STUDIES ON REACTIONS BETWEEN GAS AND SOLID.
III. AZOTATION OF CALCIUM CARBIDE AND THE EFFECT OF PRESSURE OF NITROGEN ON THE REACTION VELOCITY.

By Takeo AONO.

From a kinetic study of the reaction $CaC_2 + N_2 = CaCN_2 + C$, G. Bredig[1] and his coworkers found that the azotation velocity of the carbide is proportional to the N_2-pressure. But F. Foerster and H.

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(1)   Bredig, Fränkel and Wilk, *Z. Elektrochem.*, **13** (1907), 605.

Jacoby[1] stated from their experiments that „Dies zeigt, dass zwar ein Druckeinfluss bei der CaCN$_2$-bildung vorhanden, dass er aber nur von geringer Bedeutung ist." As this problem is significant for the study of the chemistry of calcium cyanamide, the present experiment has been carried out to ascertain whether this proportional relation really or to what extent exists or not.

Experimental.

A nickel boat of 1 cm. wide and 5 cm. long, containing powders or grains of technical calcium carbide mixed with CaF$_2$ (1 and 5% in weight), was placed in a porcelain tube, one end of which being sealed. The other end of the tube was connected both with a nitrogen source and a Hg manometer and an air pump through a three way cock. The tube was very carefully tested whether it was perfectly gas-tight in heated state or not. After searching several kinds, the author obtained a proper material specially made by the S.C.P. Co. N$_2$–gas which contained 0.24% of O$_2$, was purified with heated Cu, conc. H$_2$SO$_4$ and sodalime, and then dried with CaCl$_2$ and P$_2$O$_5$. After the carbide had been heated in vacuum up to a proper temperature until no gases were expelled from the carbide and the tube, the N$_2$-gas was led into it for a few minutes. At the beginning of the azotation of carbide, the reaction velocity varies considerably from time to time even at a constant N$_2$–pressure. After a certain time the change of reaction velocity becomes so slow as it may be regarded as constant in a short time interval. The measurement was executed at this stage in two ways.

The one way was as follows. Decreasing or increasing the total pressure (P) of the N$_2$–gas in the reaction tube, the time (Δt) needed for each 8 mm. of the pressure decrease (ΔP) was measured with a stop watch. The slight change of the total volume due to the change of the manometer hight was also measured and the correction (F) for it was calculated as follows. If we denote by V the total volume of the gaseous space at the manometer reading of 760 mm., and by v the volume decrease due to the change of manometer hight, then we have $F_1 = V / (V - v_1)$, $F_2 = V / (V - v_2)$, etc. at the pressure P_1, P_2, etc. respectively. And

$$dt = \frac{\Delta t}{8} F.$$

(1)   Foerster and Jacoby, *Z. Elektrochem.*, **12** (1907), 101.

The pressure P was determined from the following equation

$$P = B - \left[2(h-a) + \frac{\Delta P}{2} + (c-c') \right],$$

where B: the barometer reading of the atmosphere; a: mean hight of the manometer reading; c, c': hights of the meniscuses; h: reading of the circular edge of the meniscus of the higher column.

The other way was to measure the rate of decrease of the N_2–pressure as G. Bredig had done; but as this method takes longer time to accomplish one set of measurement, and from fear that the reactivity of the material might change during the course of measurement, the former way was preferred.

Experimental Results. At a constant temperature the velocity of the reaction

$$CaC_2 + N_2 = CaCN_2 + C$$
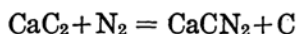
will be a function of both the pressure of N_2 and the reactive solid material. In a proper condition and in a small time interval the reactivity of the carbide may be regarded as constant, and the reaction velocity will change solely with the N_2–pressure. If there holds the proportional law between them, then we must have the following relation at constant N_2–volume:

$$-\frac{dP}{dt} = kP \quad \dots\dots\dots\dots\dots\dots\dots (1)$$

where $-dP$ means the decrease of N_2–pressure during the small time dt, and k the velocity constant. From equation (1) we have

$$k_2 = -\frac{dP}{P\,dt} \quad \dots\dots\dots\dots\dots\dots\dots\dots (2),$$

or

$$k_3 = \frac{2.303}{t_2 - t_1} \log \frac{P_1}{P_2} \quad \dots\dots\dots\dots\dots\dots (3).$$

Some of the results of two sets of the measurements are given in Tables 1, 2, 3 and 4. Each in Tables 1 and 2, 3 and 4 belongs to the same series respectively.

Table 1.

Method 1. Powdered carbide ($CaC_2 = 67.4\%$ and $CaF_2 = 1.2\%$)

No.	Temp. °C.	P_{N_2} mm.	Δt. sec.	F	$-P\dfrac{\Delta t}{\Delta P}$	$k_2 \times 10^3$
1	786	55.9	376	1.071	2815	0·355
2	787	271.3	95.5	1.048	3375	0.296
3	789	441.1	78.8	1.031	4476	0.233
4	790	561.5	67.8	1.019	4848	0.222
5	790	651.7	64.0	1.010	5260	0.190
6	791	753.5	60.0	1.000	5650	0.170
15	866	228.7	100	1.053	3010	0.332
16	867	395.7	61.6	1.035	3148	0.318
17	868	601.9	47	1.015	3590	0.278
18	870	749.5	40	1.001	3752	0.266
19	870	741.3	42	1.002	3904	0.256
20	870	540.1	53.6	1.021	3766	0.266
21	870	335.9	81	1.042	3545	0.282
22	870	97.3	240	1.068	3118	0.327
23	945	250.9	16.0	1.051	528	1.89
24	945	451.1	10.8	1.030	626	1.59
25	945	574.7	8.2	1.018	600	1.66
26	945	554.3	7.8	1.019	551	1.81
27	945	534.1	9.2	1.022	628	1.59
28	945	635.5	7.4	1.012	596	1.68
29	945	615.1	7.6	1.014	592	1.69
30	946	720.7	6.6	1.003	596	1.68
31	946	655.7	6.0	1.009	496	2.01
32	947	631.3	7.4	1.012	592	1.69
33	948	710.5	7.1	1.009	636	1.57
34	948	755.5	6.8	1.000	641	1·56
96	1007	749.6	6.2	1.001	581	1.72
97	1007	492.3	7.6	1.026	479	2.08
98	1007	526.3	8.6	1.023	578	1.73
99	1008	319.7	13.8	1.043	575	1.74
100	1008	153.9	27.8	1.061	568	1.76

Table 2.

Method 2.   (Continued to Table 1.)

No.	Temp. °C.	P mm.	t_2-t_1 sec.	$k_3\times10^3$
35	950°	759.7		
			61.9	1.36
38	,,	698.3		
			67.6	1.35
41	,,	637.5		
			75.0	1.35
44	,,	576.0		
			83.9	1.31
47	,,	515.9		
			94.2	1.33
50	,,	455.1		
			107.5	1.33
53	,,	394.5		
			81.5	1.32
55	,,	354.1		
			91.4	1.32
57	,,	313.7		
			102.8	1.35
59	,,	273.1		
			56.0	1.37
60	,,	252.9		

Table 3.

Method 1.   Grainy carbide[1] (61.9% CaC_2, 5% CaF_2—powder).

No.	Temp. °C.	P mm.	Δt sec.	F	$-P\dfrac{\Delta t}{\Delta P}$	$k_2\times10^3$
11	1028	528.6	50	1.022	338	2.96
12	1029	285.0	6.3	1.047	235	4.25
13	1030	709.2	4.6	1.004	410	2.44
14	1030	648.2	5.1	1.010	417	2.40

(1) This carbide was specially prepared for this research by Mr. Hibi's process. The grain had a size of 1~3 mm. in diameter and was porous, the surface being covered with a thin film of carbon.

Table 4.

Method 2.   (Continued to Table 3.)

No.	Temp. °C.	P mm.	t. sec.	t_2-t_1 sec.	$k_3 \times 10^3$
26	1028	391.0	0		
				47	1.12
27	,,	370.8	47		
				54	0.93
28	,,	352.6	101		
				56	1.05
29	,,	332.4	157		
				63	1.00
30	,,	312.2	220		
				63	1.06
31	,,	292.0	283		

Now, looking at the Tables 2 and 4, we find that the velocity constants k_3 calculated from equation (3) are gradually decreasing at first and then slightly increasing with P or time, while most of k_2 from the equation (2) increase with decreasing pressures.   The decrease or constancy of k_3 could be attributed to the decrease of active mass with time, because it takes much time to accomplish one set of measurement.   The increase of k_2 could not be attributed to any error involved in the operation such as inconstancy of temperature, change of reacting mass, etc. This can be recognized when the figures are carefully observed.   It was assumed that

$$\frac{\Delta t}{\Delta P} = \frac{dt}{dP} = 1 \bigg/ \frac{dP}{dt} \,,$$

and ΔP was taken as 8 mm., while the arithmetical mean pressure was taken as the corresponding P.   Tracing $\left(\frac{-\Delta t}{\Delta P} \sim P \right)$ curves we see that in the region of these experiments

$$\left| \frac{dP}{P\,dt} \right| \gtrapprox \left| \frac{\Delta P}{P\,\Delta t} \right| \quad \dots\dots\dots\dots\dots\dots\dots \quad (4),$$

and this difference must, if any, increase with decreasing P.   Hence the velocity constants found by this experiment would have to become rather smaller as P diminishes, which contradicts to the experiment.   From

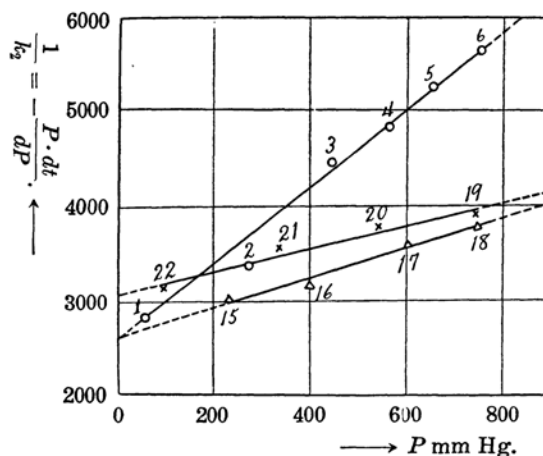these reasons, the increase of k_2 with decreasing P could not be attributed to any error.[1]

Fig. 1.

Tracing $\left(-P\dfrac{dt}{dP}\right)\sim P$ curves from these data we have, for example, Fig. 1 (from Table 1). The points lie almost on straight lines. Therefore we have

$$-P\cdot\frac{dt}{dP} = aP+b \quad\dotsb\quad (5)$$

or

$$-\frac{dP}{dt} = \frac{P}{aP+b} = K\frac{P}{1+aP} \quad\dotsb\quad (6)$$

It is important that a and α decrease with rising temperatures, as are seen in Table 5, which was calculated from the experimental values in Table 1.

Table 5.

Temp. °C.	From No.	for P in mm. Hg.				for P in atms.	
		a	b	K	α	K'	α'
790	1—6	4.07	2540	0.000394	0.00161	0.300	1.22
869	15—22	1.36	2840	0.000352	0.000479	0.268	0.364
946	23—34	0.125	530	0.00189	0.000236	1.44	0.179
1008	96—100	0.022	565	0.00177	0.000039	1.35	0.030

(1) When the data of Bredig's report (loc. cit.) are carefully observed, we can find that their k also increases with decreasing pressure.

Although the quantitative relation cannot be deduced directly from these data because the active surface and also the reactivity must change with proceeding of the reaction, we see that, the higher the temperature the greater is the effect of pressure-increase to the reaction velocity, though the effect of the pressure-increase becomes smaller at higher pressures.
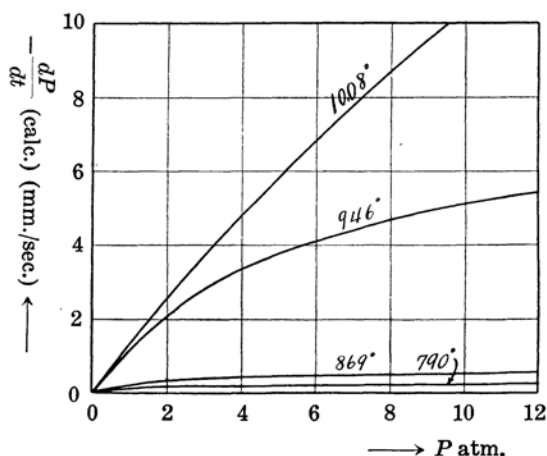

Fig. 2.—Relations btw. reaction velocity and nitrogen-pressure
at various temperatures.   (only qualitative.)

At lower pressures the reaction velocity is nearly proportional to the N_2-pressure.   From Table 5 we have Table 6 and Fig. 2.   The numerical values cannot be compared with each other, because the reactivities of the carbide in each case are not equal, but we can see the tendency of the reaction velocity influenced by the pressure.

Table 6.

Relation between $-\dfrac{dP}{dt}$ and P (atm.)   (calculated).

Temp. °C.	$-\dfrac{dP}{dt}$				
	$P = 1$ atm.	$P = 3$ atm.	$P = 5$ atm.	$P = 10$ atm.	$P = 20$ atm.
790	0.135	0.193	0.211	0.227	0.236
869	0.197	0.385	0.475	0.578	0.640
946	1.24	2.82	3.80	5.16	6.29
1008	1.31	3.72	5.87	10.38	16.88

The velocity of N_2–absorption of carbide at constant temperature and pressure increases at first to a certain limit and then gradually decreases. The maximum velocity and its position is a function of temperature, the higher the temperature the greater is the maximum value and the position comes faster. These characteristics were studied by the author in many cases, which will be reported in the following papers in details but one of them will be cited here.

Powdered carbide (CaC_2=72.97%), mixed with 10.0% of freshly ignited and dehydrated calcium chloride powder, was heated in vacuum up to 870°C. and at this constant temperature nitrogen was led in. Keeping the pressure of nitrogen constant at 775 mm., the velocity of decrease in pressure per second was measured. After 20 minutes the pressure was varied and the reaction velocity or the rate of decreasing of the pressure was measured simultaneously with the corresponding pressure. The results are shown in Table 7 and Fig. 3–5.
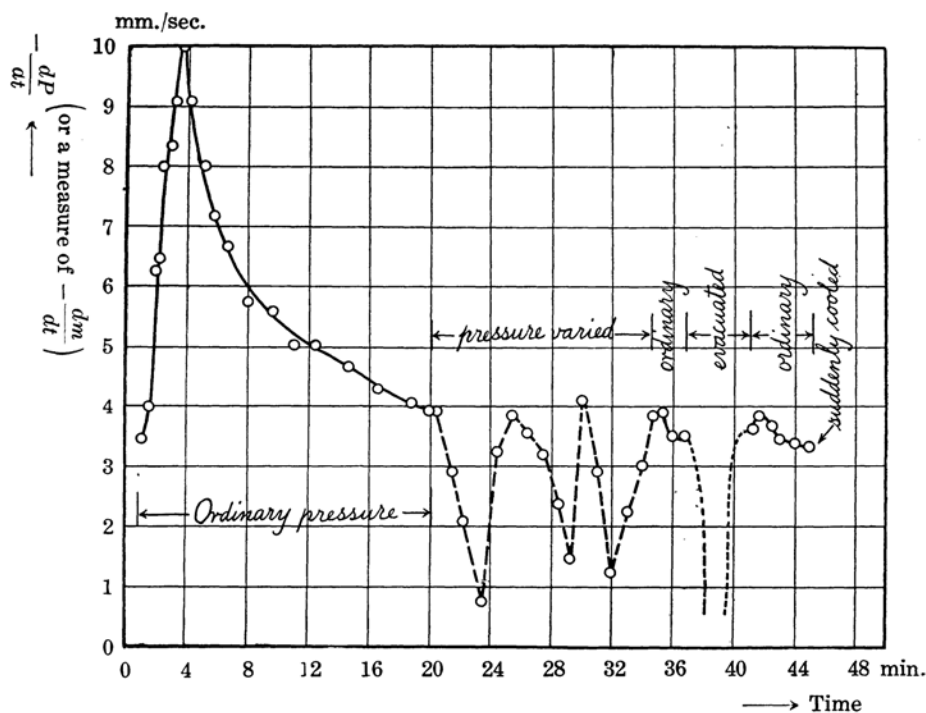

Fig. 3.—Velocity of azotation of powdered carbide
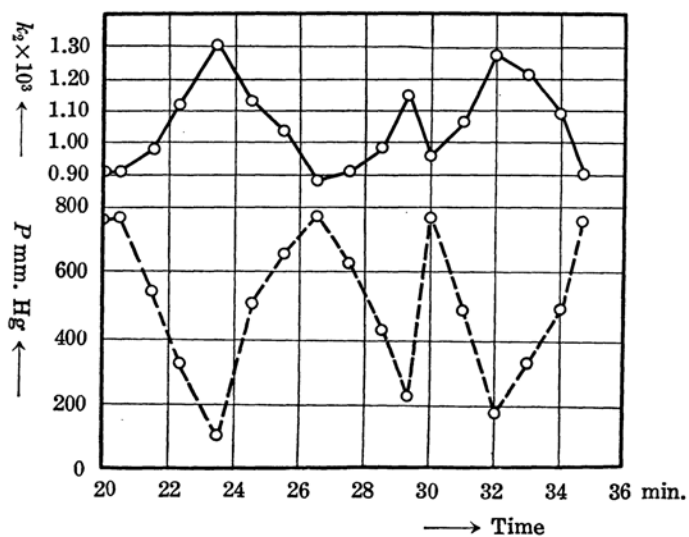with $CaCl_2$ (10%).

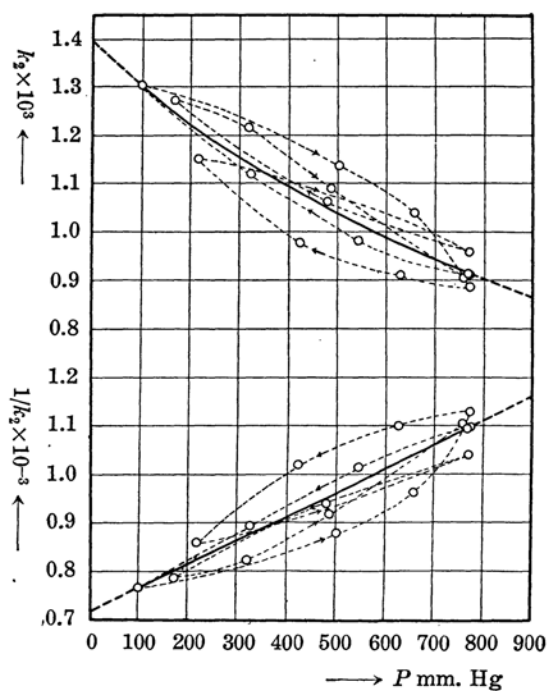Fig. 4.—Relations btw. P and k_2 with proceeding time.

Fig. 5.—Change of k_2 with varying pressures.

Table 7.   Calcium-carbide (72.97% CaC_2) + 10% $CaCl_2$.

Furnace temp. = 870°C., $-\dfrac{dP}{dt}$ = mm. α-Br-naphthalene/sec.

F = correction factor.

Time min.	P_{N_2} mm. Hg.	$-\dfrac{dP}{dt}$ mm. Br-na./sec.	$-\dfrac{dt}{dP}$ sec./mm. Hg.	F	$\dfrac{1}{k_2} = -P \cdot \dfrac{dt}{dP} \cdot F$	$k_2 \times 10^3$
0	0→775	—				
1.0	775	3.45				
1.5	,,	4.00				
2.0	,,	6.25				
2.3	,,	6.45				
2.5	,,	8.00				
3.0	,,	8.35				
3.3	,,	9.10				
3.7	,,	10.00				
4.3	,,	9.10				
5.2	,,	8.00				
5.8	,,	7.15				
6.8	,,	6.67				
8.2	,,	5.72				
9.8	,,	5.55				
11.2	,,	5.00				
12.7	,,	5.00				
14.8	,,	4.65				
16.8	,,	4.25				
19.0	,,	4.00				
20.0	769	3.90	1.42	1.002	1095	0.914
20.5	773	3.90	1.42	1.000	1097	0.913
21.5	545	2.93	1.89	1.013	1016	0.985
22.3	325	2.07	2.67	1.027	892	1.121
23.5	99	0.75	7.42	1.042	766	1.305
24.5	503	3.22	1.72	1.016	879	1.138
25.5	659	3.82	1.45	1.007	963	1.039
26.5	773	3.79	1.46	1.000	1128	0.887
27.5	627	3.18	1.74	1.009	1100	0.910
28.5	423	2.34	2.36	1.021	1020	0.981
29.3	215	1.44	3.85	1.035	857	1.154
30.0	771	4.10	1.35	1.000	1041	0.961
31.0	481	2.88	1.92	1.017	939	1.065
32.0	169	1.24	4.47	1.038	785	1.275
33.0	319	2.21	2.50	1.028	821	1.218
34.0	487	2.99	1.85	1.017	917	1.091
34.7	759	3.82	1.45	1.005	1105	0.906
35.5	775	3.92				
36.0	,,	3.51				
36.3	,,	3.51				
36.8	,,	3.51	evacuated			
41.3	775	3.64				
41.6	,,	3.85				
42.5	,,	3.70				
43.0	,,	3.45				
44.0	,,	3.39				
45.0	,,	3.33				

It is interesting that when the pressure was changed suddenly, and $-\dfrac{dP}{dt}$ was measured without delay, then k_2 was greater than the value of k_2 corresponding to the equation at the elevation stage of the pressure and k_2 was smaller at the lowering stage of the pressure, or it has a hysteresis character.   These interesting facts, together with other phenomena, have been treated by the author theoretically,[1] which will be reported in this bulletin in near future.   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.   Mr. I. Kobayashi assisted him during the experiments.

Summary.

It has been experimentally determined that the velocity of reaction between nitrogen and calcium carbide at high temperatures is not directly proportional to the nitrogen-pressure, but there exists the following relation:

$$-\frac{dP}{dt} = K\frac{P}{1+aP},$$

where P denotes the pressure, K and a certain constants depending upon temperature and other conditions of the reaction.

It has also been found that the higher the temperature the greater is the effect of pressure-increase to the velocity of reaction, though the effect of the pressure-increase becomes smaller at higher pressures.   At lower pressures the velocity of the reaction is nearly proportional to the pressure.

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