or smaller than, ($\epsilon$), the convergence at that point is considered satisfactory.

The data obtained from theoretically known laminar pipe-flow velocity-distribution calculations indicate that for a given grid size the computational accuracy increases with decreasing magnitude of tolerance requirement. As the tolerance becomes equal to, or smaller than, 0.05, the computation predicts the theoretical value approximately within 1%.

For tolerances less than 0.05 the computational accuracy also appears to be less affected by the grid size. In cases relating to extremely small grid sizes (that is, 40 or more increments per major geometric dimension), however, there are not enough data available to permit evaluating the effect of tolerance requirements.

The availability of as many as 1,000 interior and 800 boundary points, the average computational speed and accuracy proved in several case studies, indicate that this method is practical and useful in a large number of one- or two-dimensional steady state problems satisfying general Laplace-type differential equations. In addition, problems satisfying equations of the type of Equation (4) can also be solved by this digital technique.

The apparent rate of convergence is much faster in Laplace's equation than in Poisson's, or Equation (4). This is consistently observed in all calculated cases. Decreasing the tolerance scarcely affects the approximate results of the Laplace equations, but the approximate results of the Poisson-type equations are affected more drastically. Therefore one should be very careful in solving boundary-value problems satisfying Poisson's equation, since the fact that two consecutive iterations at each point differ by a very small quantity ($\epsilon$) does not necessarily mean that the unknown function is as close as ($\epsilon$) to its true value. The proved case studies in pipe-flow calculation however should give a fair indication of the nature of accuracy expected in solving the Poisson type of equation by this routine.

Table 1 summarizes the number of grid points used, tolerance requirements, the number of iterations, and time requirements on several types of problems solved.

## ACKNOWLEDGMENT

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## NOTATION

$a$ = function of $x$ and $y$
$D/D_t$ = substantial time derivative
$F_z$ = extraneous body force per unit mass
$f$ = constant
$g$ = constant
$g(x, y)$ = function of $x$ and $y$ variables
$h$ = increment on a square grid
$i$ = subscript
$j$ = superscript or a subscript
$n$ = interger representing the number of grid points considered
$P$ = pressure, a dependent variable
$r$ = radius, a polar coordinate
$T$ = temperature, a dependent variable
$u$ = dependent variable, function of $x$ and $y$
$w$ = velocity function in pipe flow
$x$ = independent space variable
$y$ = independent space variable
$z$ = independent space variable
$\partial/\partial x$ = partial differentiation
$\nabla^2$ = Laplacian in Cartesian coordinates $\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2$ $\partial^2/\partial z^2$
$\Delta$ = finite difference, or increment
$\rho$ = mass density
$\mu$ = viscosity
$\sum$ = summation
$\theta$ = divergence of the velocity vector
$\epsilon$ = tolerance requirement on dependent variable

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# Kinetics of the Thermal Decomposition of Calcium Carbonate

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There is considerable indication that the decomposition of calcium carbonate in the shape of, say, a sphere takes place essentially in the following manner. The reaction starts at the outside surface and proceeds towards the center in a relatively thin spherical reaction zone (Figure 1). At a given instant the center core is undecomposed calcium carbonate and the outer shell calcium oxide. The observed reaction rate is presumably determined by the interrelationships between three major rate processes:

1. *Heat Transfer.* Heat must first be transferred to the surface of the mass and then through the outer layer of calcium oxide to the reaction zone.

2. *Mass Transfer.* The carbon dioxide released at the reaction zone must escape through the outer shell of calcium oxide. Consequently, at finite rates of decomposition the pressure at the reaction zone must be greater than that at the surface of the sphere. The increase in pressure requires an increase in the temperature of the reaction zone to maintain decomposition. This in turn decreases the temperature difference causing heat transfer and consequently decreases the rate of reaction.

3. *Chemical Reaction.* The question here is whether any process associated with the decomposition reaction itself can be an over-all rate-limiting factor, for example whether the rate of nucleation or the nature of the interfacial surface at the reaction zone can affect the over-all rate of decomposition.

A considerable number of studies of calcination of calcium carbonate have been reported (*3, 5, 21, 22*), but the experimental results have usually been treated as though chemical kinetics were the only rate-limiting step. Conversely, in one case the decomposition has been treated as a problem of heat transfer alone with mass transfer and chemical kinetics neglected (*8*).

The purpose of the present study was to elucidate the nature of the calcination process with careful consideration of the various possible rate-limiting factors and their interrelationships. Gas-solid reactions in general characteristically involve these three possible rate-limiting steps. Therefore the method of analysis and kind of results obtained may be of interest as typical of this class of chemical reaction. Rate measurements were made on cylinders and spheres formed by agglomeration of powdered calcium carbonate under high pressure. Use of such agglomerates made it possible to employ high-purity material, to form suitable shapes and sizes that would permit heat and mass transfer characteristics to be calculated, and to measure internal temperatures by compressing the powder around a thermocouple.

## SAMPLE PREPARATION

Unless otherwise specified Mallinckrodt reagent grade calcium carbonate was used in all studies. A microscopic examination indicated that the crystal type was calcite, and the average particle diameter was 10 to 15 $\mu$. The B.E.T. (Brunauer, Emmett, Teller) nitrogen surface area was found to be 0.7 sq. meter/g. In several runs calcium carbonate with an average particle diameter of 0.2 $\mu$ was used. This was prepared by the rapid mixing of equimolar quantities of calcium chloride (as a solution containing 55.5 g. calcium chloride/100 g. water) and sodium carbonate (as a solution containing 18 g. sodium carbonate/100 g. water) at temperatures below 30°C. The crystals were washed with water before drying and had a sodium chloride content of 0.25% by weight.

The dry calcium carbonate was compressed around a platinum–10%-rhodium-in-platinum thermocouple in the axial position. The technique involved packing the calcium carbonate into a metal cylinder pierced with 1/16-in. holes, lined with Gooch rubber tubing, and fitted at one end with a sintered glass filter stick through which air was removed by vacuum during the packing operation. Final degassing was achieved through a hypodermic needle inserted into the mass, and the assembly was then sealed and subjected to 27,000 lb./sq. in. in a press containing glycerine. This method provided dense and reproducible packing and masses that were hard and mechanically strong. Light turning was sufficient to produce a cylinder with diameter variations of less than 0.002 in. If required, spheres could be shaped from the cylinder obtained.

## CALCINATION APPARATUS

Figure 2 shows a schematic representation of the calcination apparatus. In its final form the furnace was of double porcelain tube construction, the inner tube being 36 in. long, 2 in. I.D., and 2-¼ in. O.D. The outer tube was 2-½ in. I.D., 2-¾ O.D., and 33 in. long. This double-tube arrangement reduced diffusion of gas through the porcelain to a negligible figure. Both porcelain tubes were wound for 30 in. of their center lengths with 3/32- by 1/32-in. Kanthal A ribbon set in alundum cement. The outer winding was used as a constant heater to supply the major fraction of the heat requirements of the furnace. The inner winding was used as an on-off control heater and was controlled by the potential from a platinum-10%-rhodium thermocouple placed near the center of the winding of the inner heater. Heating was by direct instead of alternating current to avoid induced currents from being picked up by the control thermocouple. The outer porcelain tube was sealed against the inner tube with neoprene O rings. The outer section of the furnace was insulated for a length of 30 in. with a 6-in. thickness of insulating brick. Two insulating plugs 12 in. long and 1-15/16 in. in diameter were used to insulate the inner section of the center tube. The plugs also served to reduce the gas volume of the furnace. The exit plug, on the left hand side in Figure 2, was an alundum-clay mixture baked at a high temperature. It had a ⅜-in.–diameter hole down the center axis to carry a thermocouple to the main furnace zone. The entrance plug, on the right hand side of Figure 2, was firebrick 12 in. long and 1-⅞ in. in diameter. It was grooved along the upper edge to allow space for an alundum rod used to support the calcium carbonate sample and to carry the sample thermocouple leads out of the furnace. Both ends of the furnace were sealed with rubber stoppers kept cool by water coils on the adjacent area of the porcelain tube.

Carbon dioxide generated during the reaction passed out of the furnace, through a water-cooled condenser, through a capillary flow meter, and into a flexible rubber balloon immersed in water saturated with carbon dioxide. The flow of water from the sealed jar which contained the balloon was regulated to maintain constant pressure in the system, as indicated by the manometer. By measuring the weight of water removed with time, one could accurately determine the amount and rate of carbon dioxide evolution. Instantaneous gas-flow rates were also available from the capillary flowmeter, and the total gas evolved could be checked against the total loss in weight of the calcium carbonate sample. Gas-volume measurements were accurate to ±1 cc., and temperatures measured were reproducible and considered accurate to ±2°F.

For each run the furnace was maintained at the desired temperature for about 1 hr. to achieve normal temperature distribution throughout the apparatus. The system was then purged with a stream of dry carbon dioxide added in such a manner that, after the carbon dioxide volume-measuring equipment had been purged, carbon dioxide could be blown through the furnace during the sample-loading operation. After thorough purging, the insulating plug at the entrance end of the furnace was rapidly pulled out of the furnace onto an external support. The calcium carbonate sample, which had previously been weighed, measured, and loaded onto the thermocouple insulating rod, was quickly placed in the insulating-plug groove and the assembly returned to the furnace. The flow of carbon dioxide was then stopped and the rubber stopper at the entrance pushed into the porcelain tube to seal the furnace. The loading operation required less than ½ min. Some slight cooling of the furnace necessarily took place during this time, but it was not sufficient to affect the results.

After reaction was complete and generation of carbon dioxide had ceased, the seal on the furnace was broken and the carbon dioxide removed with a helium purge. This prevented readsorption of carbon dioxide during removal of the calcined product. On some occasions the sample was allowed to cool in the helium atmosphere overnight before removal. Otherwise it was removed at the completion of gas generation while still at furnace temperature. When this latter procedure was used, the sample was allowed to cool in a desiccator before it was weighed and the length and diameter were measured.

## RESULTS

### Nature of the Reaction Pattern

Furnas (*5*) and others have suggested the *shell* model (Figure 1) for the decomposition of calcium carbonate. In the decomposition of crystals of calcite this model is certainly applicable. Visual observation of a section through a partially decomposed crystal shows the outer edges of the crystal to be white, amorphous, and opaque; the inner section remains crystalline, transparent, and completely undecomposed. The interface between the oxide layer and undecomposed calcite is sharply defined.

However with the more porous agglomerates the decomposition should tend to be shell-like and more uniform in nature. It seems reasonable to assume that completely uniform decomposition rates would be obtained throughout a highly porous powder of calcium carbonate heated slowly to a temperature just above the decomposition temperature. Under these conditions temperature and carbon dioxide pressure gradients would be negligible, and decomposition should proceed at substantially equal rates in all sections of the mass. On the basis of this reasoning the conditions which favor *shell-like* decomposition should be (1) a high ratio of carbon dioxide permeability in the calcium oxide to that in the undecomposed carbonate and (2) a rapid increase in the rate of decomposition with temperature. Since heat must be transferred to the carbonate for decomposition, higher temperatures in general exist in the outer sections of a sample than in the inner sections. The greater the temperature coefficient of the reaction, the more the decomposition pattern would become shell-like.

As a test of the foregoing reasoning, masses of calcium carbonate of different porosities were partially calcined, and samples taken at various radial distances from the center were ana-

TABLE 1. COMPOSITION OF PARTIALLY CALCINED MASSES OF CALCIUM CARBONATE

| Distance of sample from center, cm. | Calcination, % Theoretically expected for shell-like reaction | Calcination, % By analysis |
|---|---|---|
| Run 13: sphere; minus 200 mesh Iceland spar, unpressed; furnace temperature 1,748°F.; 79.5% over-all conversion | | |
| 0.00 to 0.40 | 0.0 | 16.8 |
| 0.40 to 0.60 | 0.0 | 18.7 |
| 0.60 to 0.75 | 100.0 | 40.3 |
| 0.75 to 1.05 | 100.0 | 89.4 |
| 1.05 to 1.25 | 100.0 | 92.8 |
| Run 40: Cylinder; 10-$\mu$ Mallinckrodt calcium carbonate: pressed at 27,000 lb./sq. in.; furnace temperature 1,901°F.; 50.1% over-all conversion. | | |
| 0.00 to 0.30 | 0.0 | 3.9 |
| 0.30 to 0.50 | 0.0 | 2.1 |
| 0.90 to 1.00 | 100.0 | 77.8 |

lyzed to determine the oxide-carbonate ratio.

Table 1 summarizes the results obtained with two typical masses. In agreement with the preceding discussion, the more tightly packed calcium carbonate mass (run 40) shows a much closer approach to the shell-type model. Indeed, it is very likely that the actual decomposition in both cases was closer to the shell-like model than shown by the analyses because, although the mass was withdrawn from the furnace rapidly and cooled in air, it is possible that some carbon dioxide could have transferred from the hotter inner core to the cooler outer shell during the cooling.

Attempts were also made to test this reaction model by sealing a small cylinder of radioactive $CaC^{14}O_3$ concentrically inside a larger cylinder of calcium carbonate and measuring the radioactivity of the gas evolved as reaction proceeded. However the results are inconclusive since considerable exchange of radioactive carbon dioxide was found to take place at temperatures slightly below the decomposition temperature. Haul (*9*) and coworkers have also observed considerable interchange between radioactive $C^{13}O_2$ and solid calcium carbonate at temperatures below the decomposition temperature.

The agglomerates used in this study were pressed under conditions similar to run 40 of Table 1, and it is probable that decomposition followed the shell-like model quite closely. For calcite crystals and dense limestones it is probably a good engineering assumption to consider the decomposition shell-like.

When a cylinder or sphere of calcium carbonate was calcined, considerable shrinkage took place, the amount of which increased with higher decomposition temperatures. For example, a series of nine runs was made with calcium carbonate with a particle size of about 10 $\mu$, pressed to 27,000 lb./sq. in., shaped into spheres of 0.5- to 1.4-in. diameter, and completely calcined at atmospheric pressure. The calcium carbonate densities varied from 1.90 to 1.95 g./cc. The final oxide densities increased almost linearly with furnace temperature, from about 1.26 for a furnace temperature of 1,673°F. to about 1.47 at 1,897°F.

In view of the shell-like decomposition pattern the shrinkage which occurs on decomposition must set up strains within the sample. Consider, for example, the decomposition of a sphere of calcium carbonate. Initially the reaction is most rapid at the outer surface of the sphere. But the calcium oxide which is formed contracts, and cracks form in the outer layer. Fresh carbonate is then exposed, and the decomposition is facilitated. However the oxide layer, once formed, has radial dimensions determined by the radius of the underlying calcium carbonate. Consequently as the reaction proceeds and shrinkage continues to take place at the reaction zone, the cracks in the outer layer will close. The completely reacted sphere will then have a smaller radius than the original carbonate sphere, and the outer surface will appear smooth and uncracked. But if the shrinkage has been considerable, as occurs at high temperatures, the inside of the sphere will be partially hollowed out and irregularly cracked. This characteristic has also been noticed in the decomposition of crystals of calcite. The oxide tends to retain the hexagonal form of the original crystal, but the center of the oxide mass is often hollow and extensively cracked.

### **Effect of Mass Transfer on the Rate of Reaction**

The aim of this part of the investigation was to determine the extent to which the outer layer of calcium oxide hinders the escape of carbon dioxide from the reaction zone, thereby increasing the gas pressure and consequently decreasing the rate of decomposition. Direct measurements were made of the permeability of calcium oxide prepared under conditions identical with those used for the over-all rate determinations. These measurements permitted an estimation to be made of the increase in pressure at the reaction zone for each measured rate of carbon dioxide evolution. By assuming that the decomposition followed the shell model and that the effect of pressure on the decomposition temperature followed that at equilibrium conditions (*11*), one could estimate the increase in temperature at the reaction zone for various rates and degrees of decomposition.

Permeability measurements of the calcium oxide were made in three different ways:

1. The pressure-drop–flow-rate relationship was determined for the flow of carbon dioxide through a plug of calcium oxide held at the furnace temperature used for the preparation of the oxide sample. Attempts were made to use gold and silver foil to seal the plug in the pressure-drop apparatus, but deformation of the oxide occured at the high temperatures. The permeability values obtained by this method were so high that presumably leakage around the seals occurred.
2. The pressure-drop–flow-rate relationships for carbon dioxide at the reaction temperatures were calculated from pressure-drop–flow-rate measurements made with argon, helium, and hydrogen at room temperatures. An apparatus similar to that used by Russell (*19*) was used in these tests. With these three gases it was possible to calculate both the Poiseuille and Knudsen contributions to flow and hence the effect of temperature, viscosity, and molecular weight.
3. The procedure outlined by Kraus, Ross, and Girifalco (*14*) was used to calculate the permeability from measured values of the surface area of the calcium oxide (B. E. T. krypton adsorption).

Method 2 gave values for the permeability to carbon dioxide at 1,800°F. of 0.0076 to 0.0096 moles/(hr.)(ft.)(mm. Hg); two measurements by method 3 gave values of 0.0023 and 0.00066. These results indicate that the value of the permeability of the calcium oxide is probably of the order of 0.01 mole/(hr.)(ft.)(mm. Hg) and almost certainly not less than 0.001 mole/(hr.)(ft.)(mm. Hg). However, even for the latter value, the average reaction temperature was calculated to increase by only 0.4°F. for decomposition at a furnace temperature of 1,782°F. and an equilibrium decomposition temperature of 1,652°F. Under these circumstances the resistance offered by the calcium oxide layer has a negligible effect on the reaction rate.

With the use of the B. E. T. surface-area measurements of Murray, Fischer, and Sabean (*17*), the pressure drop effect was also calculated for the decomposition of a single crystal of pure calcite, which represents the form of calcium carbonate for which a mass transfer effect would presumably be of greatest importance. When one takes representative values such as

| | |
|---|---|
| Surface area | 16 sq. meters/g. |
| Specific gravity, CaO | 1.74 |
| Specific gravity, $CaCO_3$ | 2.73 |
| Porosity, CaO | 48% |

the permeability is calculated to be 0.00008 mole/(hr.)(ft.)(mm. Hg). The resulting effect on the reaction temperature is such that the average difference between the furnace and reaction temperatures throughout decomposition would have been decreased by about 3.4% from that expected for complete decomposition at the equilibrium pressure. Consequently the resistance offered to the passage of carbon dioxide through

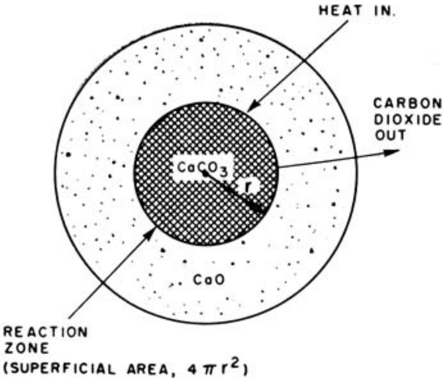

Fig. 1. Decomposition of a sphere of calcium carbonate (shell or layer model).

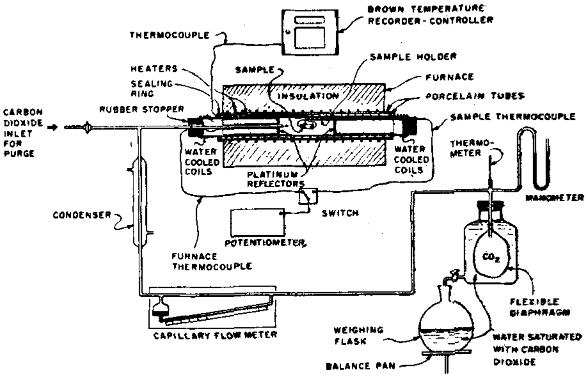

Fig. 2. Schematic arrangement of furnace and ancillary equipment.

the calcium oxide has only a minor effect on the over-all rate of decomposition of any form of calcium carbonate.

#### Effect of Heat Transfer and Chemical Kinetics

To make a quantitative analysis of these rate-determining factors, a group of tests, summarized in Table 2, was made in which the temperature at the center of the sample (mostly cylinders) was measured. Usually bare platinum–platinum-10%-rhodium thermocouples with a diameter of 0.010 in. were used. However identical results were obtained with thermocouples of a diameter of only 0.001 in., an indication that heat conduction along the thermocouples did not affect the measured temperatures.

Figure 3 illustrates a typical time-center temperature history for the studies made with agglomerates formed from 10 to 15-μ calcium carbonate. There are two striking observations which were common to this entire series of runs. (1) After the sample had been placed in the furnace, the temperature at the center of the sample rose rapidly, passed through a sharp maximum, and then, after a small temperature drop, through a minimum. The temperature then remained practically constant for the major part of the reaction time. (2) This center temperature remained substantially in excess of the equilibrium decomposition temperature throughout the run.

The plot indicates that the time required to heat the calcium carbonate from room temperature to the equilibrium decomposition temperature (1,652°F. at 769 mm. Hg pressure carbon dioxide) was about 11 min., or less than 10% of that required for complete decomposition. The major fraction of the reaction occurred during the time interval between the initial maximum in the center temperature and the final rise to the furnace temperature.

Also included in Figure 3 are two plots of the calculated value of the reaction temperature that would be predicted during shell-like decomposition, for a permeability of the calcium oxide outer layer to carbon dioxide of 0.001 or 0.0001 mole/(hr.)(ft.)(mm. Hg), respectively. The plots show that even for a permeability as low as 0.0001 mole/(hr.)(ft.)(mm. Hg) the theoretical reaction temperature is only slightly above the equilibrium decomposition temperature of 1,652°F. for the ambient pressure of 769 mm. Hg of carbon dioxide. Since the calcium oxide formed in these studies had a permeability not less than 0.001 mole/(hr.)(ft.)(mm. Hg), the resistance offered by the calcium oxide to the escape of carbon dioxide is clearly *not* the cause of the increase of the center temperature above that of equilibrium (1,652°F.).

The reaction temperature is determined by a balance between two rate processes, the rate of heat transfer to the reaction zone and the rate of heat consumption by the endothermic reaction. The existence of a *maximum* in the center temperature at an early stage of the decomposition reflects the effect of one or both of the following factors:

1. The rate of heat transfer to the reaction zone is highest at the beginning of a run. Thereafter the rate of heat transfer is reduced by the development of a layer of calcium oxide through which heat must be transferred by conduction.
2. The rate of reaction increases with an increase in temperature and possibly also with the extent to which the reaction zone has penetrated into the mass (because of an increase in available reaction area, to be discussed later).

For all the 10 to 15-μ agglomerates studied (runs 39 to 45) the temperature at the center of the mass was consistently

Table 2. Calcium Carbonate Decomposition Studies, Summarized Data

| Run | Shape | Radius, cm. | Length, cm. | Thermo-couple diam., in. | Density $CaCO_3$ g./cc. | Density CaO, g./cc. | Furnace temp., °F. | $CO_2$ Pressure mm. Hg. | % reacted | Reaction[1] time, hr. | Temperatures inside reaction mass, °F. Max. | Min. | Equil. temp. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Series A (agglomerates of 10- to 15-μ diameter) | | | | | | | | | | | | | |
| 39 | Cylinder | 1.06 | 6.79 | 0.010 | 1.86 | 1.31 | 1,782 ± 2 | 769 | 100 | 1.84 | 1,683 | 1,672 | 1,652 |
| 40 | Cylinder | 1.04 | 6.14 | 0.010 | 1.90 | —[5] | 1,901 ± 2 | 765 | 50.1 | 0.28 | 1,690 | 1,677[6] | 1,651 |
| 41 | Cylinder | 1.07 | 6.69 | 0.010 | 1.85 | 1.28 | 1,705 ± 4 | 762 | 100 | 4.34 | 1,673 | 1,657 | 1,650 |
| 42 | Sphere | 1.08 | — | 0.010[2] | 1.84 | 1.34 | 1,835 ± 5 | 770 | 100 | 0.75 | 1,688 | 1,674 | 1,652 |
| 43 | Cylinder | 1.09 | 6.62 | —[3] | 1.87 | —[5] | 1,751 ± 3 | 765 | 100 | 2.02 | 1,679 | 1,660[7] | 1,651 |
| 45 | Cylinder | 1.04 | 6.84 | 0.001[4] | 1.80 | 1.43 | 1,814 ± 3 | 772 | 100 | 1.36 | 1,685 | 1,673 | 1,652 |
| Series B (agglomerates of approx. 0.2-μ diameter) | | | | | | | | | | | | | |
| 48 | Cylinder | 1.09 | 6.52 | 0.010 | 1.64 | —[5] | 1,844 ± 4 | 760 | 100 | 0.70 | | | |
| 49 | Cylinder | 1.105 | 7.59 | 0.010 | 1.68 | —[5] | 1,905 ± 5 | 774 | 100 | 0.63 | | | |

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[1] Reaction time, the time during which gas evolution occurred.
[2] In run 42 the sphere was made by turning down a cylinder, and it was later found that the thermocouple junction was at 0.37 of the diameter instead of 0.50.
[3] In run 43 0.010-in.–diameter wire was used, but two 1-in. sections on each side of the junction were flattened to a cross section of 0.003 in. × 0.026 in.
[4] In run 45 four strands of 0.001-in.–diam. wire were used for mechanical strength.
[5] In runs 40, 43, 48, and 49 the calcium oxide was so extensively cracked that density figures were not determined. The cracking in runs 39 and 45 was negligible.
[6] Reaction carried only to 50% completion mark, and minimum center temperature was not reached. Minimum was estimated at 1,677°F.
[7] Later in this run a second minimum of 1,655°F. was obtained. The results of this run were probably affected by extensive cracking.

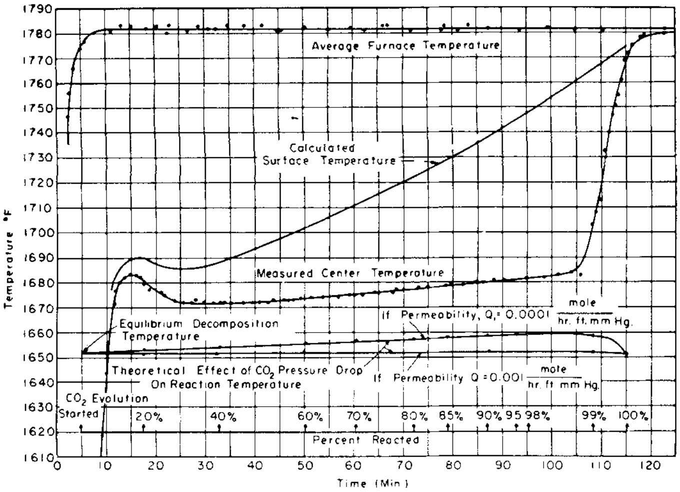

Fig. 3. Time-temperature variations in decomposition of cylinder of agglomerated 10- to 15-$\mu$ calcium carbonate; run 39.

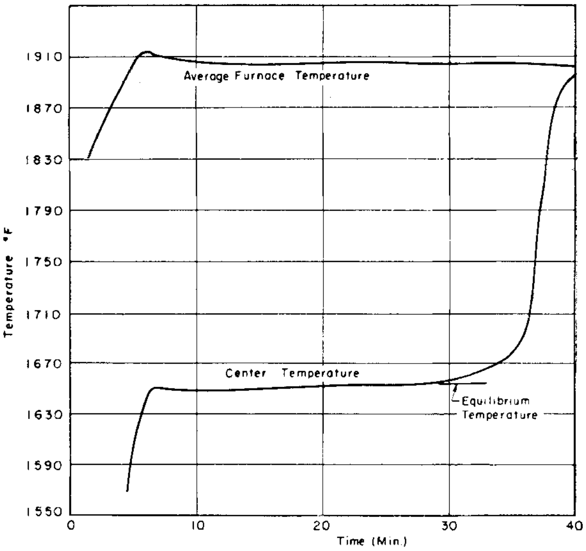

Fig. 4. Time-temperature variation in decomposition of cylinder of agglomerated 0.2-$\mu$ calcium carbonate; run 49.

greater than the equilibrium decomposition temperature throughout the reaction. This excess in temperature over the equilibrium value increased with higher furnace temperatures. On the other hand when agglomerated calcium carbonate of a smaller particle size (approximately 0.2 $\mu$) was studied, the center temperature-time curve was considerably different (Figure 4) from that for the coarser material. The temperature maximum in the early part of the run is almost nonexistent, and in addition the center temperature remained practically constant for the major part of the reaction time at a temperature substantially equal to that of the equilibrium decomposition temperature. This occurred even when the furnace temperature was as high as 1,905°F. It therefore appears that the size of the crystal present in the agglomerate has a pronounced effect on the temperature at the center of the reaction mass. For the major part of the decomposition time the sensible heat requirements of the undecomposed carbonate are negligible. Consequently it is evident that the decomposition is dependent upon the size of the crystals in the agglomerate. Calcium carbonate with a small particle size (0.2 $\mu$) decomposes, even at the high rates, at reaction temperatures and carbon dioxide pressures approximating those of equilibrium. Consequently this is a case in which reaction rate is determined by the rate of heat transfer alone.

However calcium carbonate agglomerates of 10 to 15-$\mu$ particles require temperatures considerably in excess of equilibrium. It is apparent that here some nucleation or chemical activation process plays a part in the over-all rate of the reaction. One method of obtaining a measure of the relative importance of heat transfer and the chemical activation effect on the over-all rate of reaction is to compare the temperature drop actually available for heat transfer with that which would have resulted if there had been no chemical resistance, that is, if the reaction had proceeded at the equilibrium temperature. Several such comparisons are summarized in Table 3.

These results indicate that the increase in the temperature at the reaction zone decreased the over-all temperature difference theoretically available for heat transfer ($T_F - T_E$) by about 10 to 20%. Hence although heat transfer still remains the major rate-controlling factor, a chemical reaction effect does become important for larger crystal sizes of calcium carbonate; this is discussed in more detail later.

It has been assumed here that the temperature measured at the center of the sample equals the reaction temperature. This seems reasonable considering that for the major fraction of the decomposition time the center temperature changed relatively slowly. Moreover the thermal diffusivity of the calcium carbonate is relatively high, and so the center temperature does not greatly lag behind even during the transient heating periods at the beginning and end of the run. For instance, if the surface temperature of a 1-in.-diameter calcium carbonate sphere were instantaneously raised 5°F., thermal diffusivity calculations indicate that the center temperature would be raised 4°F. within 0.8 min.

### Thermal Properties of the Solid Phases

When one assumes shell-like decomposition, it is possible to calculate both the thermal absorptivity of the surface of the sample and the thermal conductivity of the outer layer of calcium oxide. From the rate of evolution of carbon dioxide the rate of heat intake by the sample can be calculated. A value is assumed for the thermal conductivity of the calcium oxide, and from the temperature at the reaction zone (equal to the center temperature) and the heat flux it is possible to calculate the surface temperature. Consequently, with a knowledge of the surface area and the furnace temperature it is then possible to calculate the thermal absorptivity of the surface. These calculations are made for conditions at some instant during the early part of the run. At this time the outer layer of calcium oxide is thin, the temperature drop through it is small, and the value obtained for the thermal absorptivity is insensitive to the value assumed for the thermal conductivity of the calcium oxide. In practice it was possible to extend this type of calculation (1) to estimate the change in thermal absorptivity of the surface with time and (2) to check the assumed value of the thermal conductivity of the calcium oxide by reversing the calculational procedure for a time late in the decomposition run, when the surface temperature is less sensitive to the thermal absorptivity value and more strongly dependent on the conductivity value. In the latter case a value could be assumed for the absorptivity, and the thermal conductivity could be calculated. This trial-and-error procedure was repeated until consistent values were obtained for the thermal absorptivity of the surface and the thermal conductivity of the calcium oxide layer.

The variation of calculated absorptivity of the surface with the extent of reaction is shown in Figure 5. Variations with time and temperature in the extent of sintering of the oxide surface and of surface cracking will affect the absorptivity. However it seems reasonable to assume that the decrease shown in Figure 5 was caused primarily by a change in the thermal absorptivity as the surface changed from calcium carbonate to calcium oxide. The only reliable value for the emissivity of calcium carbonate appears to be the value of 0.93 quoted by McAdams (*16*)

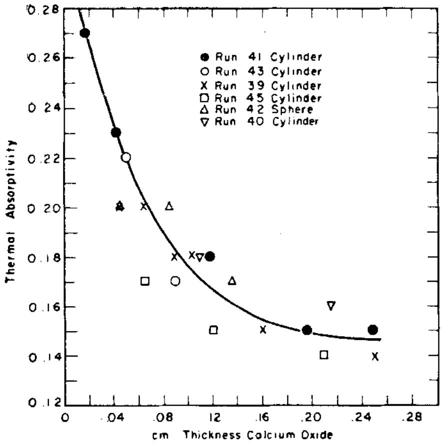

**Fig. 5. Variation of thermal absorptivity with thickness of calcium oxide layer.**

for marble at 72°F. The absorptivity of the calcium carbonate used in this investigation is probably not too different from that of marble. According to the literature few determinations of the absorptivity of calcium oxide have been made in the past. The most reliable is probably that of Hild (*10*), who found the emissivity of a calcium oxide powder with a particle size of 3 to 5 $\mu$ to be 0.27 in the range of 900° to 1300°C. In any case the absorptivity of the surface is low enough to require a very substantial temperature difference between the furnace wall and the oxide surface at the rates of heat transfer called for by the reaction rates observed here. The calculated variation in oxide surface temperature with time, for a typical run, is shown on Figure 3.

The values calculated for the thermal conductivity of the outer layer of calcium oxide were within the range 0.36 ± 0.06 B.t.u./(hr.)(ft./°F.) for calcium oxide with a bulk density of 1.30 g./cc. The shrinkage which occurred during calcination very probably caused fine cracks to form in this calcium oxide, which would lower the thermal conductivity below that expected for a homogeneous mass.

To test this hypothesis, a sample of calcium carbonate was calcined at 1,417°F. at a total pressure of 60 mm. Hg pressure of carbon dioxide. The resulting oxide had a density of 1.14 g./cc. and had undergone less than 8% shrinkage during calcination. A sample of this oxide was found to have a thermal conductivity of 0.46 B.t.u./(hr.)(ft./°F.) at 690°C. when compared to a zirconia standard in an apparatus similar to that described by Francl and Kingery (*4*).

These values generally agree with the value of 0.4 B.t.u./(hr.)(ft./°F.) quoted by Tadokaro (*23*) for lime.

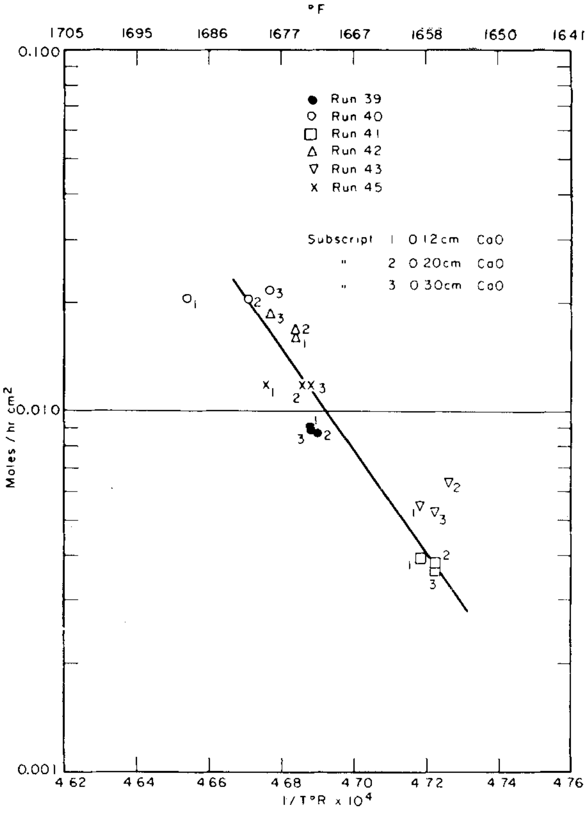

**Fig. 6. Variation of rate of decomposition of agglomerated 10- to 15-$\mu$ calcium carbonate with reaction temperature.**

#### Chemical Kinetics

It has been shown that with the calcium carbonate of small particle size (0.2 $\mu$) the chemical reaction rate (or nucleation rate) was sufficiently high to offer no resistance to the over-all rate of decomposition. Under these conditions the reaction rate was completely heat transfer controlled. However for the calcium carbonate with a larger size (10 to 15 $\mu$) the average temperature difference available for heat transfer was decreased some 10 to 20% by a rise in the reaction temperature over the equilibrium temperature of decomposition corresponding to the pressure of carbon dioxide present at the reaction zone.

Table 4. Variation of Reaction Rate During Decomposition

| Run 39 |  | Run 45 |  |
|---|---|---|---|
| CaO thickness, cm. | $M$ moles (hr.)(sq. cm.) | CaO thickness, cm. | $M$ moles (hr.)(sq. cm.) |
| 0.047 | 0.00996 | 0.064 | 0.0126 |
| 0.052 | 0.00975 | 0.119 | 0.0118 |
| 0.074 | 0.00938 | 0.209 | 0.0124 |
| 0.082 | 0.00933 | 0.298 | 0.0121 |
| 0.130 | 0.00883 | 0.454 | 0.0136 |
| 0.208 | 0.00997 |  |  |
| 0.372 | 0.00970 |  |  |
| 0.534 | 0.01080 |  |  |

Table 3. Relative Effect of Heat Transfer and Chemical Reaction on Over-all Reaction Rate

Agglomerated Calcium Carbonate, Particle Size of 10 to 15 $\mu$

| Run | Furnace temperature* $T_F$, °F. | Reaction temperature* $T_R$, °F. | Equilibrium decomposition temperature $T_E$, °F. | Ratio $\frac{T_F - T_R}{T_F - T_E}$ |
|---|---|---|---|---|
| 39 | 1,782 | 1,677 | 1,652 | 0.81 |
| 41 | 1,705 | 1,658 | 1,650 | 0.80 |
| 42 | 1,835 | 1,679 | 1,652 | 0.85 |
| 43 | 1,751 | 1,661 | 1,651 | 0.90 |
| 45 | 1,814 | 1,682 | 1,652 | 0.82 |

*The furnace and reaction temperatures quoted are time-average values for the period 10 to 98% of total decomposition. These limits were taken to exclude transient temperature effects.

A considerable number of previous workers have used an equation developed by Polanyi and Wigner (*18*) to correlate the rate of decomposition of carbonates. For the purposes of this discussion the equation may be simplified to

$$M = ke^{(-E/RT)}$$

where

$M$ = reaction rate, expressed as mole/(hr.)(sq. cm.) of reaction area

$k$ = reaction rate constant
$E$ = activation energy, cal./g.-mole
$R$ = gas constant
$T$ = absolute temperature, °K.

To test the applicability of an equation of this type, values were calculated for the reaction rate $M$ (expressed as moles of carbon dioxide evolved per hour per square centimeter of superficial reaction area $4\pi r^2$ as indicated for the sphere in Figure 1) at three different thicknesses of penetration of the reaction zone for each of the runs. The depths taken for the calculation of $M$ were 0.12, 0.20, and 0.30 cm., respectively. The values thus calculated are plotted in Figure 6 against the reciprocal of the respective absolute temperature (°R) existing at the center of the sample. In general for any one run the variation of $M$ with the degree of penetration of the reaction zone was small, as shown by the data in Table 4 for two typical runs. This supports the Polanyi-Wigner analysis. However the rate of change of the reaction rate $M$ with temperature was large. The "activation energy" corresponding to the straight line drawn in Figure 6 is 360 kcal./g.-mole. (Rather lower weight was given to the results of run 43, because it is possible that here surface cracking increased the value of $M$.) Such an activation energy is exceedingly high, and being an order of magnitude greater than the enthalpy change for the reaction, 39.4 kcal./g.-mole, it is rather unbelievable. On the other hand the determinations of the activation energy by several previous workers have approximated the enthalpy change for the reaction. A summary of their results follows:

| Ref. | Activation energy reported kcal./g.-mole |
|---|---|
| *3* | 35.5 to 41.6 |
| *21* | 40.8 to 44.3 |
| *13* | 48.7 to 50.1 |
| *22* | 37.0 |

However these workers assumed that the reaction temperature equaled the furnace temperature and indeed, if this assumption is used with the results of the present investigation, an activation energy of 48.2 kcal./g.-mole is obtained. But it has been conclusively shown in this work that the reaction temperature is not equal to the furnace temperature. It appears merely fortuitous that the activation energies reported by previous workers on the basis of furnace temperatures should approximate the enthalpy change.

On the other hand the abnormally high activation energy obtained here, when one uses a reaction area equal to the superficial area (or a constant ratio of the actual reaction area to the superficial area), does not seem at all reasonable. Rather the value of 360 kcal./g.-mole is a reflection of the inadequacy of the simplified model, which assumes that all the reaction occurs on a spherical surface of vanishingly small thickness. Consider, for instance, a small part of the decomposition zone of a calcite crystal. After partial decomposition the model assumed in the analysis up to this point has been that depicted in Figure 7*a*; that is, the reaction has been pictured as proceeding at an interface which gradually penetrates into the calcite. However microscopic examination of the decomposition of crystals of calcite has indicated that the decomposition region is, in fact, a complex zone. Cracks very frequently are formed in the calcite (Figure 7*b*), and the reaction then proceeds also at the new surface formed (Figure 7*c*). In many cases it appears that whole blocks of calcite are broken out of the parent crystal. As a result the total area on which the reaction is proceeding at any given instant is strongly dependent on the degree to which cracking and block formation is occurring.

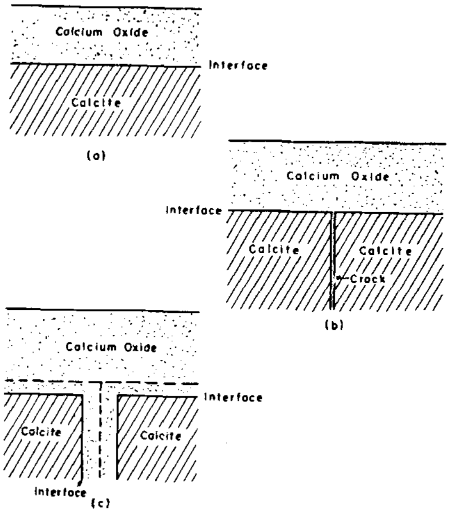

Fig. 7. Mechanism of increase in reaction area by formation of cracks.

Within any one run at a constant furnace temperature (and substantially constant reaction temperature) the calculated value of the reaction rate $M$ remained practically constant (Figure 6 and Table 4). This indicates that the ratio of the true reaction area (along all the surfaces of cracks and blocks) to the superficial area of the model remained virtually constant within a run. However the tremendous increase in the value of $M$ with the reaction temperature suggests that the increase largely results from an increase in the degree of cracking and block formation rather than from an increase in the rate of penetration of an interface into the parent crystal. This in turn suggests that the rate of new surface generation by cracking, etc., is strongly dependent on temperature.

The splitting-out mechanism for the progress of the reaction zone in a decomposing solid was predicted by Garner and Hailes (*6*) in 1933, and its importance has been emphasized recently in the theoretical work of Schultz and Dekker (*20*). Bowden and Singh (*2*) have recently published data on the decomposition of lead azide, for which they obtained electron micrographs indicating that the crystal breaks up into small blocks, about $10^{-5}$ cm. across, at the decomposition interface. Decomposition appeared to take place at the surface of these blocks. Without some knowledge of the degree to which surface development takes place, experimental verification of theoretical rate equations is impossible.

In conjunction with the present investigation Jones (*12*) studied the decomposition of calcite and obtained a number of photomicrographs of well-developed calcium oxide nuclei. Each developed nucleus was square in section, and the appearance of many suggested that they were inverted pyramids hollowed out of the calcite, possibly by successive block removals. The similarity to the nuclei found on the 001 face of alum by Garner (*7*) is remarkable.

The present investigation did not yield any quantitative information on the kinetics of the nucleation process. However the qualitative results suggest that nucleation does play an important role, particularly with the larger crystal sizes; it is also important during the initial stages of decomposition and for high rates of decomposition. A resistance to nucleation appears to be the most reasonable explanation for the early maximum in the time-reaction temperature curve (Figure 3). Apparently a considerable amount of superheat is required to increase the rate of nucleation to the degree that the rate of decomposition is commensurate with the heat input. Once this condition is reached, nuclei continue to form, since the temperature decreases despite the high reaction rate now in effect. During the latter part of a calcination run it is difficult to determine whether or not nucleation plays an important role. However it is well known (*1*) that larger crystals of pure calcite require higher temperatures and longer times for decomposition than the more amorphous limestone. This again appears to represent a case of nucleation acting as a rate-limiting process.

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# Rates of Thermal Decomposition of Barium Carbonate–Carbon Mixtures

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The thermal decomposition of pure barium carbonate to form barium oxide and carbon dioxide requires relatively high temperatures; for example, at 1,030°C. the equilibrium partial pressure of carbon dioxide is only 2 mm. Hg (*3*). Unfortunately temperatures in excess of 1,030°C. tend to produce a dense, nonporous form of barium oxide. According to Lander (*3*), a barium carbonate–barium oxide eutectic exists at 1,030°C., and apparently above this temperature barium carbonate–barium oxide solutions form which continue to exist as solid solutions below the melting point. Therefore the thermal decomposition of barium carbonate is usually facilitated by the addition of carbon (*1, 2*). The carbon dioxide partial pressure becomes greatly reduced, since the following reaction proceeds far to the right:

$$C + CO_2 \rightarrow 2CO \qquad (1)$$

The observed rate of the over-all reaction may therefore be affected by heat or mass transfer rates or by the kinetics of two separate reactions.

## EXPERIMENTAL

Barium carbonate was mixed with one of several forms of carbon, and the mixture was pressed (at 27,000 lb./sq. in.) into a cylinder around a platinum, rhodium–in–platinum thermocouple. The cylinder was calcined in a constant-temperature furnace of special design, and the rate of reaction was determined by the rate of the evolution of gas. The apparatus and methods employed were substantially the same as those used previously for studying the decomposition of calcium carbonate (*6*). This earlier paper also discusses the accuracy of the experimental data.

Lieberson and Oster (*5*) found that the rate of reaction of barium carbonate and carbon mixtures was not greatly influenced by the amount of carbon used in excess of that stoichiometrically required for the over-all reaction:

$$BaCO_3 + C \rightarrow BaO + 2CO \qquad (2)$$

(The stoichiometric ratio is 6.085 g. carbon/100 g. barium carbonate.) However to decrease the possibility of the carbon content being a rate-controlling factor, and also to decrease the effect of imperfect mixing, a 50% excess of carbon over the stoichiometric quantity was used in each run beyond the first.

Since it was also desirable to carry out the reaction at temperatures below that of the barium carbonate–barium oxide eutectic (1,030°C. or 1,886°F.), vacuum conditions were required. A mechanical vacuum pump was used to exhaust the furnace, and a Cartesian Diver manostat reduced pressure fluctuations. The rate of the evolution of gas (which was almost 100% carbon monoxide) was measured with a capillary flow meter. The over-all degree of decomposition of the barium carbonate was determined by measuring the weight of the sample before and after reaction.

Mallinckrodt reagent-grade barium carbonate was used in all runs. The average particle diameter was found to be about 0.13 μ; the B.E.T. surface area (by nitrogen adsorption) was about 10 sq. m./g. The properties of the different types of carbon studied are outlined in Table 1. The components were mixed dry, then wet (with water), and then again dry after removing the water by evaporation. The most efficient mixing probably took place when the mass was a thick paste. However despite the considerable care devoted to obtaining good mixing the degree of mixing was not so high as desired. Small "islands" of white barium carbonate, up to approximately 0.15 mm. in diameter, were visible in the pressed samples. Nevertheless, the degree of mixing was apparently sufficient to give complete decomposition of the barium carbonate, if reaction conditions were favorable.

In all cases a 0.010-in.-diameter platinum, 10% rhodium-in-platinum thermo-

TABLE 1. PROPERTIES OF CARBON BLACKS AND GRAPHITES STUDIED

Carbon Blacks

| Code name | Type | Surface area, sq. m./g., by B.E.T.-Nitrogen Method | Mean particle diameter, (μ) | Ash content, wt. % |
|---|---|---|---|---|
| Elftex 5 | Furnace black | 77 | 0.03 | 0.5 |
| Elf 8 | Channel black | 100 | 0.03 | 0.1 |
| Sterling FT | Thermal black | 15.7 | 0.20 | 0.1 |
| Same-after partial graphitization | | 12.7 | 0.20 | 0.1 |

Graphites

| Code name | Minimum graphitic carbon content, wt. % | Maximum ash, wt. % | Particle size |
|---|---|---|---|
| Dixon 2 | 94 | 5 | 30% + 100 mesh<br>30% − 200 mesh |
| Microfyne | 94 | 5 | 97% − 325 mesh |