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EXTRACTION METALLURGY DIVISION

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Kinetic Studies on the Thermal Decomposition of Calcium Carbonate[1]

T. R. INGRAHAM[2] *and P. MARIER*[2]

Kinetic studies have been made of the thermal decomposition of precipitated calcium carbonate, powdered calcite, and regular fragments of calcite crystals. The powdered materials were examined in the form of pellets, which were prepared by compacting the powder to about 70% of its theoretical density. The work was done at one atmosphere of pressure in a flow of air containing various amounts of carbon dioxide. It was observed that the decomposition of the pellets, which were prepared in a variety of shapes, was characterized by the same advancing interface mechanism as that observed for single specimens of crystal fragments. When the rates of decomposition were normalized for the change in of interfacial area accompanying decomposition, it was possible to correlate the observed rates of decomposition for a variety of pellet shapes, and to relate these rates, as a function of particle size and pellet roughness, to the rates of decomposition of large fragments of calcite crystals. The activation energy for the decomposition reaction was found to be 40.6 kcal./mole. At a constant temperature, the decrease in reaction rate with increasing carbon dioxide pressure was found to be proportional to the difference between the equilibrium dissociation pressure and the back pressure of carbon dioxide. A reaction mechanism based on diffusion through a constant thickness of active calcium oxide is suggested.

Une étude cinétique de la décomposition thermique du carbonate de calcium précipité, de la calcite en poudre et de crystaux fragmentés de calcite est présentée. Les substances en poudre ont été compactées sous forme de pastilles, de formes diverses, jusqu'à 70% de la densité théorique avant d'être étudiées. La décomposition a eu lieu à pression atmosphérique dans un courant d'air contenant des proportions variables de gaz carbonique. Cette décomposition des pastilles est caractérisée par le même mécanisme d'interface progressive observé sur les crystaux fragmentés individuels. Lorsque les taux de décomposition sont ajustés pour la variation de surface interfaciale lors de la décomposition il est possible d'établir une relation entre les taux de décomposition des diverses formes de pastilles. La relation entre ces taux, en fonction des dimensions des particules et de la rugosité des pastilles, et les taux de décomposition de fragments de calcite peut aussi être établie. L'énergie d'activation de la réaction de décomposition a été déterminée comme étant 40.6 kilo calories/mole. A température constante, la réduction dans le taux de réaction avec l'augmentation du gaz carbonique est proportionnelle à la différence entre la pression de dissociation à l'équilibre et la pression initiale du gaz carbonique. Il est proposé un mécanisme basé sur la diffusion au-travers d'une couche constante d'oxyde de calcium.

The thermal decomposition of calcium carbonate has been the subject of many investigations, from which it is evident that in the normal range of calcination temperatures (700 to 1000°C.) the only products of decomposition are carbon dioxide and solid calcium oxide.

The most influential paper related to the mechanism of decomposition of calcium carbonate is that of Langmuir(1), who determined that if the Phase Rule were to apply, and no solid solutions were involved, the decomposition reaction must take place at an interface between the two solid phases, calcium carbonate and calcium oxide. This was confirmed by Furnas(2) for the decomposition of limestone, and it was also shown that the rate of migration of the interface under isothermal conditions was almost constant, in agreement with the observations of Spenser and Topley(3) on the decomposition of silver carbonate. On the basis of the uniform rate of migration of the interface, it has been concluded by MacDonald(4), and by Hyatt, Cutler and Wadsworth(5), that the rate of decomposition was controlled by some stage of the process occurring in the interface. At temperatures above 950°C., Furnas(2) and Narsimhan(6) have shown that the rate of the decomposition reaction is probably determined by the rate of transfer of heat across the layer of reaction product.

Furnas(2) did not detect any variations in the rate of decomposition attributable to variations in gas composition, but from work on fragments of calcite crystals, Hyatt, Cutler and Wadsworth(5) suggested that the rate of decomposition might be correlated with the partial pressure of carbon dioxide in the sweeping gas, by a relationship based on an adsorption expression. The activation energies determined by various investigators vary from a low of about 35 kcal./mole, determined by Britton, Gregg and Winsor(7), to a high of 230 kcal./mole, recently reported by Hashimoto(8). The majority of the values reported lie in the range 37 to 53 kcal./mole(9–15).

It was recognized by Spenser and Topley(3), from their work on the thermal decomposition of silver carbonate, that if the rate of movement of a reaction interface were constant, it could be correlated, for spherical particles, with the 1/3 power of the weight change of the particle. A similar concept has been used by Britton, Gregg and Winsor(7), Freeman and Carroll(13), and Cremer and Nitsch(16). However, in these latter papers, the results were correlated on the basis of interfacial area, which, for solid spherical particles, varies with the 2/3 power of the weight of the particle. The 2/3 power has been referred to as an "order" of reaction by the authors(7,13,14,16). Gomes(17) has stated that the term "order" has no significance when used to refer to a heterogeneous process.

To obtain a more reliable value for the activation energy of the decomposition reaction, and to broaden the concept of applying surface area corrections to the decomposition of powdered

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materials, it was decided to re-investigate the thermal decomposition of calcium carbonate, using a variety of regular shapes of powder compacts. This technique was used by Warner and Ingraham(18) in studies of the decomposition of ferric sulphate and aluminum sulphate.

All the experiments reported here were done at temperatures below that at which the transfer of heat into the sample is rate-controlling. This was ascertained from linearity of the log rate versus reciprocal temperature relationship.

Experimental Procedure

Since there is a substantial loss in weight as a result of the liberation of carbon dioxide during the conversion of calcium carbonate to calcium oxide, thermogravimetric methods are suitable for following the progress of the reaction. The instrument used in these experiments was an automatic recording balance-and-furnace unit manufactured by the American Instrument Company under the trade name "Thermo-Grav".

Calcium carbonate from two sources was used. In some experiments, regular fragments of clear natural calcite crystals were used. In others, ground calcite, or reagent-grade precipitated calcium carbonate, was used. For both materials, the weight loss was the theoretical quantity of carbon dioxide, within the experimental error of measurement (±1%). Samples weighing about 0.455 gm. were used to obtain a weight loss of about 200 mg., the full-scale deflection of the instrument. All of the particles of the reagent-grade calcium carbonate were less than 56 microns in equivalent diameter, and 64% were less than 14 microns. Unless otherwise specified, this material was used with the as-received size distribution. For some experiments, sized fractions of the ground calcite were prepared with a Roller Particle Size Analyzer.

All experiments using ground calcite or powdered calcium carbonate were done with pellets. These were prepared in a ¼ in. diameter cylindrical die, and were adjusted to the required dimensions by careful filing.

In making an experiment, the pellet was supported in the apparatus on a platinum mesh sample-holder and brought to a predetermined constant temperature. Then the run was begun by changing the composition of the sweeping gas from carbon dioxide to either pure dry air or some fixed composition of air and carbon dioxide. A constant flow rate of about 50 ml./min. of pre-heated gas was used. A series of flow rates was tested in preliminary experiments, and it was shown that, at the most rapid rate of decomposition examined, flow rates in excess of 40 ml./min. do not affect the rate of decomposition.

The weight loss as a function of time was obtained from the instrument in the form of a graph. From the ratio of the weight loss up to a given time, *t*, and the weight loss at the termination of an experiment, the fractional amount of decomposition, α, was calculated. The fractional amount of decomposition, α, was converted into weight loss per unit area of interface by relating the interfacial area to a parameter of the sample. The earlier methods of conversion suggested by Spenser and Topley(3), Mample(19) and Massoth and Hensel(20) have been superseded by the equations suggested by McKewan(21). Working from the general rate equation,

$$r_o d_o f = kt, \qquad (1)$$

in which r_o and d_o are respectively the initial size parameter and density of the sample, t is the time of reaction, and k is the reaction rate constant, McKewan has made substitutions for f, the fractional thickness of the layer of reacted material, to relate the rate of reaction to the fractional decomposition, α.

For spherical particles, and cylindrical particles with the height equal to the diameter,

$$\alpha = 1 - (1 - f)^3 \qquad (2)$$

For cylindrical particles of other height-to-diameter ratios,

$$\alpha = 1 - (1 - f)^2 \left(\frac{a - f}{a}\right) \qquad (3)$$

where a is the ratio of pellet height to pellet diameter.

For bar-shaped particles,

$$\alpha = 1 - (1 - f)\left(\frac{a - f}{a}\right)\left(\frac{b - f}{b}\right) \qquad (4)$$

where a and b are the ratios of each of two dimensions to a third.

Although all of the foregoing expressions were developed for use with single solid particles, it has been shown by Warner and Ingraham(18) that Equations (1) and (3) can be used, with certain restrictions, to describe the rate of decomposition of cylindrical compacts of powdered ferric sulphate and aluminum sulphate. Incorporation of the density term in Equation (1) is particularly useful for resolving the results from pelletized powder samples, because it obviates the problem of preparing pellets of identical density. It is evident, from Equation (1), that if the expression were applicable to the decomposition of calcium carbonate, then the graphical relationship of $r\,d\,f$ to t would be linear and the slope of the line would be numerically equal to the rate constant, k, for the decomposition.

Results and Discussion

The results obtained from a series of experiments done at 850°C., using an air sweep to remove the evolved carbon dioxide from the vicinity of the sample, are shown in Figure 1. The experiments included cylindrical, bar-shaped, and cubic samples. It is evident from the linearity of the relationship that the mathematical expressions proposed for various shapes of solid samples by McKewan(21) are also applicable, under the conditions of these experiments, to powder compacts of calcium carbonate. Since the pellets used in the experiments had a range of densities which did not exceed 76% of the theoretical density of natural calcite, it seems reasonable to believe that a stagnant layer of carbon dioxide was retained in the vicinity of the interface, and that the presence of this layer prevented decomposition from taking place within the body of the sample. This belief was substantiated by sectioning and polishing a pellet and developing the interface with an alcohol solution of methyl red indicator. The interface was clearly defined, and in cross-section tended to a circular form for symmetrical cylindrical samples. A clearly defined interface was obtainable only when sweep gases were used. When the decomposition was studied under reduced pressures, the simple geometric treatment could not be used to correlate the results. The results could be correlated only by a logarithmic treatment similar to that used by Evans(22) to resolve the results of experiments in which the reaction rate is controlled by the diffusion of gases through a porous material.

The activation energy for the decomposition was obtained from a series of experiments done at temperatures between about 790 and 850°C. To minimize the effect of the reverse reaction, an air sweep was used to remove the evolved carbon dioxide. The relationship between the logarithm of the rate constant and reciprocal temperature is linear, as shown in Figure 2, and can be expressed by the equation

$$\log k = 5.851 - \frac{40{,}565}{2.303\,RT} \qquad (5)$$

The activation energy of 40.6 kcal./mole is in reasonable agreement with the majority of values reported in the literature (37-53 kcal./mole), and it is in good agreement with the value of 39.8 ± 1.2 kcal./mole calculated from the data of Kelley and Anderson(23) for the heat of reaction at the midpoint temperature of the range used in these experiments. This agreement has been noted previously by Zawadski and Bretsnajder(15).

The effect of carbon dioxide pressure on the rates of formation and decomposition of a number of metal carbonates has been studied by Zawadski and Bretsznajder(15). They showed that the velocity of reversible formation and decomposition reactions is proportional to the difference between the equilibrium pressure of carbon dioxide and the back pressure of carbon dioxide applied to the sample.

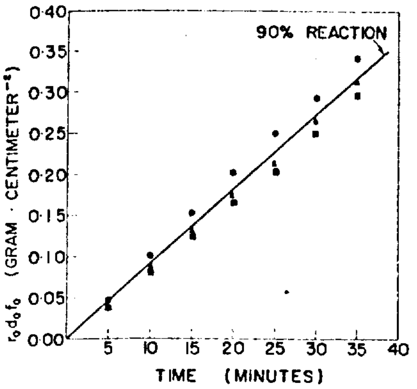

Figure 1 — Rate of decomposition, in an air stream at 850°C., of precipitated calcium carbonate, pelletized in the form of :

● a cylinder, ▲ a bar and ▣ a cube.

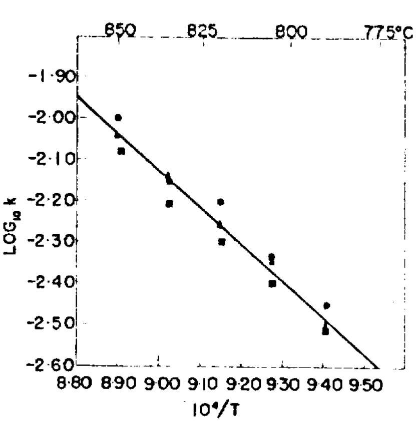

Figure 2 — Arrhenius plot for determining activation energies; ▣ cube = 38.9 kcal, ● cylinder = 41.0 kcal, ▲ bar = 41.8 kcal.; average 40.6 kcal.

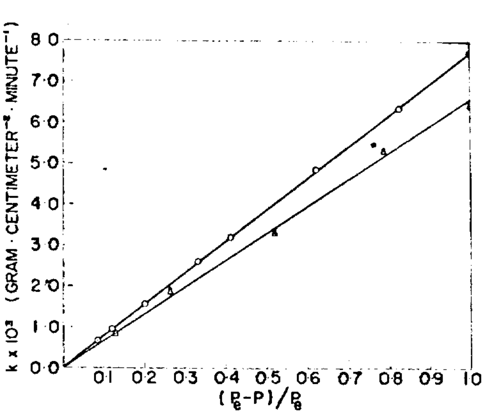

Figure 3 — Variation in the rate constant for decomposition, caused by changes in the partial equilibrium pressure of carbon dioxide in the air-carbon dioxoide sweeping gas. Total pressure, one atmosphere.

⊙ 850°C. △ 835°C.

$$v = k(P_e - P) \ldots\ldots\ldots\ldots (6)$$

The application of this relationship to the decomposition of pellets of calcite or powdered calcium carbonate has been assessed at two temperatures for different back pressures of carbon dioxide. This was done by diluting the sweep gas with known amounts of carbon dioxide. The equilibrium pressure of carbon dioxide over the sample was calculated from the equations suggested by Hill and Winter(24). For convenience in plotting the results at two temperatures, the rate was plotted against the fractional equilibrium pressure. The value of P_e is the one appropriate to the temperature of the experiment. The results are shown in Figure 3. The linearity of the relationships in Figure 3 confirms the suitability of the Zawadski-Bretsznajder(15) relationship and permits expression of the effects on reaction rate of changes in pellet size, shape and density and of the back pressure of carbon dioxide. For a spherical pellet or a symmetrical cylinder or cube, the equation is:

$$r_o d_o [1 - (1 - \alpha)^{1/3}]\, P_e/(P_e - P) = 7.10 \times 10^5 \exp(-40{,}565/RT)t \quad (7)$$

The frequency factor and the activation energy constant in Equation (7) were established from experiments done with finely divided reagent-grade calcium carbonate. To correlate the results with those for the decomposition of single crystals of calcite, a group of experiments was done with pellets prepared from ground calcite which had been fractionated to recover the particles within a narrow size range. The results of the experiments are shown in Figure 4. From the linearity of the relationship it is evident that the particles in the pellet do not behave as single particles. If they did, then the rate of the decomposition would be expected to increase in proportion to the decrease of particle size. Based on an experimental measurement of the rate of decomposition of large single calcite crystals, which gave a rate constant of 4.80×10^{-3} gm. of calcium carbonate decomposed per minute per nominal square centimeter of interfacial area, the rate of decomposition for pellets containing various size fractions of calcite can be expressed by the following equation:

$$k = (4.80 \times 10^{-3} \times 1.56) + 2.53 \times 10^{-6}\,\mu, \ldots\ldots (8)$$

where μ is the particle size, 1.56 is a surface roughness factor, and 2.53×10^{-6} is the rate of variation of surface roughness with particle size. It is particularly interesting to note that the nominal surface area as indicated by the surface roughness factor is only about one and a half times the geometric surface area.

In another group of experiments, studies were made to detect any changes in the rate of decomposition which might be caused by the presence of impurities in the pellet. The impurities were mixed with the calcium carbonate prior to the pressing operation. Two varieties were used, a potentially inert impurity and a potentially reactive impurity. For the experiments with an inert impurity, 2, 5, 10 and 15% by weight of barium carbonate was mixed with the calcium carbonate. The results of the experiments showed no change in the rate of the decomposition reaction. All of the results were well represented by the same straight line used to describe the rate in the absence of impurity.

The potentially reactive impurity selected for study was finely divided silica. Since the results of the experiments could not be resolved by the same kinetic treatment used for the pure carbonate, it was concluded that reaction between the calcium oxide and silica probably destroyed the normal interface between the calcium oxide and calcium carbonate.

During the experiments in which back pressures of carbon dioxide were used, it was noted that although the $r_o d_o f$ versus t relationships continued to be linear, the intercept no longer passed through zero. With increasing back pressures of carbon dioxide, there was a progressive movement of the intercept from zero to increasing values of t. When graphs of α versus t were prepared, it was evident that there was a substantial induction period in the decomposition reaction at the higher back pressures of carbon dioxide. According to Jacobs and Tompkins(25), induction periods are to be considered typical of many solid reactions. Various explanations have been advanced for the causes of these induction periods. Garner(26) has suggested that a slow growth of nuclei, during their early stages of growth, may be involved. Recently a relatively simple concept has been advanced by Voge and Atkins(27) which explains both the apparent autocatalytic behavior and the slow growth of nuclei, by considering simple changes in geometry which occur during the growth of a disc-shaped nucleus. The same reasoning has been applied to the decomposition of calcium carbonate, and the relationship $\alpha^{1/2}$ versus t has been found to be linear. Hence, it seems reasonable to suggest that in the initial stages of the decomposition of a pellet of calcium carbonate, a few small shallow patches of calcium oxide are formed on the surface of the pellet. Until these patches grow sufficiently to cover the surface of the pellet with a layer of calcium oxide, the kinetics of the reaction are controlled by the laws governing the linear rate of advance of an interface in two dimensions from a point source.

In the second stage of the decomposition reaction, the calcium oxide-calcium carbonate interface advances at a uniform rate from the surface of the pellet toward its centre, following the law of a contracting sphere for relating the decreasing interfacial area to the fractional amount of reaction.

Mechanisms of Reaction

On the basis of the experimental results of this investigation, it is not possible to make a decisive selection of the mechanism for the decomposition reaction. From the fact that the reaction

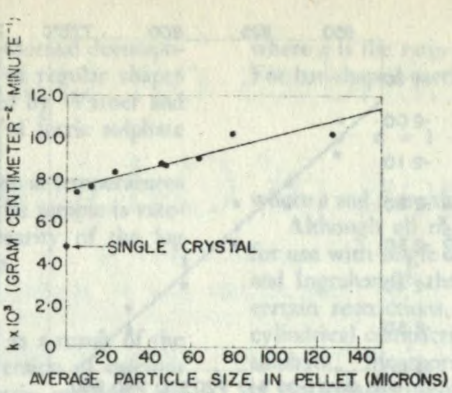

Figure 4

Figure 4 — Variation in the rate constant for decomposition, caused by altering the particle size of the ground natural calcite used to prepare symmetrical ¼-in. cylindrical pellets.

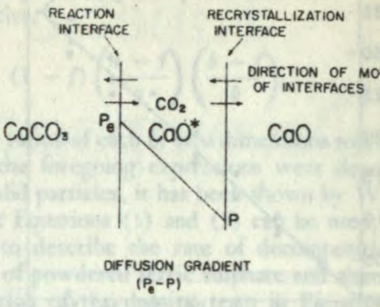
REACTION INTERFACE
RECRYSTALLIZATION INTERFACE
DIRECTION OF MOVEMENT OF INTERFACES
CO₂
Pₑ
CaCO₃
CaO*
CaO
P
DIFFUSION GRADIENT
(Pₑ–P)

Figure 5

Figure 5 — Representation of double interface decomposition mechanism.

obeys linear kinetics, it may be argued that the reaction rate is controlled by some process occurring in the interface that separates the two solid phases. On the basis of the pressure dependency of the reaction rate, it was argued by Hyatt, Cutler and Wadsworth(5) that the rate was controlled by the population of active calcium oxide groups in the interface. It was argued that the number of these groups is controlled by a Langmuir-type of dependence on the pressure of carbon dioxide. Another equally probably mechanism can be postulated on the basis of the pressure dependency observed in this investigation. The mechanism is illustrated in Figure 5.

From Figure 5, it will be evident that the postulated mechanism is based on the presence of two interfaces, both of which move at the same velocity. The first interface is between calcium carbonate and active calcium oxide. By active calcium oxide is meant calcium and oxygen groups still arranged in the original positions they occupied in the calcium carbonate lattice. Because of the loss of carbon dioxide from this lattice, the resulting metastable structure should be porous and very reactive. The second interface is that between the active calcium oxide and the calcium oxide which has recrystallized to its stable crystal habit. It is likely that under most circumstances the recrystallization process is rapid and that the recrystallization interface follows the reaction interface closely. It is reasonable to believe that the constant distance between the interfaces is of the same order as the distance through which the molecular forces of the calcium oxide lattice extend. Since carbon dioxide must be released through this layer of active calcium oxide, there will be a pressure gradient across it of $(P_e - P)$, where P_e is the equilibrium pressure of carbon dioxide at the temperature of experiment and P the partial pressure of carbon dioxide in the bulk of the gas phase. It is presumed that P never increased beyond the partial pressure in the bulk of the gas because the layer of recrystallized calcium oxide is open and porous as a result of the presence of cracks and fissures caused by shrinkage to a more compact lattice habit.

Conclusions

When the thermal decomposition of calcium carbonate was studied kinetically in an air stream at temperatures between 750° and 900°C., using powdered material which had been compressed to form a pellet, the pellet behaved as a solid mass even though it had an appreciable amount of void space. When the results were normalized to remove the variable of decreasing surface area as the decomposition reaction progressed, they were consistent with the hypothesis that both the rate of the initial stage of the reaction, when small patches of product were growing, and the rate of the final stages of the reaction, when the carbonate-oxide interface was receding into the specimen, are governed by a rate of interface migration which is constant at a constant temperature.

At any specified temperature, the decrease in the rate of decomposition with increasing back pressure of carbon dioxide is directly proportional to the difference between the back pressure and the equilibrium decomposition pressure. This observation suggests that the rate of the reaction is controlled by the rate of diffusion of carbon dioxide through a layer of active calcium oxide of constant thickness. Since the calcium oxide is highly reactive, it is reasonable to believe that the escape of carbon dioxide is a series of adsorption-desorption processes, each of which is the equivalent of chemical reaction.

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