STUDIES ON REACTIONS BETWEEN GAS AND SOLID. V. AZOTATION OF CALCIUM CARBIDE AND THE EFFECT OF SIZE OF GRAIN ON ITS VELOCITY.

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Experimental.

Experimant A. A block of a technical carbide was crushed by a mill and sieved in three parts: H = (less than 80 mesh), I = (48–80 mesh) and J = (larger than 48 mesh), and H and I were put in reaction with nitrogen in the same reaction tube at 1030°C. for 3 hrs. "Granular carbide"(1) (larger than 48 mesh) added with 5% of calcium fluoride was also subjected to azotation at 1030°C. for 4 hours. Table 5_1 shows the results.

If we assume that the particles are spheres of initial mean radius r_0, which was changed chemically to the depth r', then the ratio of the remaining carbide to the initial is given by Equation (5_1) :

Table 5_1.

	Crushed carbide		Granular carbide	
No. and date of the exp.	No. 302 (June 18, 1930)		No. 304 (June 20, 1930)	
	H	I	I	H
Sieves (mesh)	<80	80—48	5—8	8—48
Mean radius (r_0) mm.	0.044	0.117	1.59	0.664
Yield of acetylene (G) c.c./gr. at 15°C.	219.5	264.9	228.0	229.4
Temp. (°C.) and time (hrs.)	1030°; 3	1030°; 3	1030°; 4	1030°; 4
Gr. of samples taken (W)	2.3908	3.3696	2.6606	2.9925
Increase in weight ÷ W = (w)	0.0644	0.0321	0.0602	0.1150
Degrees of azotation %	36.0	12.7	23.6	48.7
Yield of acetylene G c.c./gr.	67.6	189.1	139.5	67.3
$(1+w)G'/G = \alpha$	0.325	0.750	0.650	0.337
α, corrected for efflorescence*	0.413	—	—	—
$1-\sqrt[3]{\alpha}$	0.255	0.091	0.134	0.304
Thickness of reacted layer (r') mm.	0.011	0.011	0.213	0.201

* This correction is due to the change $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$, $Ca(OH)_2 + CaC_2 = 2CaO + C_2H_2$ (by heating) and $C_2H_2 = 2C + H_2$, which has been determined by the author. The numerical value is given by

$$\frac{67.6 \times 1.0644}{219.5-(264.9-219.5)} = 0.413 .$$

(1) Vid. the former paper.

$$\alpha = \frac{(r_0 - r')^3}{r_0^3} = \frac{G'(1+w)}{G}, \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (5_1)$$

$$r' = (1 - \sqrt[3]{\alpha})\, r_0 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (5_2)$$

From these experiments r', namely $\int_0^t \left(\frac{dr'}{dt}\right) dt$, is found to be independent of the initial size r_0 of the particles (at 1030°C.). Whether the value $\left(\frac{dr'}{dt}\right)$ is dependent on time or not is the next problem to be determined, mined.

Experiment B. The method was the same as that of reported in the former papers,(1) the velocity of azotation being determined from time to time by measuring the absorption speed of nitrogen at constant temperature (1140°C.) and pressure (1 atm.). The samples were the "granular" of diameters (0.175–1.0), (1.0–2.0), (2.0–3.0) mm. respectively. The sample of Exp. 376 was (3.17–0.84 mm.) different from others, all being free from catalysers. Table 5_2 and Fig. 1 show the results.

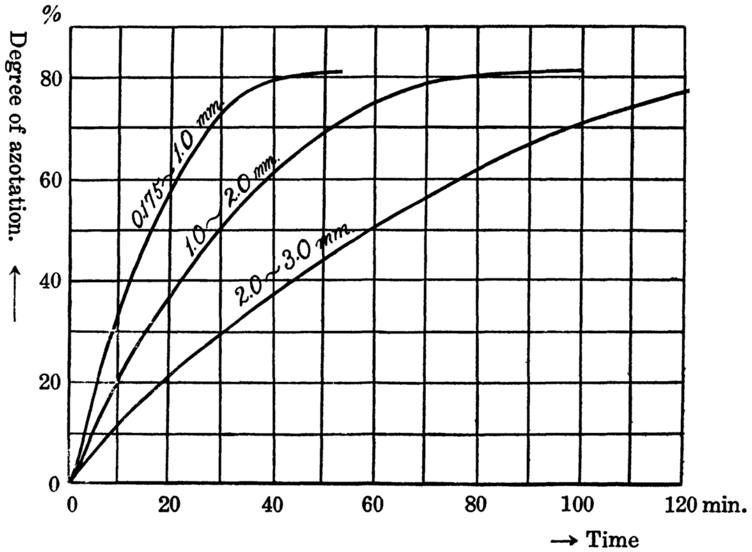

Fig. 1.—Azotation of "granular carbide" of varying size at 1140°C.

(1) This bulletin, **7** (1932), 143.

Table 5_2.

Velocity of azotation of "Granular carbide" of various size at constant temp. (1140°C.) and pressure (1 atm.) of nitrogen (without catalysers).

Exp. No.	389		390		386		376	
Dia. mm.	0.175–1.0		1.0–2.0		2.0–3.0		3.17–0.84	
Purity %	63.9		71.3		72.6		62.9	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1	(1.0)	1.18	1.07	1.05	0.578	0.73	1.11	1.70
2	(2.00)	4.86	1.25	3.48	0.695	2.08	1.30	4.08
3	2.00	9.61	1.25	6.10	0.688	3.53	1.35	6.61
4	1.80	14.23	1.19	8.65	0.660	4.94	1.36	9.19
5	1.60	18.26	1.07	10.98	0.623	6.28	1.35	11.75
6	1.47	21.88	1.04	13.17	0.595	7.55	1.33	14.28
7	1.36	25.27	1.00		0.578		1.32	16.78
8	1.30	28.46	1.00	17.36	0.540	9.93	1.29	19.25
9	1.24		0.909		0.525		1.27	21.68
10	1.20	34.38	0.909	21.29	0.525	12.18	1.24	24.05
12	1.11		0.862		0.510		1.18	28.63
14	1.03	45.00	0.833		0.490		1.12	33.02
15	0.99		0.815	30.17	0.475	17.40		
16	0.95		0.769		0.461		1.06	37.40
18	0.885		0.685		0.438		0.995	41.10
20	0.81	58.10	0.699	37.92	0.422	21.99	0.939	44.75
25	0.64	66.60	0.614	44.73	0.390	26.22		
30	0.45	73.30	0.570	50.90	0.370	30.18	0.703	60.02
35	0.265	77.55			0.360	33.98		
40	0.110	79.65	0.440	61.50	0.350	37.66	0.464	71.1
45	0 060		0.377		0.339			
50	0.020	81.00	0.350	69.65	0.325	44.78	0.192	77.0
60	0.000	81.15	0.220	75.30	0.300	51.30	0.064	79.2
70			0.110	78.90	0.270	57.30	0.028	79.9
80			0.047	80.40	0.240	62.65	0.000	80.0
90			0.023	81.10	0.210	67.35		
100			0.000	81.35	0.180	71.35		
120					0.105	77.35		
140					0.042	80.15		
160					0.014	81.10		

If we calculate the values

$$\left\{n_{\infty}^{\frac{1}{3}}-(n_{\infty}-n_t)^{\frac{1}{3}}\right\}/t = k_5 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (5_3)$$

where n_t denotes the degree of azotation in % at time t, and n_{∞} the final value of n_t, k_5 is found to be nearly constant. (Table 5_3).

Table 5_3.

Velocity constant k_5 for granular carbide at 1140°C.

Exp. No.	389		390		386		376		385	
Dia. mm.	0.18—1		2—1		3—2		3.17—0.84		2—1	
$+CaF_2$, %	0		0		0		0		4	
Time, min.	n_t	k_5	n_t	k_5	n_t	k_5	n_t	k_5	n_t	k_5
5	18.26	0.0704	10.98	0.0408	6.28	0.0230	11.75	0.044	10.92	0.040
10	34.38	0.0725	21.29	0.0417	12.18	0.0228	24.05	0.048	23.25	0.046
20	58.10	0.0742	37.92	0.0408	21.99	0.0216	44.75	0.051	39.70	0.043
30	73.30	0.0780	50.90	0.0403					53.07	0.043
40	79.65	0.0796	61.50	0.0406	37.66	0.0202	71.1	0.056	64.10	0.043
50	81.00	0.0760	69.65	0.0412					72.35	0.044
60			75.30	0.0418	51.30	0.0204	79.2	0.055	77.70	0.045
70			78.90	0.0426					80.40	0.045
80			80.40	0.0418	62.65	0.0210	80.0	0.056		
90			81.10	0.0410					81.70	0.044
100			81.35	0.0412	71.35	0.0217				
120					77.35	0.0228				
140					80.15	0.0230				
160					81.10	0.0227				
∞	81.15		81.36		81.45		80.0		81.90	
mean k_5		(0.0751)		0.0413		0.0219		0.052		0.0435

Theoretical considerations.

For the velocity of azotation of a spherical carbide grain of an initial mean radius r_0 at a given temperature and pressure, we suppose the following relations:

Case a.

The linear velocity of azotation in the direction of r is constant:

$$-\frac{dr}{dt}=\kappa \qquad (5_a)$$

where r : radius at any time t,
κ : velocity constant.

$$\therefore \quad \kappa=\frac{r_1-r}{t-t_1} \qquad (6_a)$$

If $r_1=r_o$ at $t_1=0$, then

$$\kappa_0=\frac{r_0-r}{t} \qquad (7_a)$$

$$\therefore \quad k_5=\frac{\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\}}{t} \qquad (8_a)$$

Case b.

the linear velocity is inversely proportional to the thickness of the layer of the product:

$$-\frac{dr}{dt}=\frac{\kappa'}{r_0-r} \qquad (5_b)$$

$(r_o-r) \propto$ resistance to the proceeding of the reaction.

$$\kappa'=\frac{(r_1-r)\left\{r_0-\frac{1}{2}(r_1+r)\right\}}{t-t_1} \qquad (6_b)$$

$$\kappa_0'=\frac{(r_0-r)^2}{t} \qquad (7_b)$$

$$\therefore \quad k_5'=\frac{\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\}^2}{t} \qquad (8_b)$$

because $r=\nu m^{\frac{1}{3}}=\mu(n_\infty-n_t)^{\frac{1}{3}}$ and $r_0=\nu m_0^{\frac{1}{3}}=\mu n_\infty^{\frac{1}{3}}$; m: mass of a grain; n_∞, n_t: degree of nitrogen-fixation, and ν, μ: constants.

From the experimental results, shown in Table 5_3., we see that at temperature of 1140°C. k_5 are almost constant at any time after $t=10$ minutes from the beginning. Hence, in case of the "granular carbide," the linear velocity of azotation of the carbide towards the center is constant at 1140°C. If we denote the mass of a carbide granule with m, the reactive surface with A, and the density with δ, then from Equation (5_a) we have:

$$-\frac{dm}{dt}=-A\cdot\delta\cdot\frac{dr}{dt}=\kappa\cdot A\cdot\delta\,, \qquad (9_a)$$

and also $$-\frac{dm}{mdt}=-\frac{d\ln m}{dt}=\kappa\cdot F\cdot\delta\,, \qquad (10_a)$$

where $F=A/m=$ specific surface of the remaining carbide. Hence, the rate of change of the carbide to cyanamide at these higher temperatures and under a constant pressure is proportional to the surface area.

It was already pointed out in the former paper(1) that at temperatures lower than 950°C. and in case of powdered carbide without effective catalysers, the following relation holds good:

$$n_t = n_\infty - \left\{ n_\infty^{\frac{1}{3}} - \sqrt{k_5'(t-t')} \right\}^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4_8)$$

or

$$\frac{\{ n_\infty^{\frac{1}{3}} - (n_\infty - n_t)^{\frac{1}{3}} \}^2}{t-t'} = k_5' = \text{constant} \quad \ldots\ldots\ldots\ldots\ldots \quad (4_7)$$

This equation coinsides with (8_b), although it has a term $(t\text{-}t')$ instead of t. This t' is a correction due to the initial disturbance of the velocity, which starts with very low values, and attains a maximum after several minutes. This shows that at temperatures lower than about 950°C., the layer of the products hinders the further progress of the reaction proportionally to the thickness of the layer.

At temperatures, where the products melt partly with the carbide, or when some catalysers such as $CaCl_2$ were added, the relation is of course different from the above. (See the former papers.(1)).

Even at moderate temperatures, it is sometimes found that a velocity-curve at constant pressure involves several fragments of different nature: starting from an initial acceleration- or induction-curve, it passes a maximum point and then describes either a constant linear velocity curve or a curve of the first order and turns finally to a parabolic curve.

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 the directors and engineers of the Co. on that day.

Summary.

The effect of size of powder and grain of carbide on the velocity of azotation was experimentally discussed, and it was also experimentally determined that the velocity of azotation of carbide at constant temperature and pressure is

1. proportional to the surface area of individual grains, in case of the "granular" carbide, and the radial velocity of azotation is constant at about 1140°C. or

(1) Aono, loc. cit.

2. the radial velocity is inversely proportional to the thickness of changed layer at 950°C. and lower temperatures.

3. In some cases, there are several types of character in the velocity.

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