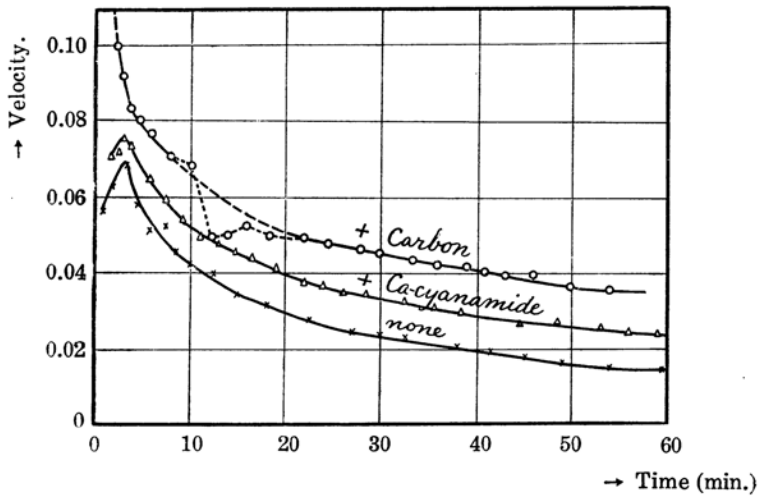

Fig. 5. Azotation velocity of powdered carbide at 870°C. with various catalysers.

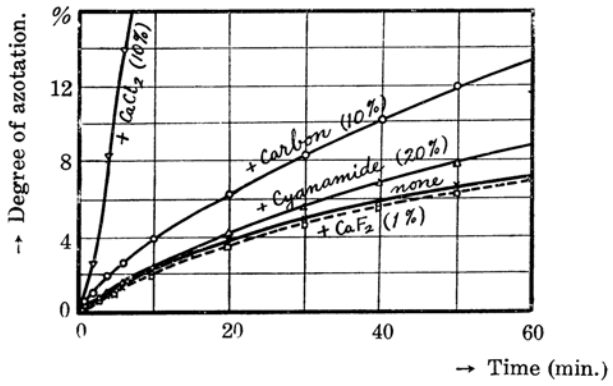

Fig. 6. Effect of various catalysers upon the azotation of powdered carbide at 870°C.

Table 6.

Effect of catalysers on the azotation of carbide power at 870°C. and 1 atm. pressure.

Exp. No.	524		525		521		523		361**	
Catalyser added %	0		Cyanamide, 20		"Darco C," 10		$CaCl_2$, 10		CaF_2, 1	
Sample. gr.	2.7023		2.702+0.543		2.741+0.274		2.736+0.274		4.043	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	0.0567	0.22					0.345	1.09		0.17
2	0.0633	0.46	0.0715	0.50	0.1070	1.10	0.625	2.62	0.0512	0.40
3	0.0690		0.0752	0.78	0 0925		0.835	5.05	0.0530	0.65
4	0.0655	1.02	0.0727	1.06	0.0830	1.91	1.000	8.35	0.0528	0.90
6	0.0520	1.49	0.0640	1.57	0.0770	2.61	0.715	13.90	0.0462	1.37
	0.0470		0.0578	2.03	0.0714		0.600	18.33	0.0396	1.77
10	0.0424	2.28	0.0525	2.45	0.0680	3.89	0.545	22.20	0.0358	2.13
15	0.0345	3.12	0.0456				0.455	30.65	0.0270	2.89
20	0.0298	3.79	0.0400	4.18	0 0500	6.21	0.393	37.78	0.0250	3.53
30	0.0243	4.96	0.0333	5.59	0.0455	8.34	*		0.0208	4.63
40	0.0195	5.92	0.0287	6.82	0.0408	10.17			0.0170	5.58
50	0.0158	6.75	0.0252	7.89	0.0360	11.95			0.0148	6.34
62	0.0142	7.50	0.0230	8.90		13.70			0.0130	7.13
Product N %	powder 2.34		powder 5.8		sintered very slightly 3.72		sintered slightly. >15		powder	

* N_2-pressure was changed after 20 minutes and the change of velocity with pressure was measured. The result was already reported in this bulletin, **7** (1932), 143–154.

** The carbide and the velocity unit are different from the other four; its purity is 68.2%.

It is evident from the table and figures, that addition of an active carbon not only accelerates the reaction, but also almost puts out the maximum point of velocity. In experiment No. 521 the maximum velocity did not appear after two minutes before which the velocity was not measured, while without carbon the maximum velocity appears after more than 3 minutes at this temperature. The accelerating action of carbon, especially at the earlier stage of the azotation may be recognized to be conspicuous. The action of the cyanamide at this lower temperature can also be attributed to the carbon contained in the cyanamide. It should be weak, because its quantity ($13.3 \times 0.2 = 2.66\%$) is small with respect to the carbide, and as the carbon in the cyanamide is in the form of graphite with

some amorphous carbon, and as it had been subjected to higher temperatures, the activity will be but weak. Calcium fluoride had no effect at 870°C., while calcium chloride accelerated the reaction extraordinally, which will be partly due to the action of decomposing the carbide, and setting carbon free. As to this problem, the discussion will be given later in this bulletin.

The most of these experiments were carried out in the research laboratory of the Denki-Kagaku-Kogyo Co. Ltd. Tokyo, before Sept. 10th (1930), and reported to the meeting of engineers and directors of the Co. on that day.

Summary.

The effects of some catalytic substances to the velocity of azotation of both powdered and "granular" carbide were experimentally determined.

1. There is an optimum quantity of calcium fluoride to be added to the carbide to get the highest velocity of azotation, the quantity of which is a function of both carbide and reaction temperature.

2. The added substances not only have some influence upon the velocity, but also change the characteristics of the velocity curves of azotation.

3. Carbon and carbon containing substances or those which sets carbon free from carbide show strong catalytic action to the azotation of calcium carbide. The opinion that the nascent carbon must be acting as a catalyser is supported.

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