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Thermal Decomposition of Lead Carbonate Tablets Prepared by Compressing Fine Particles

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The thermal decomposition of lead carbonate tablets was kinetically studied in a nitrogen gas stream at temperatures of 240, 320, and 360°C. The tablets used in this work were prepared by compressing lead carbonate particles in a steel mold under pressures of 2—15 ton/cm^2. The decomposition reaction for the tablet was represented in two ways. Rate expressions were developed from the unreacted-core shrinking model applied to the individual particles (for the first of the two decomposition processes) and to the whole tablet (for the second). The effect of the pressure applied in preparing the tablet on the decomposition rate was attributed to the deviation in the pressure profile for carbon dioxide in a tablet (for the first process) or to the variation in the effective diffusivity and bulk density of the tablet (for the second).

Publications have appeared on the non-isothermal decomposition of lead carbonate, reporting the existence of such intermediate phases as $PbO \cdot 2PbCO_3$, $PbO \cdot PbCO_3$, and $2PbO \cdot PbCO_3$ in a carbon dioxide atmosphere at 1 atm.[1-3] In 1964 Crisafe and White[4] examined the thermal decomposition of lead carbonate by equilibrium methods and found the presence of $3PbO \cdot 4PbCO_3$, which is stable under very high P-T conditions. It was recently shown, from isothermal decomposition studies[5,6] in a nitrogen-gas flow or under reduced pressure, that a mass of lead carbonate particles decomposed to form two intermediate phases, $PbO \cdot PbCO_3$ at high partial pressures of carbon dioxide and $2PbO \cdot PbCO_3$ at low partial pressures. One of the basic lead carbonates, $PbO \cdot 2PbCO_3$, is formed only in the decomposition of lead carbonate hydroxide, $2PbCO_3 \cdot Pb(OH)_2$.[7]

Few studies had been published on the rate of the decomposition of lead carbonates; therefore, kinetic studies of the thermal decomposition of these samples were previously made by the present authors,[5-7] showing that the unreacted-core shrinking model provided a good explanation for the decomposition of the samples. The thermal decomposition of a packed mass of lead carbonate particles in a small glass tube[8] was also investigated in a nitrogen-gas stream and was found to be:

$$2PbCO_3(s) \longrightarrow PbO \cdot PbCO_3(s) + CO_2(g) \qquad (1)$$

$$PbO \cdot PbCO_3(s) \longrightarrow 2PbO(s, \text{litharge}) + CO_2(g) \qquad (2)$$

We will refer to these processes, for convenience, as the first and second processes respectively. It was shown previously that the over-all rate of the decomposition of each process was influenced by the dissociation pressure of the reactant(s)-product(s)-product(g) system, and that it was also influenced to some extent by the carbon dioxide pressure at the gas-solid interface.[8]

In the present study, lead carbonate tablets prepared by compacting lead carbonate particles under different pressures were decomposed isothermally, and a kinetic study of the decomposition of these tablets was made in order to evaluate the effect of the compacting pressure.

Experimental

The disk-shaped tablets used in this work (11.3 mm in diameter, *ca.* 2 mm thick, and *ca.* 1 g in weight) were prepared by compressing lead carbonate particles

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1) E. A. Peretti, *J. Amer. Ceram. Soc.*, **40**, 171 (1957).

2) S. St. J. Warne and P. Bayliss, *Amer. Mineralogist*, **47**, 1011 (1962).

3) G. Pannetier, S. Fénistein and G. Djega-Mariadassou, *Bull. Soc. Chim. France*, **1964**, 701 (1964).

4) D. A. Grisafe and W. B. White, *Amer. Mineralogist*, **49**, 1184 (1964).

5) R. Komoda, Y. Nishi and M. Kano, *Nippon Kagaku Zasshi*, **88**, 1038 (1967).

6) R. Komoda, Y. Nishi and M. Kano, *ibid.*, **89**, 478 (1968).

7) R. Komoda, Y. Nishi and M. Kano, *ibid.*, **90**, 30 (1969).

8) R. Komoda, Y. Nishi and M. Kano, *Kogyo Kagaku Zasshi*, **71**, 475 (1968).

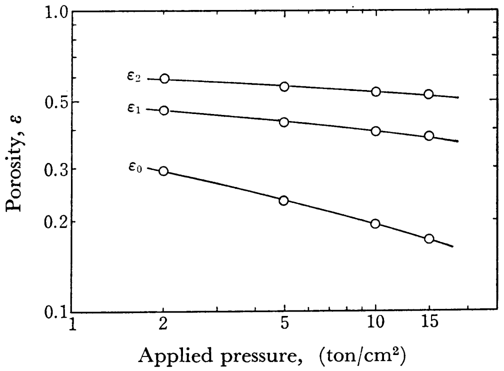

Fig. 1. Correlation between the applied pressure and porosity.

uniformly in a steel mold which consisted of a cylindrical die with two punches, lower and upper. The lead carbonate particles used (3—4 μ in diameter, as determined under an electron microscope) were prepared from cold aqueous solutions of lead acetate and ammonium carbonate, and were then compressed under pressures of 2—15 ton/cm^2 for 5 min by a hydraulic press. The lead carbonate tablets thus prepared were porous and had different porosity values as Fig. 1 shows. The porosity of the tablet was calculated from its bulk density and the theoretical net density of the sample. Some of the porosities of the tablets before decomposition, ε_0, were smaller than 0.2595, the minimum value of the theoretical porosities corresponding to that of the closest packing of equal-sized rigid spheres. This may be attributed to the fact that not all the lead carbonate particles in these tablets were exactly spherical or the same size. No change in the X-ray diffraction pattern was observed between two different lead carbonate samples, compressed and uncompressed. This fact suggests the absence of any appreciable effect of the applied pressure on the crystal structure.

The thermogravimetric apparatus used was an ordinary one consisting of a helical quartz spring and a 38-mm-i.d.×*ca.* 1-m-long quartz tube whose lower half was enclosed in an electrically-heated furnace. Preheated nitrogen-gas flows of 0.03—0.80 *l*/min were led, at 1 atm, into the vertical quartz tube at the bottom in order to sweep off the product gas or the carbon dioxide gas evolved during the decomposition runs. The tablet was supported on a stainless-steel wire sample-holder and was so suspended in the apparatus that the base of the tablet was parallel to the axis of the vertical tube. The extension of the spring was measured with a cathetometer during the decomposition reaction. The sample was also weighed exactly both before and after the run. The temperature of the sweeping gas was assumed to be close to the sample temperature and was measured with a chromel-alumel thermocouple. The decomposition runs were carried out at the constant temperatures of 240°C (for the first process) and 320 and 360°C (for the second process).

An X-ray diffractmeter was also used to identify the decomposition products and to ascertain whether or not a decomposition reaction occurred.

Results and Discussion

Preliminary runs showed that the thermal decomposition of lead carbonate tablets proceeded according to Eqs. (1) and (2); this finding was in agreement with the results of the decomposition studies of the powdered mass packed tightly into a glass tube.[8] In this paper the two processes represented by Eqs. (1) and (2) are designated as the first process and the second process respectively.

For the thermal decomposition of the powdered mass, two simple, idealized models can be considered. One of them is chosen for the case where all the particles in the powdered mass decompose at all times. The other is applicable when only some particles in the outer shell of the powdered mass decompose at first, and then the decomposition zone (in which some particles are decomposing) moves inwards, leaving a completely decomposed solid behind.

In slicing and examining the inside of the partly-decomposed tablets, as will be described below, the thermal decomposition of lead carbonate (the first process) was found to occur at every individual particle within the tablet. Thus, the thermal decomposition study of the first process was made by selecting the former model, or by simultaneously applying the unreacted-core shrinking model to the individual particles within the tablet. However, the second process was found to occur at the particles localized in the outer shell of the tablet. The kinetic study of this process was made by employing the latter model.

A number of decomposition studies of solid materials have been made assuming a profile of a uniform temperature throughout the powdered mass.[8–12] This assumption is acceptable when a small amount of the sample is used and when its rate of decomposition is small, as in the present case. The theoretical expression for the effective thermal conductivity within a powdered mass[13] indicates that the effective thermal conductivity decreases with an increase in the porosity. Consequently, the rate of the heat transfer may be more rapid with the tablet compressed at the pressure of 15 ton/cm^2 than with that compressed at 2 ton/cm^2. On the other hand, experimental runs showed that the over-all rate of decomposition for the former tablet was much slower than that for the latter.

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9) T. R. Ingraham and P. Marier, *Can. J. Chem. Eng.*, **41**, 170 (1963).

10) N. A. Warner and T. R. Ingraham, *ibid.*, **40**, 263 (1962).

11) A. W. Coats and N. F. H. Bright, *Can. J. Chem.*, **44**, 1191 (1966).

12) M. Hasatani and S. Sugiyama, *Kagaku Kōgaku*, **30**, 734 (1966).

13) D. Kunii and J. M. Smith, *AIChE J.*, **6**, 71 (1960).

These facts suggest that the step of heat transfer played no appreciable role in determining the rate of the decomposition reaction in our experiment. In addition, the following facts suggest the important role of the carbon dioxide pressure: during the thermal decomposition of the lead carbonate mass in a glass tube, as has been reported previously,[8] no decomposition reaction of the second process occurred at the lateral face of the cylindrical pellet, this face being surrounded by glass through which the product gas (carbon dioxide) could not be removed but through which heat could be transported. Moreover, no decomposition reaction occurred at elevated pressures of carbon dioxide. For these reasons, the temperatures within a tablet were presumed to be uniform throughout the tablet during the decomposition reaction and not practically affect the over-all rate of the decomposition. The temperature profile in each particle was also presumed to be uniform, since the expression for heat-transfer control did not fit the experimental data satisfactorily. In view of the above considerations, only the pressure profile for carbon dioxide was considered in the treatment to be described below.

Nitrogen flow rates in the range studied were found to influence the rate of the decomposition. It is obvious that the partial pressure, P_i, of carbon dioxide at the tablet surface decreases as the rate of nitrogen-gas flow increases. Therefore, the effect of carbon dioxide pressure on the decomposition rate was evaluated in this paper on the basis of the partial pressure, P_i, which was determined by means of equations to be described below.

The rate of the decomposition reaction of the lead carbonate tablet was very small; therefore, in the present work we can assume that the sample temperature is almost equal to that of the gas stream.[14]

No significant reduction in the size of the tablet during decomposition was observed, while L was constant throughout the decomposition run.

The First Process. The thermal decomposition of some solid materials occurs at an interface advancing from the outside of the particle toward the interior. The unreacted-core shrinking model proposed earlier by Yagi and Kunii[15] provides a good representation of this phenomenon. When the over-all rate of the thermal decomposition is virtually independent of the mass-transfer rates of gases through the porous solid layer, as well as across the gas-film surrounding the particle, but is controlled solely by the inherent chemical reactivity of the solid reactant, the following equation for the single particle can be developed from the model:

$$1-(1-F)^{1/3}=kt \tag{3}$$

where k is a constant which is a function of the temperature, the particle size, the specific properties of the reactant, and so on. This expression is also applicable to the powdered mass in applying the model simultaneously to all the individual particles in the powdered mass, whose constituents are practically equal in size and in the same conditions. When the decomposition of each particle in the mass is controlled by the surface phenomenon and only the partial pressure of carbon dioxide outside the particles changes, an expression of the type of Eq. (3) is still useful for the decomposition of the particles.

If the pressure profile for carbon dioxide is uniform throughout the tablet, all the individual particles in the tablet should be under essentially the same conditions. Therefore, the relationship between the conversion of the whole tablet and the decomposition time for the first process should be:

$$1-(1-F_1)^{1/3}=k_1t_1 \tag{4}$$

where the constant, k_1, comprises a decomposition rate constant which is proportional to the difference between the equilibrium partial pressure of carbon dioxide and the partial pressure of carbon dioxide within the tablet; k_1 can then be expressed as follows:

$$k_1=k_1'P_{e1}(1-P/P_{e1}) \tag{5}$$

These two expressions, (4) and (5), are useful for the decomposition study of the lead carbonate tablet with a uniform internal-pressure profile.[8]

When the pressure profile for carbon dioxide within the tablet is not uniform, consider the pressure, P, of carbon dioxide within an arbitrary volume element in the tablet ($\Delta r\cdot r\Delta\theta\cdot\Delta l$ in cylindrical coordinates) and take an average value throughout the whole tablet; then:

$$k_1=k_1'P_{e1}\frac{1}{2R^2\pi L}\int_0^R\int_0^{2\pi}\int_{-L}^{L}(1-P/P_{e1})r\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}l \tag{6}$$

This expression is simple and is useful for an engineer in developing approximate rate expressions without undue complexities; nevertheless, it is not strictly accurate from the mathematical standpoint.

A partly-decomposed tablet was sliced off and examined by exposing the cross-sectional surface to X-rays. In the tablet compressed at the pressure of 2 ton/cm², little difference was detected between the heights of the corresponding peaks of the two X-ray diffraction patterns[4,5] for the particles located in the center and near the surface, each X-ray diffraction pattern showing the existence of only two phases, $PbCO_3$ and $PbO\cdot PbCO_3$. On the contrary, a great difference between the corresponding peak heights was observed in the tablet compacted at the pressure of 15 ton/cm². Further experiments were made by roasting the central part of the partly-decomposed tablet and by deter-

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[14] N. J. Themelis and W. H. Gauvin, *Can. J. Chem. Eng.*, **41**, 1 (1963).

[15] S. Yagi and D. Kunii, *Kogyo Kagaku Zasshi*, **56**, 131 (1953); "Proc. 5th Int. Symp. on Combustion," Reinhold, New York (1955), p. 231.

Table 1. Fractional decompositions for the whole tablet and for its central part

Applied pressure, (ton/cm^2)	2	2	5	10	15
Weight of the whole tablet undecomposed, U_u (g)	1057.4	949.4	1075.9	1071.2	1042.2
Weight of the whole tablet decomposed partly, U_p (g)[a]	1016.5	909.0	1033.4	1032.1	1002.9
Time for decomposition, t_1 (min)	16	17	20	21	25
Fractional decomposition for the whole tablet, F_1 (dimensionless)[b]	0.470	0.517	0.480	0.443	0.458
Weight of the sample: the central part of the partly decomposed tablet, U_p' (g)	143.4	123.7	127.9	82.8	134.2
Weight of the sample at the completion of decomposition, U_c (g)[c]	124.6	107.8	110.9	71.3	115.5
Fractional decomposition for the central part of the partly decomposed tablet, F_1' (dimensionless)[d]	0.470	0.504	0.445	0.364	0.358
Ratio of F_1' to F_1 at about $F_1=0.5$, F_1'/F_1 (dimensionless)	1.000	0.975	0.928	0.821	0.781

a) The decomposition runs were carried out at the temperature of 240°C in the nitrogen-gas flow of 0.40 l/min.

b) $F_1 = 2\times\left(\frac{U_u-U_p}{44.01}\right)\Big/\left(\frac{U_u}{267.2}\right)$

c) The samples were decomposed at 400°C in the nitrogen-gas stream for 70 min.

d) $F_1' = 2\times\left\{1-\left(\frac{U_p'-U_c}{44.01}\right)\Big/\left(\frac{U_c}{223.2}\right)\right\}$

mining its fractional decomposition. The results obtained from these experiments (see Table 1) as well as the observation of the X-ray diffraction patterns showed that the difference between the degrees of decomposition of particles at the two locations became greater with an increase in the compacting pressure (*viz.*, with a decrease in the porosity of the tablet). This fact suggests that the carbon dioxide pressure profile within a tablet becomes less uniform with a decrease in the porosity of the tablet.

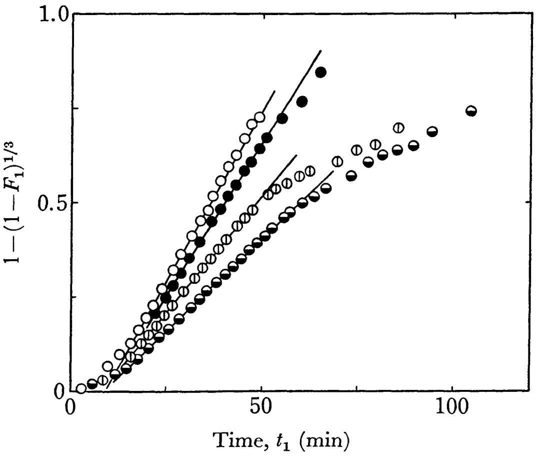

Fig. 2. Plots of $1-(1-F_1)^{1/3}$ *vs.* decomposition time for the first process at 240°C.
○: P=2 ton/cm^2, $G\times10^4$=2.09 g/(cm^2)(sec)
●: P=2 ton/cm^2, $G\times10^4$=0.74 g/(cm^2)(sec)
⦶: P=15 ton/cm^2, $G\times10^4$=4.01 g/(cm^2)(sec)
◒: P=15 ton/cm^2, $G\times10^4$=2.51 g/(cm^2)(sec)

Figure 2 shows some typical results obtained from the two series of experiments for the tablets prepared under two different compacting pressures. Similar plots, illustrated in Fig. 2, were obtained in the other runs, and in all cases, good, straight lines were obtained. It is evident from the linearity of the relationship in Fig. 2 that the approximate expression of Eq. (4) is applicable to the major period of the decomposition run. The slight deviations of the experimental plots from the linearity in the beginning of the decomposition reaction may be attributed to the formation and the growth of the nuclei of $PbO\cdot PbCO_3$; this initial period is usually termed an induction period. Deviations of the plots were also observed at the end of the decomposition of the tablets compressed at higher pressures, partially because of a lack of mathematical accuracy in deriving Eqs. (4) and (6). However, for the sake of simplicity, the approximate expressions of Eqs. (4) and (6) were used successfully in this work by being applied only to the experimental data in the major period.

It is now necessary to determine the partial pressure, P_i, of carbon dioxide at the external surface of the tablet. The values of P_i under the different experimental conditions were determined by calculating the following equations concerning a dimensionless factor of j_d:[16]

$$j_d = \alpha\left(\frac{\sqrt{a_p}\cdot G}{\mu}\right)^{-\beta} \tag{7}$$

in which:

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16) K. H. Yang and O. A. Hougen, *Chem. Eng. Prog.*, **46**, 146 (1950).

$$N_{\mathrm{Re}} = \sqrt{a_p} \cdot G/\mu > 620;\ \alpha = 1.25,\ \beta = 0.41$$

$$N_{\mathrm{Re}} < 620;\ \alpha = 2.44,\ \beta = 0.51$$

$$j_d = \left(\frac{k_f \cdot M_m \cdot P_f}{G}\right)\left(\frac{\mu}{\rho_N \cdot D}\right)^{2/3} \tag{8}$$

The rate of mass transfer in a boundary film, N', which is presumed to be equal to the apparent rate of the thermal decomposition, can be expressed as:

$$N' = k_f \cdot a_m(P_i - P_g) = r_a \tag{9}$$

Equations (7), (8), and (9) are combined to give an appropriate expression for the partial pressure:

$$P_i - P_g = \frac{1}{\alpha}\left(\frac{r_a \cdot \sqrt{a_p} \cdot M_m \cdot P_f}{\mu \cdot a_m}\right)\left(\frac{\mu}{\rho_N \cdot D}\right)^{2/3}\left(\frac{\sqrt{a_p} \cdot G}{\mu}\right)^{\beta - 1} \tag{10}$$

The specific values of M_m, G, μ, and ρ_{N} in this equation are represented by those of nitrogen-gas at the temperature of 240°C, since the partial pressure of carbon dioxide in the bulk-gas phase was so low as to be negligible compared with that of nitrogen. The partial pressure of carbon dioxide in the main stream, P_g, was successfully regarded as zero. Let the film pressure factor, P_f, be equal to 1 atm because of the small value of P_i compared with the partial pressure of nitrogen at the solid-gas interface. The binary molecular diffusivity of interest was predicted by means of the appropriate method.[17] In this procedure, an empirical value of D, estimated at 0.6050 cm^2/sec at 600°K by Walker and Westenberg,[18] was also used for the prediction. The overall rate, r_a, was empirically determined at the major period corresponding to F_1 of 0.4—0.7. The value of P_i in each run was then obtained by the substitution of the appropriate properties and empirically-determined variables into Eq. (10).

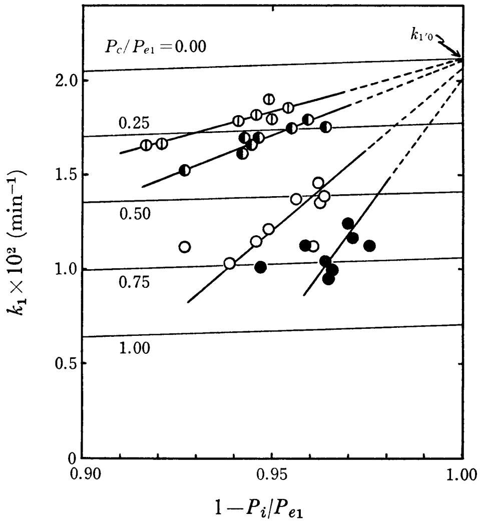
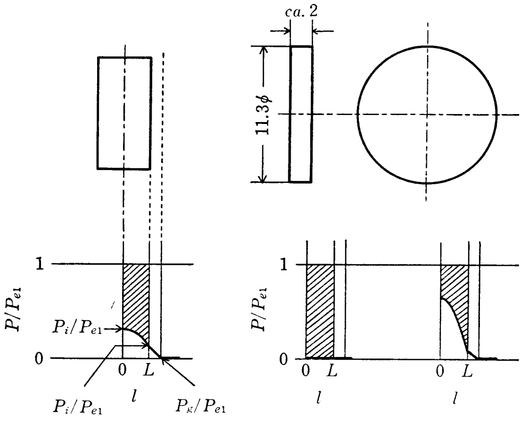


Fig. 3. Correlation between k_1 and $(1 - P_i/P_{e1})$ for the first process at 240°C.
⦶: $P = 2$ ton/cm^2: ◐: $P = 5$ ton/cm^2
○: $P = 10$ ton/cm^2: ●: $P = 15$ ton/cm^2

Figure 3 shows the relationship between k_1, the slope of each line illustrated in Fig. 2, and $(1 - P_i/P_{e1})$, the dimensionless pressure term at the solid-gas interface as evaluated from the empirically-determined value of P_i. In estimating the $(1 - P_i/P_{e1})$ quantity, the dissociation pressure of lead carbonate was determined from the experimental data by Peretti.[1] Good, straight lines were obtained in the two series of decomposition runs carried out with the tablets compacted at the pressures of 2 and 5 ton/cm^2. However, the empirical plots obtained from the tablets compacted at the pressures of 10 and 15 ton/cm^2 were scattered to some extent. This may be attributed to the large deviations of the tablet porosities. Figure 3 also shows that the rate of the decomposition, which was represented by k_1, apparently increased with the $(1 - P_i/P_{e1})$ term, the function of the partial pressure at the solid-gas interface. Furthermore, it is shown that the pressure term $(1 - P_i/P_{e1})$ apparently had a more significant effect on the rate of the decomposition when the compacting pressure was high (*viz.*, the porosity of the tablet was small).

It is obvious that the mean value of $(1 - P/P_{e1})$, averaged through the whole tablet, necessarily exerts an influence upon the overall rate of decomposition. Since it comprises the decomposition rate constant, the k_1 constant should be affected by the averaged term of $(1 - P/P_{e1})$, as is to be expected from Eq. (6). Therefore, the empirical value of k_1 gives useful information about the pressure profile within a tablet.

The dimensionless-pressure profile for carbon di-



(a) (b) (c)

Fig. 4. Sketch of the tablet and pressure profiles for carbon dioxide.

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17) E. N. Fuller, P. D. Schettler and J. C. Giddings, *Ind. Eng. Chem.*, **58(5)**, 19 (1966).

18) R. E. Walker and A. A. Westenberg, *J. Chem. Phys.*, **29**, 1139 (1958).

oxide in the *l*-direction (the axial direction of the tablet) for the first process may be shown analogously as Profile (a) in Fig. 4, since the local pressure of carbon dioxide may be higher at the center than at the surface. It can reasonably be considered that, in estimating the rate of the decomposition of the lead carbonate tablet, the transfer of carbon dioxide in the *l*-direction is more important than in the *r*-direction (the radial direction of the tablet) because of the very small length-to-diameter ratio (L/R) of the tablet used in this work. These considerations and the symmetrical pressure distribution in the θ coordinate lead to the conclusion that Eq. (6) can be rewritten as a function of only one coordinate direction. Hence:

$$k_1 = \frac{k_1'\cdot P_{e1}}{2L}\int_{-L}^{L}(1-P/P_{e1})\mathrm{d}l \tag{11}$$

In Fig. 3 the straight line for the tablets compacted at the pressure of 2 ton/cm² is extrapolated to the point $(1-P_i/P_{e1})=1$; thereby, $k_{1,0}$ is estimated at 2.12×10^{-2} min^{-1}. This constant, $k_{1,0}$, is assumed to be identical with the k_1 at $P=0$ in Eq. (11), which corresponds to that of the carbon dioxide-pressure profile (b) in Fig. 4. This assumption is reasonable because there was little difference, as has already been mentioned, between the local pressures of carbon dioxide with the tablet compressed at the pressure of 2 ton/cm² and because the partial pressure of carbon dioxide at the center of this tablet is, thereby, negligibly low when the partial pressure at the surface approaches zero. The integration of Eq. (11) at $P=0$ and the application of this assumption give the following equation:

$$k_{1,0} = k_1'\cdot P_{e1} \tag{12}$$

The ratio of k_1 to $k_{1,0}$ can then be expressed as follows:

$$\frac{k_1}{k_{1,0}} = \frac{1}{L}\int_{0}^{L}(1-P/P_{e1})\mathrm{d}l \tag{13}$$

in which the integral from zero to L with respect to l is satisfactorily used because of the symmetrical pressure profile. The integral term in Eq. (13) gives the shaded area illustrated in Profile (a) in Fig. 4 as a typical example, while the denominator, L, which is given by the integration from zero to L of the $(1-P/P_{e1})=1$ quantity, shows the area of the rectangle indicated as Profile (b) in Fig. 4. Therefore, the expression of Eq. (13) indicates that the ratio of k_1 to $k_{1,0}$ is equal to the ratio of one area to the other, each area corresponding to the overall pressure-driving force to decomposition.

It was impossible to determine the real pressure profile within a tablet because of the experimental difficulties. However, it is obvious that the partial pressure, P, of carbon dioxide at an arbitrary situation, l, varies with l; this is expressed as a continuous function of l ($-L\leqq l\leqq L$). On introducing a dimensionless coordinate, $z=l/L$, the pressure profile within a tablet is given as $P(z)$. Noting that $P(z)=P(-z)$, the expression for $P(z)$ at $0\leqq|z|\leqq1$ can be represented by a "power series" of the type:

$$P(z) = a_0 + a_2z^2 + a_4z^4 + \cdots + a_{2n}z^{2n} + \cdots \tag{14}$$

where:

$$\frac{a_{2n}}{a_{2n+2}z^2} > \frac{P_c}{P_c-P_i} > 1$$

for all n's greater than or equal to m.

The absolute value of the nth term in this infinite series approaches zero as $n\rightarrow\infty$. The terms with a large n value are, then, negligibly small and the approximate expression for $P(z)$ can be written with the first several terms in Eq. (14). Many of the terms should be employed for the very close approximation to $P(z)$, especially when $|z|$ approaches unity, while the value of $P(z)$ at $z=1$ is determined from the experimental data. However, in the absence of full information about the profile, the approximate expression for $P(z)$ was assumed to be given by the first two terms on the right-hand side of Eq. (14); in addition, the integral term in Eq. (13) was also assumed to give the following area in place of the real area corresponding to the overall pressure-driving force: the area being surrounded by a curved line (defined by Eq. (15)) and three straight lines ($z=l/L=0$, $z=1$, and $P/P_{e1}=1$). On the basis of these assumptions, the pressure profile in a tablet can be outlined without deviating too greatly from reality.

From the above considerations, the approximate expression presumed for the pressure profile at $0\leqq|z|\leqq1$ is:

$$P(z) = a_0 + a_2z^2 \tag{15}$$

The boundary conditions employed are:

$$\left.\frac{\mathrm{d}P}{\mathrm{d}z}\right|_{z=0} = 0$$

$$P(0) = P_c$$

$$P(1) = P(-1) = P_i$$

The solution to Eq. (15) with these conditions is:

$$P(z) = P_c + (P_i-P_c)z^2 \tag{16}$$

so that Eq. (13) becomes:

$$\frac{k_1}{k_{1,0}} = \frac{(1-P_i/P_{e1}) + 2(1-P_c/P_{e1})}{3} \tag{17}$$

Since the value of $(1-P_i/P_{e1})$ in each run had already been calculated from Eq. (10), the value of $(1-P_c/P_{e1})$ in each run could be determined from the approximate expression of Eq. (17). The results for the dimensionless pressure, P_c/P_{e1}, as well as the experimental values of $k_1/k_{1,0}$ at $(1-P_i/P_{e1})=0.97$, are illustrated in Fig. 5 against the porosity, ε_1.

It is shown in Fig. 5 that the partial pressure of carbon dioxide at the center of the tablet rises with a decrease in the porosity, as was suggested earlier by the diffractmetrical and the thermogravimetrical analyses, in spite of these being the same pressure at the solid-gas interface (*viz.*, $P_i/P_{e1}=0.03$).

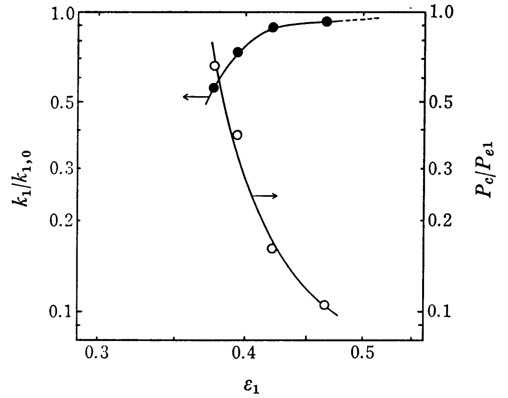

Fig. 5. Effect of porosity ε_1 on dimensionless ratios, $k_1/k_{1,0}$ (●) and P_c/P_{e1} (○).

Equation (17) with a given parameter of P_c/P_{e1} is, then, plotted in Fig. 3. The series of lines thus obtained shows how high the P_c/P_{e1} ratio was in each run. It is apparent from Fig. 3 that the carbon dioxide pressure at the center becomes higher, on the whole, with an increase in the compacting pressure; therefore, the pressure profile for carbon dioxide during the decomposition reaction is less uniform for the tablets of a lesser porosity.

The empirical plots of k_1 against $(1-P_i/P_{e1})$ for the tablets compacted at the pressure of 15 ton/cm^2 (*cf.* Fig. 3) show that the averaged value of P_c/P_{e1} can be estimated to be approximately 0.7. This fact shows that the carbon dioxide-pressure profile of this tablet might be represented analogously as Profile (c) in Fig. 4. No attempt has been made to demonstrate this simplified pressure profile, whereas these considerations are supported by the fact that the plots of $1-(1-F_1)^{1/3}$ against t_1, which give a straight line in the case of a uniform pressure profile, deviated to some extent with the tablets compacted at higher pressures. It was also considered that the simple expressions of Eqs. (4) and (11) were useful for the first process of the thermal decomposition of only the lead carbonate tablets with a greater porosity. However, these expressions proved applicable also to tablets compressed at the pressure of 15 ton/cm^2.

The Second Process. The thermal decomposition study of a mass of basic lead carbonate ($PbO\cdot PbCO_3$) particles[5)] showed that the decomposition reaction of the materials occurred only at low partial pressures of carbon dioxide, and the rate of the decomposition for every single particle was found, at small nitrogen-flow rates, to be controlled by the step of the mass transfer of carbon dioxide through the atmosphere within the mass of particles. It was, then, reasonably considered that the decomposition rate of a tightly-compacted mass of the basic lead carbonate particles was controlled by the diffusional step through the powdered mass. Visual observation and the X-ray diffraction data showed that the decomposition product, PbO (litharge), formed a shell of a reddish brown color sharply separated from the grey-colored reactant, $PbO\cdot PbCO_3$, inside the shell, and that the decomposition front advanced from the outside of the lump, or of the whole tablet, to the interior. Hence, the diffusional step through the product layer (the porosity of which is given as ε_2) proves to have a significant connection with the rate of the decomposition. When the decomposition of one particle is subject to the gas-film-diffusion controlling step, the specific rate of the decomposition of this particle is constant at any given time during the decomposition run, irrespective of the size of the undecomposed-core in the particle. It can, then, be concluded that all the rates of decomposition for the particles of any conversion under the same conditions are equal during the decomposition. Therefore, the thermal decomposition of the whole tablet was reasonably considered, from a macroscopic point of view, to occur at the interface between decomposed and undecomposed materials. It is also reasonable to suppose that the decomposition interface moved inward only in the direction normal to the base of the tablet since the decomposition front, curved slightly like a lens, was taken to be almost parallel to the base of a tablet because of its small height-to-diameter ratio. Therefore, only the *l* component of the mass transport will be considered in this paper.

The moler flux with respect to a stationary coordinate, N_p in g-mol/(cm^2)(sec), of carbon dioxide diffusing through the porous layer of the decomposition product is expressed by the following expression, which is called Fick's first law of diffusion:

$$N_p = y_p(N_p+N_N)-c\bar{D}_e(\mathrm{d}y_p/\mathrm{d}l) \tag{18}$$

There may be a net motion of carbon dioxide away from the decomposition interface during the decomposition run, and nitrogen-gas is stationary in a pseudo-steady-state condition; these things were assumed successfully by previous workers[19–21)] and were also applicable to the present study. The molar flux of nitrogen was, thereby, taken to be zero. Then, by substituting $N_N=0$ in Eq. (18) and solving for N_p, we obtain:

$$N_p = -\frac{c\bar{D}_e}{1-y_p}\cdot\frac{\mathrm{d}y_p}{\mathrm{d}l} \tag{19}$$

With the pseudo-steady-state approximation valid for the solid-gas system, the rate of the decomposition at any instant is, in the present case, given by the rate of diffusion of the product gas away from the decomposition interface through the product layer; therefore:

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19) O. Levenspiel, "Chemical Reaction Engineering," John Wiley, New York (1962), p. 346.

20) K. B. Bischoff, *Chem. Eng. Sci.*, **18**, 711 (1963).

21) C. Y. Wen, *Ind. Eng. Chem.*, **60**(**9**), 34 (1968).

$$-\frac{\mathrm{d}W_r}{\mathrm{d}t} = \frac{\mathrm{d}W_p}{\mathrm{d}t} = 2SN_p = \text{constant} \tag{20}$$

The amount of the reactant present in a tablet is expressed as the product of the molar bulk density and the volume of the undecomposed mass. The disappearance of a small amount of the solid reactant is accompanied by the decrease in its volume; thus:

$$-\mathrm{d}W_r = \mathrm{d}W_p = -2S\rho_a \mathrm{d}l \tag{21}$$

Noting that the decomposition interface was taken to advance only in the l-direction, the fractional conversion for the second process can be written as follows:

$$F_2 = \frac{L-l}{L} \tag{22}$$

By substituting Eqs. (19) and (21) into Eq. (20), solving with the pseudo steady-state approximation, and using the appropriate expression for F_2 we obtain the conversion-time expression for the second process of the decomposition of the tablet, or:

$$(F_2)^2 = k_2 t_2 \tag{23}$$

where:

$$k_2 = \frac{2\bar{D}_e P_{e2} P_t}{RT\rho_a L^2 (P_N)_{\ln}} (1 - P_i/P_{e2}) \tag{24}$$

The $(P_N)_{ln}$ term in this expression is the logarithmic mean of the partial pressures of nitrogen-gas at the solid-gas interface and at the decomposition interface, defined by the following equation:

$$(P_N)_{\ln} = \frac{P_{N,i} - P_{N,l}}{\ln(P_{N,i}/P_{N,l})} = \frac{(1-P_i)-(1-P_{e2})}{\ln\frac{1-P_i}{1-P_{e2}}} \tag{25}$$

in which the subscripts i and l refer to the solid-gas interface and the decomposition interface respectively.

Some typical correlations between $(F_2)^2$ and t_2 for the decomposition of a lead carbonate tablet are shown in Fig. 6. These plots, as well as the similar plots from the other runs, indicate that the experimental data gave a linear relationship in almost all regions of the decomposition run, showing that Eq. (23) is valid under the present experimental conditions and can be used for the second process of the decomposition of a lead carbonate tablet. Each slope of the straight lines in Fig. 6 gives the experimental value of k_2.

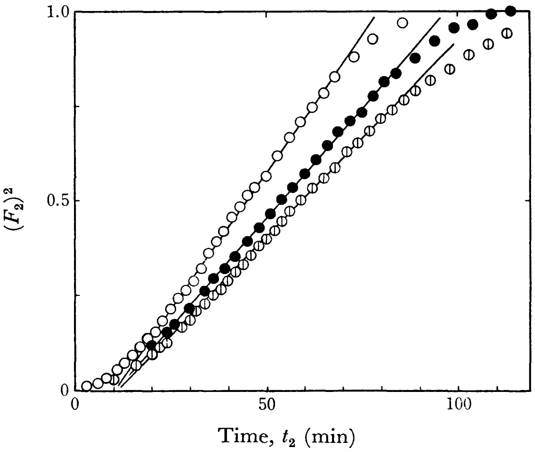

Fig. 6. Plots of $(F_2)^2$ *vs.* decomposition time for the second process at 320°C.
applied pressure $P=5$ ton/cm^2;
○: $G\times10^4=7.71$ g/(cm^2)(sec)
●: $G\times10^4=2.67$ g/(cm^2)(sec)
◐: $G=10^4=2.01$ g/(cm^2)(sec)

It is now necessary to examine the effect of the compacting pressure on the decomposition rate. All the variables in Eq. (24), except for $\bar{D}_e$ and ρ_a, are naturally independent of the compacting pressure. Some variables, such as L, $(P_N)_{\ln}$, and P_i, are expected to have different values varying in every run, while the rest of the variables give constant values in a series of runs carried out with tablets of the same compacting pressure. All the numerical values of $(P_N)_{\ln}$ were, however, found to be almost equal in every run with the tablets of the same

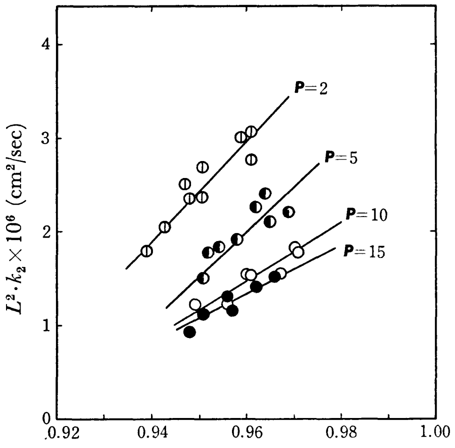

Fig. 7. Correlation between $L^2\cdot k_2$ and $(1-P_i/P_{e2})$ for the second process at 320°C.

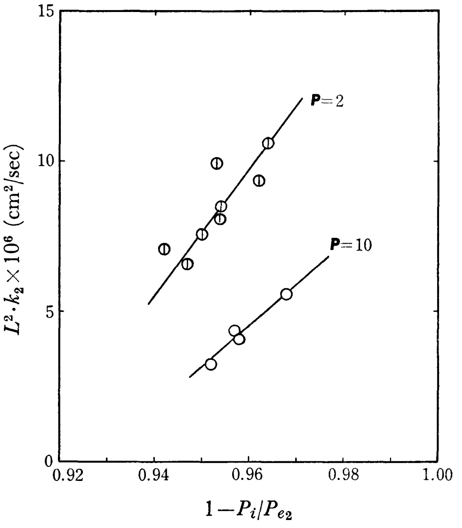

Fig. 8. Correlation between $L^2\cdot k_2$ and $(1-P_i/P_{e2})$ for the second process at 360°C.

compacting pressure (an error to within 0.2%). Consequently, a constant value of $(P_N)_{\text{ln}}$ was used for each series of runs. The plots of $L^2 \cdot k_2$ against $(1-P_i/P_{e2})$ are, then, illustrated in Fig. 7, where each experimental value of P_i was obtained from the calculation of Eq. (10). Figure 8 also shows the experimental correlation between the $L^2 \cdot k_2$ and $(1-P_i/P_{e2})$ values obtained from the other two series of experimental runs done at 360°C. Each value of the slopes in Figs. 7 and 8 was incorporated into Eq. (24); the subsequent substitution of appropriate values in the equation gave the numerical values of the mean effective diffusivity, which were subject to the influence of the compacting pressure used in the preparation of the tablet. These values of $\bar{D}_e$ are plotted against ε_2 in Fig. 9. It is apparent from Fig. 9 that the decrease in ε_2 (attributed to the increase in applied pressure) corresponds to the decrease in $\bar{D}_e$.

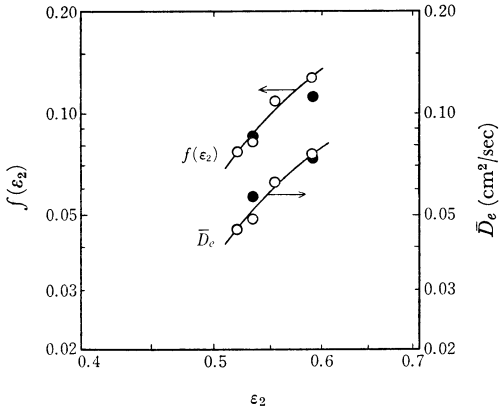

Fig. 9. Effect of Porosity ε_2 on $\bar{D}_e$ and $f(\varepsilon_2)$ at 320°C (○) and 360°C (●).

It can reasonably be concluded, on the basis of the previous considerations, that the effect of the applied pressure on the decomposition rate is reduced to that on the term $\bar{D}_e/\rho_a$ in Eq. (24). The values of $\bar{D}_e/\rho_a$ calculated from the slopes in Figs. 7 and 8 were not identical; this indicates that $\bar{D}_e$ and ρ_a were affected to different degrees by the applied pressure. Many investigations have been made of the correlation between the applied pressure and the bulk density or porosity of the powdered mass compacted. These investigations are summarized comprehensively in several papers.[22,23]

An expression between the applied pressure and the porosity, ε_0, applicable to the present work was as follows:

$$-\frac{d\varepsilon_0}{d\boldsymbol{P}} = C(1-\varepsilon_0)\boldsymbol{P}^{-0.9} \tag{26}$$

This expression is Nutting's Equation as modified by Kawakita and Tsutsumi.[22] The exponent, -0.9, was derived from the text.[24] Equation (26) can be easily integrated, or:

$$\ln(1-\varepsilon_0) = C_1 \cdot \boldsymbol{P}^{0.1} + C_2 \tag{27}$$

The relationship between $\boldsymbol{p}$ and ρ_a can be analogously derived from Eq. (26) by noting that:

$$\varepsilon_0 = 1 - \rho_a/\rho_r \tag{28}$$

thus:

$$\ln \rho_a = C_3 \cdot \boldsymbol{P}^{0.1} + C_4 \tag{29}$$

The good fits of Eqs. (27) and (29) are illustrated in Fig. 10.

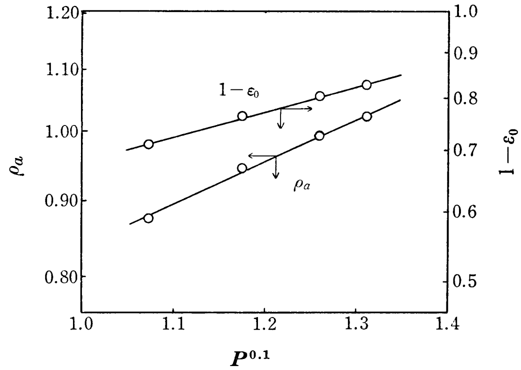

Fig. 10. Plots of log ρ_a and log $(1-\varepsilon_0)$ against $\boldsymbol{P}^{0.1}$.

The mean effective diffusivity, $\bar{D}_e$, on the other hand, is a function of several variables, such as ε_2, the molecular diffusivity, the Knudsen diffusivity, and the surface diffusivity, among which ε_2 is influenced by the applied pressure, as is shown in Fig. 1. A useful study of the surface diffusion in a porous solid was made by Sakashita, Arai, and Kobayashi,[25] who concluded that the amount of carbon dioxide transported by the surface diffusion increases as the pressure of carbon dioxide rises. They also reported that, for the diffusion of carbon dioxide through a sintered mass of glass beads ($\varepsilon = 0.40$), the ratio of the surface diffusivity to the total effective diffusivity could be estimated to be 0.11 for CO_2–H_2 system at 1 atm. It may be analogously considered in the present case that the surface diffusion through a porous layer is almost negligible in comparison with the molecular diffusion because of the very low pressures of carbon dioxide. The empirically-determined value of $\bar{D}_e$ in the present work might include some errors due to some assumptions and errors included in Eqs. (10) or (20). For this reason and because of a lack of information about the Knudsen and surface diffusions, no explicit expression for $\bar{D}_e$ could be proposed. However, the large porosity (ε_2) values of the samples suggest that the diffusion of carbon dioxide through the product layer is predominantly

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22) K. Kawakita and Y. Tsutsumi, This Bulletin, **39**, 1364 (1966).

23) R. W. Heckel, *Trans. AIME Met.*, **221**, 1001 (1961).

24) B. S. Neumann, "Flow Properties of Disperse Systems," North-Holland Publ. Co., Amsterdam (1953), p. 397.

25) K. Sakashita, F. Arai and H. Kobayashi, *Kagaku Kogaku*, **31**, 921 (1967).

influenced by the molecular-diffusional step within a macropore produced after the decomposition reaction. The plots of $f(\varepsilon_2)$ against ε_2 are shown in Fig. 9, where $f(\varepsilon_2)$, a function of ε_2, was determined from the conventional expression for the effective diffusivity, or:

$$\bar{D}_e = f(\varepsilon_2)\cdot D \qquad (30)$$

The numerical values of $f(\varepsilon_2)$ are in good agreement with the data on some other porous materials of the same porosity.25,26)

Further information about $f(\varepsilon_2)$ or $\bar{D}_e$ should be derived from another appropriate experiment for $\bar{D}_e$. However, the approximate value of $\bar{D}_e$, varying with ε_2, was proved in the present work to be useful as a criterion by which the influence of the compacting pressure on the decomposition rate could be investigated.

Conclusions

Experiments on the rate of the thermal decomposition of a lead carbonate tablet have shown that it is possible to make kinetic studies taking into account the partial pressure distribution of carbon dioxide only in the axial direction of the tablet. It has been shown that the rate of the decomposition of the whole tablet for the first process is represented by two approximate equations, (4) and (11), which were derived from the unreacted-core shrinking model applied to the individual particles in a tablet. Consequently, the effect of the applied pressure on the decomposition rate was evaluated from the integral term in Eq. (11). The partial pressure of carbon dioxide at any location within a tablet, but outside the fine particles, was influenced by the pressure used in compressing lead carbonate particles into a tablet.

It has also been shown that the overall rate of the decomposition of the tablet for the second process is controlled by diffusion of carbon dioxide through the product layer. The rate of the decomposition for the second process was, then, expressed by two appropriate equations, (23) and (24), which were developed for the whole tablet without regard to the individual particles. The effective diffusivity and the bulk density of the tablet in Eq. (24) were affected by the applied pressure.

Notation

$a, a_2, a_4, \cdots, a_{2n}, \cdots$=coefficient in Eq. (14), atm

a_m=interfacial surface area per unit mass of the tablet undecomposed, cm^2/g

a_p=exterior surface area of the tablet, cm^2

c=total molar concentration in a gaseuous phase, g-mol/cm^3

C, C_1, C_2, C_3, C_4=constants in Eqs. (26), (27), and (29)

D=binary molecular diffusivity for the system CO_2–N_2, cm^2/sec

$\bar{D}_e$=mean effective binary diffusivity of carbon dioxide averaged throughout the product layer, cm^2/sec

F_1, F_2=fractional decomposition, or conversion, for the first and the second process respectively, dimensionless

G=mass velocity of the bulk flow, g/(cm^2)(sec)

j_d=dimensionless factor of mass transfer, see Eqs. (7) and (8)

k=constant in Eq. (3), min^{-1}

k_1, k_2=constants in Eqs. (4) and (23), min^{-1}

$k_{1,0}$=empirical constant of k_1 at $P_i=0$, min^{-1}

k_1'=proportional constant defined by Eq. (5), min^{-1} atm^{-1}

k_f=gas-film mass transfer coefficient, g-mol/(sec)(cm^2)(atm)

l=axial distance in cylindrical coordinates, cm

L=half of the thickness of a tablet, cm

m=positive integer

M_m=mean molecular weight of the gas stream, g/g-mol

n=positive integer, see Eq. (14)

N=molar flux with respect to a stationary coordinate, g-mol/(cm^2)(sec)

N'=rate of mass transfer in a boundary film, g-mol/(sec)(g)

P=partial pressure of carbon dioxide, atm, see Eq. (5) or (6)

P_e=dissociation pressure of the solid-solid-gas system, atm

P_f=film pressure factor, defined as the logarithmic mean of the partial pressures of the nondiffusing component at the solid-gas interface and in the main stream, atm

P_g, P_i=partial pressures of carbon dioxide in the main stream and at the solid-gas interface, respectively, atm

P_t=total pressure of the system, atm

$(P_N)_{\ln}$=logarithmic mean of the partial pressures, atm, see Eq. (25)

$\boldsymbol{P}$=compacting pressure used in the preparation of a tablet, ton/cm^2

r=radial distance in cylindrical coordinates, cm

r_a=over-all rate of the thermal decomposition per unit mass of the tablet undecomposed, g-mol/(sec)(g)

R=radius of a tablet, cm

$\boldsymbol{R}$=gas law constant, =82.06 (cm^3)(atm)/(g-mol)(°K)

S=macroscopic area of the base of a tablet, cm

t_1, t_2=time required for the decomposition for the first and the second process, respectively, min

T=temperature of the system, °K

W_r, W_p=amount of the reactant present in a tablet and that of the product gas, respectively, g-mol

y_p=mole fraction of carbon dioxide in a gaseous phase, dimensionless

z=dimensionless coordinate, $z=l/L$

ε_0=initial porosity of a tablet, dimensionless

ε_1, ε_2=porosities of the tablet at the completion of the first and the second process, dimensionless

θ=angle in cylindrical coordinates, radians

μ=viscosity of the bulk gas phase, g/(cm)(sec)

ρ_a=molar bulk density of the tablet, g-mol/cm^3

ρ_N=density of the bulk gas phase, g/cm^3

ρ_r=theoretical net density of the reactant, g-mol/cm^3

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26) J. Hoogschagen, *Ind. Eng. Chem.*, **47**, 906 (1955).