Studies on Reactions between Gas and Solid. VII. Nitrogenation of Calcium Carbide and Its Kinetic Discussion.

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Introduction. The velocity of nitrogenation of calcium carbide had been experimentally determined as functions of pressure, temperature, size of grain and catalysers, and was formerly reported.(1) (2) (3) (4) Some theoretical discussions upon this reaction kinetics will be given here.

Gas-Solid Reaction. The carbide which was used in these experiments* did not melt or sinter till about 1100°C when heated in vacuum for some time. When the carbide was subjected to the reaction with nitrogen the product sintered very slightly at the furnace temperature above 950°C; and the local melting was perceived above 1150°. At 870°C of the furnace temperature even slight sintering was not perceived.

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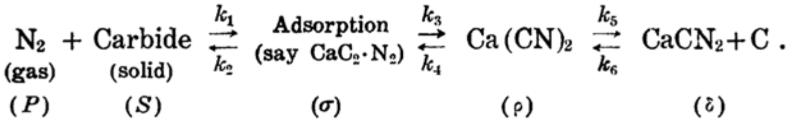
(1) T. Aono, this Bulletin, **7** (1932), 143–154.
(2) T. Aono, *ibid*, 247–255.
(3) T. Aono, *ibid*, 274–280.
(4) T. Aono, *ibid*, 287–297.
* Technical carbide powder of the composition 68.2% CaC_2, 1% CaF_2.

Therefore, beneath the furnace temperature of about 950°C, it can be thought that nitrogen is acting upon solid carbide to form solid products. In this range of temperature the reaction mechanism can be considered as follows.

The first step of the reaction will be the adsorption of nitrogen on some active spots of the carbide. Being higher temperatures the adsorption will chiefly be of chemical or activated nature and an adsorption compound, say $CaC_2\cdot N_2$, will be formed temporarily. Some of such a compound, with an energy larger than the heat of activation, will change to $Ca(CN)_2$; others will break up again into carbide and nitrogen. The $Ca(CN)_2$, thus formed, can exist also temporarily, because at such temperatures the cyanide is very unstable and goes into $CaCN_2$ and C.(5) The reaction scheme is given as follows.



$$\underset{\substack{(\text{gas})\\(P)}}{N_2} + \underset{\substack{(\text{solid})\\(S)}}{\text{Carbide}} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \underset{(\sigma)}{\text{Adsorption (say } CaC_2\cdot N_2)} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \underset{(\rho)}{Ca(CN)_2} \underset{k_6}{\overset{k_5}{\rightleftarrows}} \underset{(\delta)}{CaCN_2+C}\ .$$

Equations of the reaction velocity. Let us use the following notations:

S: the total (effective) active spots capable of formation of the adsorption compound, at time t,
σ: position occupied by the adsorption compound, say $CaC_2\cdot N_2$,
ρ: quantity of effective $Ca(CN)_2$,
δ: quantity of effective $CaCN_2$,
k_1: velocity constant of condensation of nitrogen,
k_2: velocity constant of evaporation of nitrogen,
k_3: velocity constant of $Ca(CN)_2$-formation from adsorption compound,
k_4: velocity constant of back formation of adsorption compound from $Ca(CN)_2$,
k_5: velocity constant of formation of $CaCN_2$+C from $Ca(CN)_2$,
k_6: velocity constant of formation of $Ca(CN)_2$ from $CaCN_2$+C,

all being taken in proper units. Assuming the law, which resembles that of mass-action, to hold in this case, the following equations can be written down:

$$-\frac{dN}{dt}=k_1P(S-\sigma)-k_2\sigma \qquad (1),$$

$$\frac{d\sigma}{dt}=-\frac{dN}{dt}-k_3\sigma+k_4\rho \qquad (2),$$

$$\frac{d\rho}{dt}=k_3\sigma-k_4\rho-k_5\rho+k_6\delta \qquad (3),$$

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(5) The formation of $Ca(CN)_2$ was varified by the author experimentally, and this will be discussed later. It was also reported by H. H. Franck and his co-workers in *Z. Elektrochem.* **45** (1939), 541.

$$\frac{d\delta}{dt}=k_5\rho-k_6\delta \qquad (4),$$

and

$$-\frac{d\mathrm{N}}{dt}=\frac{d\sigma}{dt}+\frac{d\rho}{dt}+\frac{d\delta}{dt} \qquad (5),$$

where $-\frac{d\mathrm{N}}{dt}$ means the rate of decrease of the gaseous nitrogen by means of the above change, and P means the pressure of nitrogen. Adsorption other than the above chemical one must also be existing, but owing to the high temperature the quantity of such will be small, and moreover, the velocity of condensation and evaporation of such kind of adsorption will be very fast, and we can consider that this kind of adsorption is always in a stationary state. Therefore the decrease of gaseous nitrogen will practically be due to the above change.

From Equations (1) and (2) we have

$$\frac{d\sigma}{dt}=(k_1PS+k_4\rho)-(k_1P+k_2+k_3)\sigma \qquad (6),$$

and then

$$\begin{aligned}\sigma &= e^{-\int(k_1P+k_2+k_3)\,dt}\left\{\int(k_1PS+k_4\rho)\,e^{\int(k_1P+k_2+k_3)\,dt}dt+const.\right\}\\ &= e^{-Kt}\left\{\int(k_1PS+k_4\rho)\,e^{Kt}dt+const.\right\} \qquad (7),\end{aligned}$$

where $K=k_1P+k_2+k_3$.

At constant temperature and pressure k_1, k_2, k_3, k_4, k_5, k_6 and P must all be constant. S is, of course, a function of time. From the experimental evidence reported formerly by the author(2)(3)(4), this change seems to be of a kind of auto-catalysis, and if we assume the following scheme:

$$\underset{(S_i)}{\text{Inactive carbide}} \xrightarrow{k} \underset{(S)}{\text{active carbide}} \xrightarrow{k_1P} \underset{(\sigma)}{\text{adsorption compound}},$$ we have

$$-\frac{dS_i}{dt}=kS_i\,; \qquad S_i=S_{i0}\,e^{-kt} \qquad (8),$$

where $S_{i0}=S_i$ at $t=0$.

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(6) The "Active and inactive" have two meanings:
- a) in case of reaction with nitrogen and solid carbide, the ordinary position is inactive, while the position adjascent to the produced nascent carbon and cyanamide or the activator, and which has the properties of fixing the nitrogen in active. The reaction will proceed principally along the contact places, that is, the active position.
- b) in case of reaction with nitrogen and carbide at higher temperatures, the carbide dissolves into the products and becomes easier to react with the nitrogen. Therefore in this case the "active" means the dissolved and activated carbide.

$$\frac{dS}{dt} = kS_i - k_1PS \tag{9}$$

from which

$$S = \frac{S_{i0}}{k_1P-k}\cdot e^{-kt} - \left(\frac{S_{i0}}{k_1P-k} - S_0\right)e^{-k_1Pt} \tag{10}$$

or

$$S = S_0' e^{-kt} - (S_0' - S_0)\, e^{-k_1Pt} \tag{10'}$$

where

$$S_0' \equiv S_{i0}\big/(k_1P-k)\,.$$

From (10) and (7) we have

$$\sigma = \sigma_0 e^{-Kt} + k_1P\left\{\frac{S_0'}{K-k}(e^{-kt}-e^{-Kt}) - \frac{S_0'-S_0}{K-k_1P}(e^{-k_1Pt}-e^{-Kt})\right\} \tag{11}$$

because, at the earlier stage of the reaction, where the change is proceeding from the left to the right, $k_4\rho$ must be very much smaller than k_1PS and can be neglected.

S_0 and σ_0 represent the values of S and σ at $t=0$. (See Fig. 1).

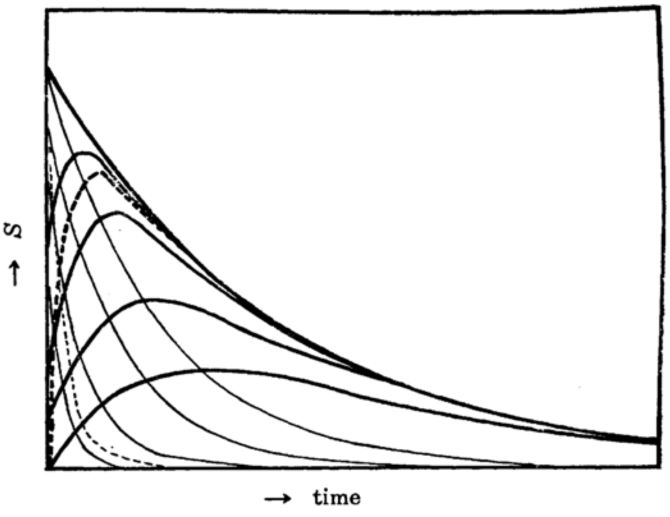

Fig. 1. Curves for "S."

Introducing Eq. (11) into (1) we have

$$-\frac{d\mathrm{N}}{dt} = \frac{k_1(k_3-k)PS_0'}{K-k}e^{-kt} - \frac{k_1P(k_3-k_1P)(S_0'-S_0)}{k_2+k_3}e^{-k_1Pt}$$
$$-(k_1P+k_2)\left\{\sigma_0 - k_1P\left(\frac{S_0'}{K-k} - \frac{S_0'-S_0}{k_2+k_3}\right)\right\}e^{-Kt} \tag{12}$$

This equation (12) gives the rate of nitrogen fixation provided that the reaction products affecting no retarding effect to the reacting substances. The characteristics of the reaction velocity-time curves found by the experiments coinside with this Eq. (11) (2)(3).

Effect of pressure. By studying the reaction in its comparatively earlier stage, whereby the influence of the layer of the product was small, it was also found by the author(1) that at a constant temperature the velocity of this reaction is not directly proportional to the pressure of nitrogen but the following relation exists.

$$-\frac{dP}{dt}=\kappa\frac{P}{1+aP}\equiv\frac{P}{aP+b} \qquad (13),$$

where $\varkappa$ and a or a and b being constants. This relation can also be derived from the above equations.

During a short time of measurement at such a lower temperature of nitrogenation as in those experiments, S can be taken as constant and $k_4\rho$ can be neglected against k_1PS, then from Eq. (7) we have

$$\sigma=\sigma_0 e^{-Kt}+\frac{k_1}{K}PS\left\{1-e^{-Kt}\right\} \qquad (14),$$

After a sufficient time e^{-Kt} becomes sufficiently small and then we have

$$\sigma_\infty=\frac{k_1}{K}PS=\frac{k_1PS}{k_1P+k_2+k_3} \qquad (15),$$

and from (1).

$$-\frac{d\mathrm{N}}{dt}=\frac{k_1k_3PS}{k_1P+k_2+k_3} \qquad (16).$$

This relation is also obtained by putting

$$-\frac{d\mathrm{N}}{dt}=k_1P(S-\sigma_\infty)-k_2\sigma_\infty=k_3\sigma_\infty \qquad (17),$$

which means that the decrease of gaseous nitrogen is merely due to the chemical change, that is, $\frac{d\sigma}{dt}=0$.

For a constant gaseous space (v) the decrease of nitrogen is proportional to the decrease of pressure and we have from (16)

$$-\frac{d\mathrm{N}}{dt}=-v\frac{dP}{dt}=\frac{k_1k_3PS}{k_1P+k_2+k_3},$$

$$\therefore\quad -\frac{dP}{dt}=\frac{P}{\left(\frac{v}{k_3S}\right)P+\left(\frac{k_2+k_3}{k_1k_3S}\right)v}\equiv\frac{P}{aP+b} \qquad (18)$$

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(1),(2),(3): *loc. cit.*

or

$$-\frac{dP}{dt}=\frac{k_1k_3S}{(k_2+k_3)v}\cdot\frac{P}{\left(\frac{k_1}{k_2+k_3}\right)P+1}\equiv\kappa\frac{P}{\alpha P+1} \qquad (18')$$

where

$$\left.\begin{aligned}\kappa&=\frac{k_1k_3S}{(k_2+k_3)v}, & \alpha&=\frac{k_1}{k_2+k_3}=\frac{a}{b}\\ a&=\frac{v}{k_3S}, & b&=\left(\frac{k_2+k_3}{k_1k_3S}\right)v\end{aligned}\right\} \qquad (19).$$

The relations (18), (18′) coinside with (13) which was experimentally obtained.

Heat of Activation. From Equation (19) we have

$$\frac{1}{a}=\frac{S}{v}k_3 \qquad (20),$$

and as k_3 represents the reaction velocity between adsorbed nitrogen and carbide, its temperature function will be given as

$$k_3=A\cdot e^{-\frac{E}{RT}} \qquad (21),$$

and then for constant S we have

$$\frac{1}{a}=A'\cdot e^{-\frac{E}{RT}} \qquad (22).$$

Therefore, if the above postulations are not wrong, log $\left(\frac{1}{a}\right)$ will stand in linear relation with $\frac{1}{T}$ and the inclination of this line to the $1/T$ axis will give the value of (−E/R), from which the temperature increment E can be calculated. From the experimental data reported in the former paper⁽¹⁾ we have Table 1 and Fig. 2.

Table 1.

Temp. °C	790	869	946	1008
a	4.07	1.36	0.125	0.022
$\frac{1}{T}\times10^3$	0.940	0.876	0.820	0.781
$\log_{10}\left(\frac{1}{a}\right)$	−0.609	−0.133	0.903	1.657

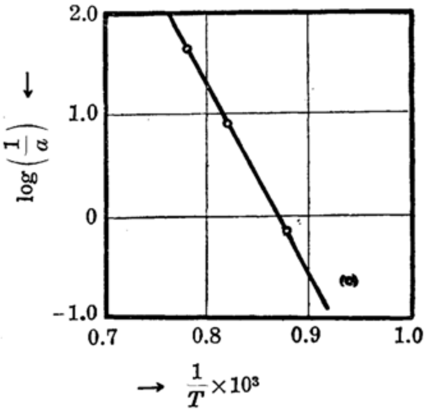

Fig. 2. Temperature increment.

Points except at the temperature of 790°C fall in a straight line, which proves the above postulation to be plausible. (The point of 790°C cannot be compared with the others, because this was taken from the measurement just at the beginning of the reaction, and which, as was formerly reported,⁽²⁾⁽³⁾ is a period of very abnormal). From the inclination of the line we have E $\approx$ 86 Cal./mol., which must be the heat of activation for the reaction of adsorbed nitrogen and calcium carbide to form calcium cyanide.

Other reaction formulae. The equations derived above are to be available for the fixation of nitrogen by very fine powder of carbide, the reaction products affecting no retarding effect to the contact between the reacting substances.

When the grain of carbide is larger, or when the temperature is high enough to make the product sinter or melt, the reaction must occur between the carbide and nitrogen which has come through the product layers. Some of the velocity formulae were already derived and discussed in the preceding papers; and was also mentioned there that it is commonly difficult to represent the complete velocity course, experimentally found, with a single equation. This will partly be due to elevation of the local temperature by dint of the reaction heat, which changes the velocity constants during the course of the reaction, and partly because the products change their physical properties during the process due to the change of temperature.

Summary.

(1) From the experimental study of the nitrogenation of calcium carbide the author concluded its mechanism to be as follows:

(a) adsorptions of nitrogen on the carbide,

(b) formation of intermediate compound $Ca(CN)_2$ temporarily,

(c) breaking of $Ca(CN)_2$ into $CaCN_2$ and C.

(2) Equations for this (gas-solid) reaction velocity were derived from the above view. For constant temperature and pressure

$$-\frac{d\mathrm{N}}{dt}=\frac{k_1P(k_3-k)S_0'}{K-k}e^{-kt}-\frac{k_1P(k_3-k_1P)(S_0'-S_0)}{k_2+k_3}e^{-k_1Pt}$$

$$-(k_1P+k_2)\left\{\sigma_0-k_1P\left(\frac{S_0'}{K-k}-\frac{S_0'-S_0}{k_2+k_3}\right)\right\}e^{-Kt}$$

and for changing pressure

$$-\frac{d\mathrm{N}}{dt}=\frac{k_1k_3PS}{k_1P+(k_2+k_3)}$$

$$-\frac{dP}{dt}=\frac{P}{aP+b}\,.$$

(3) The coincidence of these equations with the experimental results were discussed.

(4) The heat of activation for the reaction of the adsorbed nitrogen and carbide to form calcium cyanide was calculated to be approximately 86 Cal./mol.