STUDIES ON REACTIONS BETWEEN GAS AND SOLID. IV. AZOTATION OF CALCIUM CARBIDE AND THE EFFECT OF TEMPERATURE ON ITS VELOCITY.(1)

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Experimental.

Experimental Procedure. The method and apparatus of these experiments were nearly the same as those reported in the former paper.(2) But in this case the pressure of nitrogen was kept constant (1 atm.) and the velocity of the reaction was determined by measuring the speed of absorption from time to time with a second differential manometer of bromonaphthalene attached to the reaction tube. At the end of the reaction or after a difinite time the tube was rapidly cooled and the product was weighed and analysed. The content of nitrogen at a given moment was obtained by graphically integrating the $\left(-\frac{dP}{dt}\right.$ or $\left.-\frac{dm}{dt}\sim t\right)$ curve and comparing the integrated value with the final analysis.

Effect of Temperature. The effect of temperature on the reaction velocity is shown in Table 1 and Figs. 1, 2 and 3. The time was measured from the beginning of introducing nitrogen into the tube, and it took about ½–1 minute to reach 1 atm. From Fig. 1 we see that the velocity of absorption of nitrogen is very small at first and increases rapidly up to a maximum value and then gradually decreases. The results are similar to those obtained by H. H. Frank and his co-workers.(3)

The initial increase of the velocity is probably due to the following causes:

(a) liberation of the heat of reaction: $CaC_2+N_2=CaCN_2+C+54.8Cal.$,(4) which elevates the temperature of the reacting mass locally,(5) the greater the reaction velocity the greater will be the temperature elevation and consequent acceleration;

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(1) Read before the Chemical Society of Japan, Dec. 1931.

(2) T. Aono, This Bulletin, **7** (1932), 143–154.

(3) H. H. Franck, F. Hochwald and G. Hoffmann, *Z. phys. Chem.*, Bodenstein-Festband, (1931), 985.

(4) Kameyama and Oka, *J. Soc. Chem. Ind. Japan*, **34** (1931), 890.

(5) The local elevation of temperature was measured and reported by G. Bredig, *Z. Elektrochem.*, **13** (1907), 69.

Table 1.

Azotation velocity of powdered carbide ($CaC_2 = 68.2$, $CaF = 1.2\%$) at various temperatures.

Temp. °C.	867		950		1000		1060		1090		1140	
Carbide, gr.	4.0043		4.0066		4.0055		4.0068		4.0002		4.0013	
Exp. No.	361		359		362		360		363		365	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1			1.100	1.16		0.76	0.356	0.23	0.441	0.43		
2	0.256	0.40	1.116	2.44	1.242	1.93	0.664	0.75	0.619	1.00	0.346	0.40
3	.265	0.65	1.077	3.62	1.443	3.41	1.44	1.79	1.001	1.86	1.266	1.26
4	.264	0.90	1.052	4.73	1.577	5.05	2.91	4.02	2.74	3.72	3.925	4.31
5	.253	1.14	1.016	5.82	1.625	6.80	4.085	7.81	7.25	8.91	9.10	11.80
6	.231	1.37	0.983	6.87	1.613	8.55	4.63	12.56	14.93	21.43	14.29	26.15
7			0.956	7.89			4.33	17.44	14.28	27.36	13.34	44.10
8	.198	1.77	0.922	8.87	1.528	12.00	3.51	21.58	9.01	40.43	8.13	56.90
9			0.890	9.83			2.86	24.80	5.88	59.80	5.99	65.35
10	.179	2.13	0.861	10.76	1.404	15.13	2.40	27.68	4.48	70.15	4.406	71.65
12	.161	2.45	0.807	12.51	1.250	17.98	1.85	32.05	2.52	77.95	2.355	79.60
14	.148	2.75	0.749	14.19	1.146	20.58	1.585	35.66	1.34	82.10	0.833	83.20
16	.139	3.04	0.728	15.72	1.026	22.95	1.415	38.84	0.588	84.10	0.350	84.50
18	.132	3.29	0.662	17.14	0.940	25.10	1.306	41.70	0.298	85.00	0.235	85.20
20	.125	3.53	0.615	18.46	0.869	27.05	1.241	44.40	0.211	85.60	0.172	85.70
25	.111	4.11	0.518	21.39	0.738	31.37	1.104	50.57	0.127	86.45	0.093	
30	.104	4.63	0.426	23.89	0.629	35.06	0.980	56.35	0.085	87.00	0.058	86.85
35	.092	5.13	0.379	26.00	0.554	38.28	0.836	61.20	0.061	87.45	0.037	
40	.085	5.58	0.341	27.90	0.505	41.08	0.718	65.30	0.045	87.75	0.027	87.40
45	.079	5.96	0.315	29.60			0.625	68.85	0.032	87.95	0.020	
50	.074	6.34	0.291	31.17	0.438	46.16	0.539	71.90	0.020	88.05		87.60
60	.066	7.01	0.251	34.02	0.391	50.65	0.407	77.10		88.15	0.000	87.80
70	.060	7.61	0.220	36.60	0.350	54.65	0.278	80.65				
80	.055	8.16	0.197	38.82	0.314	58.25	0.197	83.15				
90	.051	8.67	0.177	40.80	0.277	61.45	0.139	84.95				
100	.048	9.14	0.157	42.55	0.247	64.25	0.086	86.20				
120	.044	10.01			0.199	69.10						
140	.040	10.81			0.165	73.00						
160	.036	11.53			0.139	76.30						
180	.044	12.21			0.119	79.15						
200	.041	13.00			0.101	81.50						
220	.037	13.74			0.079	83.45						
240	.033	14.41			0.058	84.85						
260	.030	15.03										

(b) liberation of nascent carbon, which, according to the author's opinion, acts as an efficient catalyser for this reaction;

(c) action of the boundary between the new phase of minute crystal of $CaCN_2$ formed and the reacting CaC_2.

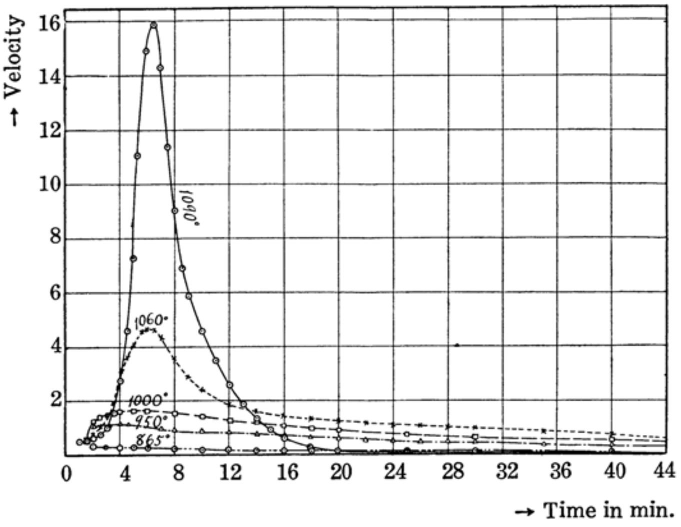

Fig. 1.—Reaction velocity and temperature.

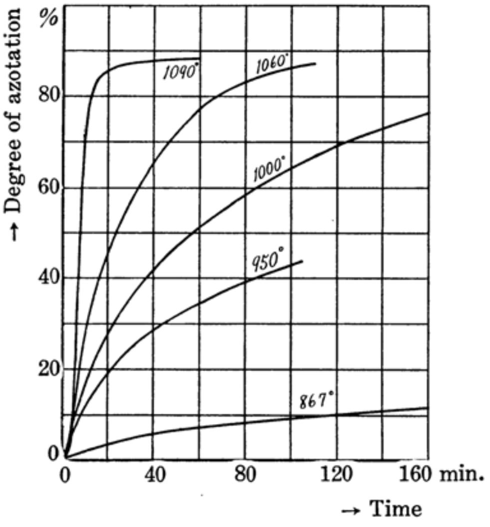

Fig. 2.—Degrees of azotation and temperature.

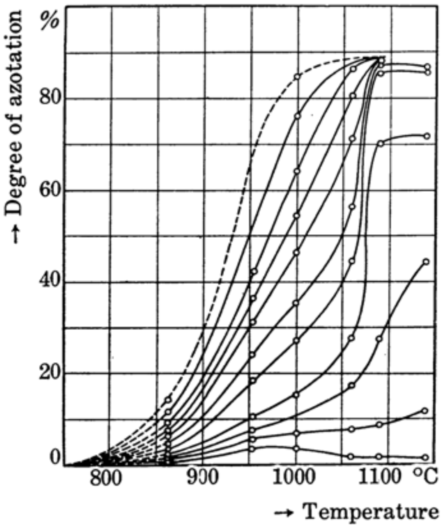

Fig. 3.—Degrees of azotation after definite times at various temperatures.

The time of the maximum velocity increases with rising temperature, and the degree of azotation (Y) at that time also increases with temperature as shown by the following equation.

$$\log Y = A - \frac{B}{T} \ ,$$

where A and B are constants and T the absolute temperature. (See Table 2 and Fig. 4).

Table 2.

Exp. No.	361	359	362	360	363	365
$1/T \times 10^4$	8.78	8.18	7.86	7.50	7.34	7.08
Y	0.65	2.44	6.80	12.56	21.43	36.0
$\log\ Y$	−0.19	0.39	0.83	1.10	1.31	1.55

The simple relation for the first order of the reaction velocity does not hold generally in this case, and the following integrated form does not give a constant value of k_4.

$$k_4 = \frac{1}{t - t_o} \ln\left(\frac{n_\infty - n_o}{n_\infty - n_t}\right) \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (4_1)$$

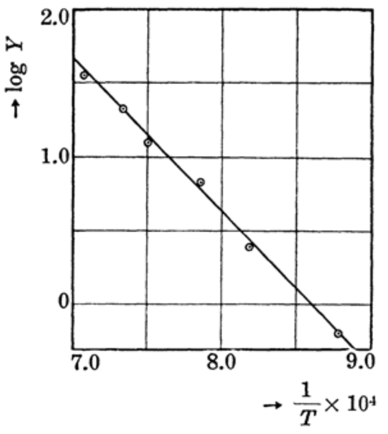

Fig. 4.—Relations btw. degrees of azotation (Y) before the time of velocity maximum and temperature.

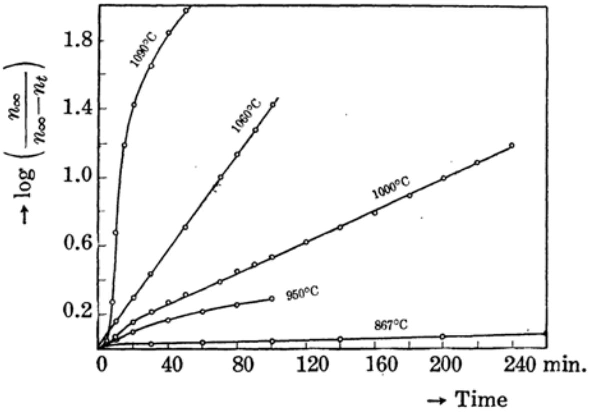

Fig. 5.—Relation btw. $\log\left(\frac{n_\infty}{n_\infty - n_t}\right)$ and time at various temps. (Powdered carbide).

where n_0 and n_t (%) are degrees of azotation at time t_0 and t (minutes) respectively, n_∞ the final maximum value of n_t, and k_4 a velocity constant.

As is shown in Fig. 5 and Table 3, the results at 1000° and 1060°C. satisfy the following relation after a certain time from the beginning,

$$k_4' = \frac{2.303}{t+t'} \log\left(\frac{n_\infty}{n_\infty - n_t}\right) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (4_2)$$

in which k_4' and t' being constant. We have then

$$n_t = n_\infty\left(1 - e^{-k_4'(t+t')}\right) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (4_3)$$

Table 3. Powdered carbide.

Relation btw. $\log_{10}\left(\frac{n_\infty}{n_\infty - n_t}\right)$ and time at various temperatures.

Exp. No.	361	359	362	360	363
Temp. °C	867	950	1000	1060	1090
t, min.					
5					0.0457
10		0.0558	0.068	0.160	0.6741
20		0.1007	0.153	0.297	1.4178
30	0.0233		0.212	0.430	1.6484
40		0.1661	0.261		1.8525
50			0.308	0.704	1.9717
60	0.0354	0.2095			
70			0.388	1.000	
80		0.2489	0.446	1.132	
90			0.490	1.284	
100	0.0469	0.2824	0.534	1.421	
120			0.620		
140	0.0561		0.708		
160			0.797		
180			0.891		
200	0.0686		0.989		
220			1.085		
220			1.183		
260	0.0806				

Applying this relation to the data obtained from Exp. 360 at 1060°C., for example, we have $k_4' = 0.0320$, $t' = 1.5$ and therefore

$$n_t = 89.6\,\{1-e^{-0.0320(t+1.5)}\} \qquad (4_4)$$

The values calculated by the equation (4_4) fairly well agree with the observed ones as shown in Table 4.

Table 4.

t	k_4'	n_t (obs.)	n_t (calc.)
10	0.0321	27.68	27.6
20	0.0318	44.40	44.5
30	0.0315	56.35	57.8
50	0.0315	71.90	72.5
70	0.0322	80.65	80.5
80	0.0323	83.15	83.0
90	0.0323	84.95	84.8
100	0.0322	86.20	86.2
110	0.0318	87.00	87.1
Mean	0.0320		

At temperatures lower and higher than 1000–1060°C., the above relation is not fulfilled. At 950° and 867°C. the following relation, which was derived from the assumption that the layer of products retards the reaction,(1) was found to be satisfied:

$$\frac{\left\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\right\}^2}{t-t'} = k_5' \qquad (4_5)$$

where t' and k_5' being constant (Table 5). If we draw curves of $\left\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\right\}^2$ against time, we have straight lines in the cases of Exp. 359 (950°C.) and 361 (867°C.). (Fig. 6).

Of course the relation 4_5 is not fulfilled at temperatures above 1000°C., and even at 867°C. it does not hold, if the carbide is mixed with catalysers such as active carbon (Exp. 521 at 867°C.) and calcium chloride (Exp. 523 at 867°C.), which are effective to accelerate the reaction. (See Table 5, Exp. No. 521; the numerical value of n_t will be found in the next paper).

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(1) Vid. the next paper.

Table 5. Powdered carbide.

Relation between $\left\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\right\}^2$ and time at 867° and 950°C.

Exp. No.	361		359		362	363	(521)
Temp. °C.	867		950		1000	1090	(867)
Time. min.	$\{\ \}^2$	$k_5' \times 10^4$	$\{\ \}^2$	$k_5' \times 10^4$	$\{\ \}^2$	$\{\ \}^2$	$\{\ \}^2$
10			0.0576	92.9		3.35	0.0036
20			0.152	93.8	0.25	9.50	.0100
30	0.00639	2.74	0.250	95.4		11.6	.0196
40			0.336	92.8		13.8	.0306
50			0.429	92.9		16.0	.0420
60	0.0146	2.74	0.518	92.2	1.145		.0566 (at $t=62$)
70			0.609	92.0			
80			0.706	92.7			
90			0.784	91.0	1.99		
100	0.0253	2.72	0.865	90.0			
120					2.92		
140	0.0361	2.71					
180					4.97		
200	0.0530	2.74					
240					7.21		
260	0.0703	2.77					
t'	6.7		3.8				
Mean k_5		2.737		92.57			

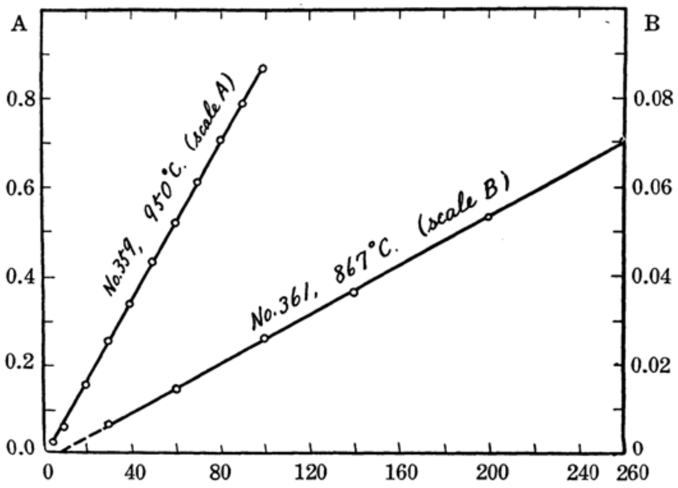

Fig. 6.—$\left\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\right\}^2$ against time.

From the equation 4_5 we have

$$n_t = n_\infty - \left\{ n_\infty^{\frac{1}{3}} - \sqrt{k_5'(t-t')} \right\}^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4_6)$$

The calculated values of n_t by this equation coinside fairly well with the observed ones. (Table 6).

Table 6. Exp. No. 361.

($n_\infty = 99.0$; $t' = 6.7$ min; $k_5' = 2.737 \times 10^{-4}$)

t. min.	30	60	100	140	200	260
n_t (obs.)	4.63	7.01	9.14	10.81	13.00	15.03
n_t (calc.)	4.68	7.00	9.21	10.93	13.05	14.82

The theoretical consideration of these relations will be given in the next paper.

Applying the Arrhenius' equation

$$\ln k = C - \frac{E}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4_7)$$

on the results obtained from Exps. No. 362 and 360, we have the apparent heat of activation E for the reaction

$$CaC_2 + N_2 = CaCN_2 + C$$

at the temperature between 1000 and 1060°C.:

$$E = 4.57 \log\left({k'_{T_1}}/{k'_{T_2}} \right) \Big/ \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \ldots\ldots\ldots\ldots \quad (4_8)$$

If we assume $N_\infty = 90.0$ in both cases, then we have $k_4 = 0.0309$ for 1060°C. and 0.0107 for 1000°C., and putting these values in the equation (4_8) we have $E = 58.6$ Cal./mol. for the temperatures between 1000 and 1060°C. Above the temperature of about 1080°C. the velocity increases suddenly and E becomes smaller (about 33 Cal./mol.). This may be due to the change in the phase of the reacting substance, e.g. partial fusion of the system $CaC_2-(CaCN_2)-CaO-CaF_2$.(1) At the same time the character of the velocity curve deviates from Equation 4_2, and

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(1) H. H. Franck and H. Heimann, *Z. Elektrochem.*, **33** (1927), 469, reported that the lowest melting point of the system (CaC_2-CaF_2-CaO) is 1070°C.

also the reaction is too fast to be measured accurately at such higher temperatures.

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 directors and engineers of the company on that day. The author expresses his best thanks to Mr. K. Hibi, who gave him the opportunity of carrying out the experiments and allowed him to publish this report now, and to Mr. I. Kobayashi, who assisted him during the experiment.

Summary.

The effect of temperature elevation to the velocity of azotation of powdered calcium carbide (with 1% CaF_2) has experimentally been determined.

1. At a constant temperature lower than about 950°C., the following relation was found:

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

where n_t means the degree of azotation (in %) after a time t, and n_∞ the final and maximum value of n_t; k_5 and t' are constants.

2. At a constant temperature between about 1000 and 1060°C., the common monomolecular course was found, namely:

$$n_t = n_\infty \left\{1-e^{-k'_4(t+t')}\right\}$$

where k_4' being a velocity constant.

3. At any temperature there is a maximum in the velocity; the time and the degree of azotation at the maximum point increase with rising temperatures. The following approximate relation was found between them.

$$\log Y = A - \frac{B}{T},$$

where Y is the degree of azotation at the maximum of the velocity, T the absolute temperature, and A and B constants.

4. From the temperature coefficient of the velocity constant, the apparent heat of activation for a powdered technical carbide (with 1% CaF_2) was calculated to be about 58.6 Cal./mol. at temperatures between 1000° and 1060°C., and about 33 Cal./mol. above 1080°C.

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