# Kinetics of Sodium Bicarbonate Decomposition

A thermal gravimetric method was used to measure rates of decomposition of $NAHCO_3$ particles. Such decomposition produces a highly porous $Na_2Co_3$ that reacts with $SO_2$ rapidly and completely at moderate temperatures. Hence, $NaHCO_3$ decomposition provides a reactant with attractive features for $SO_2$ removal. The rapid rate of decomposition combined with the high heat effect prevented determining intrinsic rates by constant temperature runs when the temperature level was above 400 K. However, rising-temperature runs, which allowed time for heat transfer to equilibrate temperatures of the thermocouple and particles, gave reliable results at high temperatures. The activation energy was 102 kJ/mol. Porosimeter data verified the large increase in pore volume (from 0.03 to $0.39 \times 10^{-3}$ $m^3/kg$) on converting the $NaHCO_3$ particles to $Na_2CO_3$. First-order kinetics were observed up to high conversions, after which the apparent order decreased. However, the sodium bicarbonate could be completely converted to $Na_2CO_3$.

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## SCOPE

It has been well established that thermal decomposition of $NaHCO_3$ particles can produce a highly porous $Na_2CO_3$ product that reacts rapidly with $SO_2$ in waste gases (Bares et al., 1970; Marecek et al., 1970). Also, rates of decomposition and of reaction with $SO_2$ have been measured separately on different samples (Subramanian et al., 1972; Guarini et al., 1973; Bares et al., 1970; Marecek et al., 1970).

Our objective was to determine the rate of decomposition of a sample of $NaHCO_3$ particles at temperatures from 373 to 473 K over the complete range of conversion. A TGA apparatus was employed since this allowed very small sample masses to be used (leading to accurate rates) and the effect of heat and mass of transfer processes could usually be eliminated. Pore-volume data also were obtained on $NaHCO_3$ and $Na_2CO_3$ particles.

## CONCLUSIONS AND SIGNIFICANCE

The rapid rate of decomposition of $NaHCO_3$ combined with a large, endothermic heat effect required careful choice of operating conditions to obtain rates unaffected by heat transfer. At temperatures above 400 K this required the TGA experiments to be conducted by the rising-temperature method. The results showed that intrinsic kinetics were first-order in mass of $NaHCO_3$ up to high conversions. The retardation of the rate beyond this point may be due to changes in the nature of the remaining $Na_2CO_3$, or the structure of the $Na_2CO_3$ product surrounding the unreacted $Na_2HCO_3$. However, the rate remained high at high conversions so that the $NaHCO_3$ was completely converted to the carbonate. The data also showed that the rate decreased when the decomposition temperature was reduced from 473 to 373 K. Corresponding pore-volume data indicated that the surface area was greater for particles decomposed at 373 K.

## Introduction

The removal of sulfur dioxide by reaction with sodium carbonate, prepared by thermal decomposition of the bicarbonate, has attractive features. Hartman et al. (1979) have pointed out that sodium carbonate can be completely utilized to remove sulfur dioxide, while only up to about 40% of calcined limestone and up to about 75% of dense limestone (from rock quarries) can be converted. These significant differences in utilization of the solid reactant are likely due to differences in initial pore structure and changes in pore structure as a result of reaction (Dogu, 1981). Hartman and Coughlin (1974, 1976) explained the incomplete conversion of limestone rock on reduction of porosity (during conversion to calcium sulfate), which limited the transport of sulfur dioxide. Indirect evidence substantiating this view is the observation of Borgwardt and Harvey (1972) that marls with very high initial porosities could be completely converted to sulfate. Sodium carbonate prepared by decomposing the bicarbonate has this same highly porous structure. A second advantage is that the reaction of sulfur dioxide occurs rapidly at 373 to 473 K, while about 1,173 K is required for reaction with limestones.

Bares et al. (1970) and Mareček et al. (1970) discovered that the reactivity of sodium carbonate is very high when it is prepared by thermal decomposition of sodium bicarbonate at temperatures from 393 to 453 K. Also, there is a fourfold decrease in solid volume in conversion of two moles of $NaHCO_3$ to one mole of $Na_2CO_3$. This greatly increases the pore volume. In contrast, $Na_2CO_3$ prepared by dehydration at low temperatures has a much lower activity for reaction with $SO_2$.

In view of the significance of the method of preparing $Na_2CO_3$ on its reaction with $SO_2$, we have measured the rate of thermal decomposition of the bicarbonate at 373 to 473 K for small particles and for pellets and compared the results with pore volume vs. pore radius (porosimeter) data.

Prior studies of the decomposition (Subramanian et al., 1972; Guarini et al., 1973) indicate that a rate equation first-order in $NaHCO_3$ explains the data, if transport effects are not involved.

Thermal gravimetric analysis has some advantages over tubular reactors for gas-solid reactions since the rate at any instant is obtained directly from the weight vs. time measurements. This avoids averaging uncertainties inherent in calculating rates from conversion data measured in tubular reactors containing a larger mass of solid reactant.

In addition to the kinetics experiment, pore-volume data were obtained for solid reactant and product in order to evaluate changes in pore structure as a result of reaction.

**Table 1. Composition of Sodium Bicarbonate***

| Constituent | Wt. % |
|---|---|
| Ammonium | 0.0005 |
| Calcium, Magnesium | 0.020 |
| Chloride | 0.003 |
| Heavy metal | 0.0005 |
| Insoluble matter | 0.015 |
| Iron | 0.001 |
| Phosphate | 0.001 |
| Potassium | 0.005 |
| Sulfate | 0.003 |
| Sodium bicarbonate | 99.7 |

*Mallinckrodt Chemical Co.

**Table 2. TGA Operating Conditions for Thermal Decomposition**

| Constant Temperature Runs | |
|---|---|
| Pressure | 101 kPa |
| Temperature | 373 to 473 K |
| Particles | |
| Size range | 1.04 to 1.47 × $10^{-4}$ m |
| Avg. diam. | 1.25 × $10^{-4}$ m |
| Sample mass | 2.2 to 50 × $10^{-6}$ kg |
| Pellet pieces | |
| Avg. dia. | 4.5 × $10^{-3}$ m |
| Avg. thickness | 3.5 × $10^{-3}$ m |
| Sample mass | 100 to 200 × $20^{-6}$ kg |
| Gas flow rate (298 K, 101 kPa) (helium 99.995%) | 0.78 × $10^{-6}$ $m^3/s$ |
| **Increasing-Temperature Runs** | |
| Pressure | 101 kPa |
| Temperature | 303 to 473 K |
| Rate of heating | 0.1 to 0.3 K/s |
| Particles, avg. dia. | 1.25 × $10^{-4}$ m |
| Gas flow rate (298 K, 101 kPa) | 0.78 × $10^{-6}$ $m^3/s$ |
| Sample mass | 2.2 to 6.0 × $10^{-6}$ kg |

## Experimental

The experimental studies consisted of three parts: sample preparation, TGA measurements for the thermal decomposition, and pore volume experiments.

### *Sample preparation*

Sodium bicarbonate in powder form (composition is given in Table 1) was first pressed into cylindrical pellets and then broken into pieces or crushed and sieved to provide samples for the TGA and porosimeter experiments. Water has to be added to

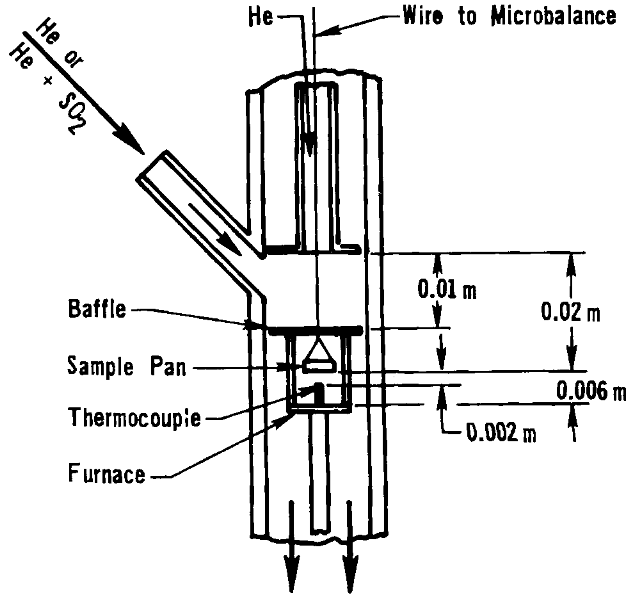

Figure 1. Detail of TGA furnace and sample pan.

the powder in order to obtain coherent pellets. The following procedure gave pellets of reproducible pore volume. Water ($10^{-3}$ kg) was added to $28 \times 10^{-3}$ kg of $NaHCO_3$ and the mixture stored in a closed container for 24 h to obtain a uniform water content. Pellets were made by adding $0.3 \times 10^{-3}$ kg of the mixture to a mold, $12 \times 10^{-3}$ m in diameter. The material was then subjected to a force of 3,630 kg which was maintained for 60 s. Finally, the pellets were dried in a desiccator for one week. For the pellet experiments these single pellets were broken into a few pieces and placed in the sample pan. For the experiments with particles the pellets were crushed, and dried before use. In this way water was eliminated from the $NA_2CO_3$ charged to the TGA.

### *TGA experiments*

Decomposition experiments were carried out with pellets and particles at constant temperature and with particles at a constant rate of temperature increase. The scope and operating conditions for the two types of temperature behavior are given in Table 2. A Perkin-Elmer (model TGS-2) TGA with System 4 Microprocessor and Controller was used for the weight vs. time measurements. Figure 1 shows the details of the furnace and platinum sample pan. A small ($3.7 \times 10^{-8}$ $m^3/s$) continuous stream of helium purges the thermobalance unit to prevent contamination with gaseous products of the decomposition. The main gas stream (helium) entered tangentially into the chamber containing the furnace and sample pan, as shown in Figure 1.

To reduce the possibility of mass transfer effects between gas and particles or pellet, a doughnut-shaped baffle (O.D. = $23 \times 10^{-3}$ m, I.D. = $10^{-2}$ m) was placed on the open top of the furnace. This arrangement prevented the gas stream from bypassing the sample. In addition, the bottom of the sample pan contained numerous small holes that permitted gas to flow past the sample. The thermocouple was located $2 \times 10^{-3}$ m below the sample pan.

A 2 min preheating period (to eliminate water) was needed to reach constant weight. This was done with the sample in place at a temperature (323 K) below that at which decomposition is appreciable.

### *Pore volume measurements*

Pore volume vs. pore diameter data were obtained in a 60,000 psi (413 MPa) porosimeter (American Instrument Co.) for samples of sodium bicarbonate and sodium carbonate prepared by thermal decomposition.

## Kinetics of $NaHCO_3$ Decomposition

The decomposition reaction $2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$ is highly endothermic, $\Delta H_{298} = 135$ kJ/mol (West, 1985). Also, the reaction is very fast at temperatures above 400 K. It is difficult to transfer energy fast enough to eliminate temperature differences between the values in the particles and the temperature of the surrounding gas stream.

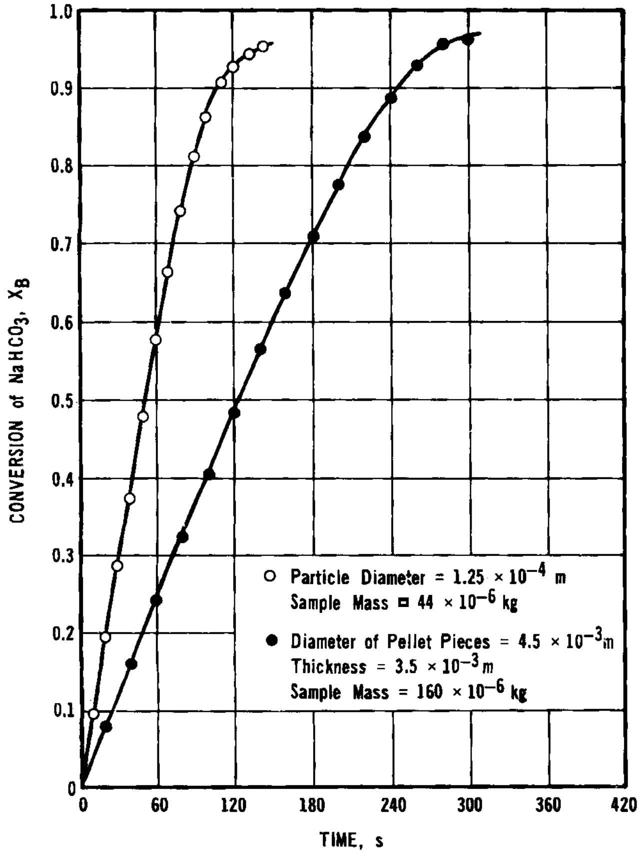

**Figure 2. Thermal decomposition of $NaHCO_3$ pellet pieces and particles at 473 K.**

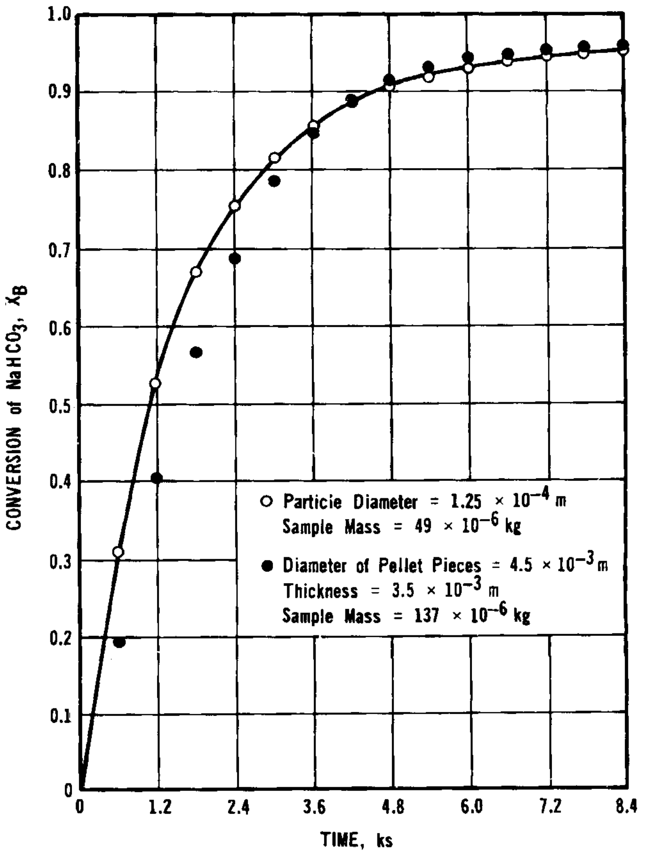

**Figure 3. Thermal decomposition of $NaHCO_3$ pellet pieces and particles at 373 K.**

Hence, the thermocouple reading in the TGA can be higher than that in the particles where the reaction occurs. Evidence for this is seen in Figure 2. This is for data obtained at a constant temperature of 473 K and shows conversion of $NaHCO_3$ vs. time data for particles ($1.25 \times 10^{-4}$ m dia.) and for the larger pellet pieces. Conversions were calculated from the decrease in sample weight, $w_{B_0} - w_B$, at any time and the equation:

$$x_B = \frac{w_{B_0} - w_B}{w_{B_0}} \frac{2\,M_B}{M_{CO_2} + M_{H_2O}} \tag{1}$$

The large difference between the curves in Figure 2 is substantially reduced at lower temperatures, as is evident from Figure 3, which is for 373 K. Additional data for an average particle diameter of $0.442 \times 10^{-3}$ m showed little change from the results at the smallest particle diameter ($0.125 \times 10^{-3}$ m) at 373 and 393 K.

Large sample mass and low gas flow rate can also introduce transport resistance. At temperatures of 373 and 393 K the effect of sample mass was within the accuracy of the data. Results at 393 K and different masses of $0.125 \times 10^{-3}$ m particles showed that there is little difference for sample masses as large as $51 \times 10^{-6}$ kg. In other runs it was found that a 100% increase in helium flow rate did not significantly change (<6%) the conversion vs. time data at 473 K.

From these measurements we concluded that the constant-temperature data provided reasonably accurate measurements of the intrinsic rate at 373 and 393 K. At higher temperatures, the results are influenced by heat transfer limitation.

To confirm these conclusions, additional runs were made using the temperature-increasing method. These experiments, which were carried out with the $0.125 \times 10^{-3}$ dia. particles and a helium rate of $0.78 \times 10^{-6}$ $m^3/s$, were started at 303 K, which is below the temperature at which decomposition rates become appreciable. The temperature was then increased, at rates of 0.1 and 0.3 K/s, to a final temperature of 433 K, where decomposition to $Na_2CO_3$ was complete. This procedure provided more time for the temperature of the particles to equilibrate with the thermocouple reading and thus eliminate the heat transfer limitation. Aiding this equilibrium was the fact that most of the decomposition occurred at temperatures below 400 K. At these lower temperatures the reaction rate and the heat transfer rate necessary to equilibrate the particle and thermocouple temperatures are both low.

## Calculation of Rate Constants

The measurements of Subramanian et al. (1972) and Guarini et al. (1973) indicated that the decomposition was first-order in mass of $NaHCO_3$. Since the reaction is not expected to be a surface phenomenon, this finding is logical. For first-order kinetics the weight vs. time data should follow the equation

$$\ln\left(\frac{W_B}{W_{B_0}}\right) = \ln\,(1 - x_B) = -\,k_d t \tag{2}$$

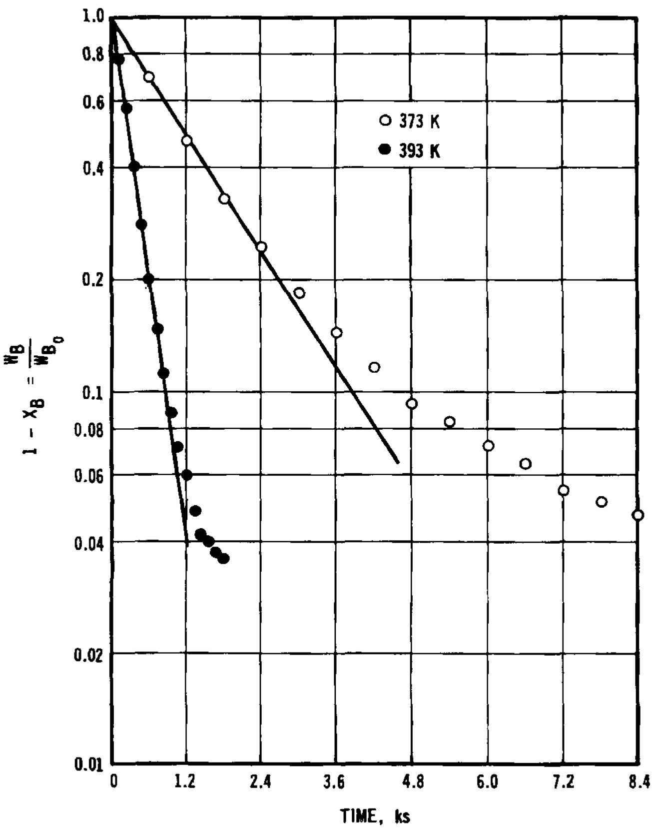

**Figure 4. First-order plot for decomposition of $NaHCO_3$ particles at 373 and 393 K.**
Particle dia. = $1.25 \times 10^{-4}$ m.

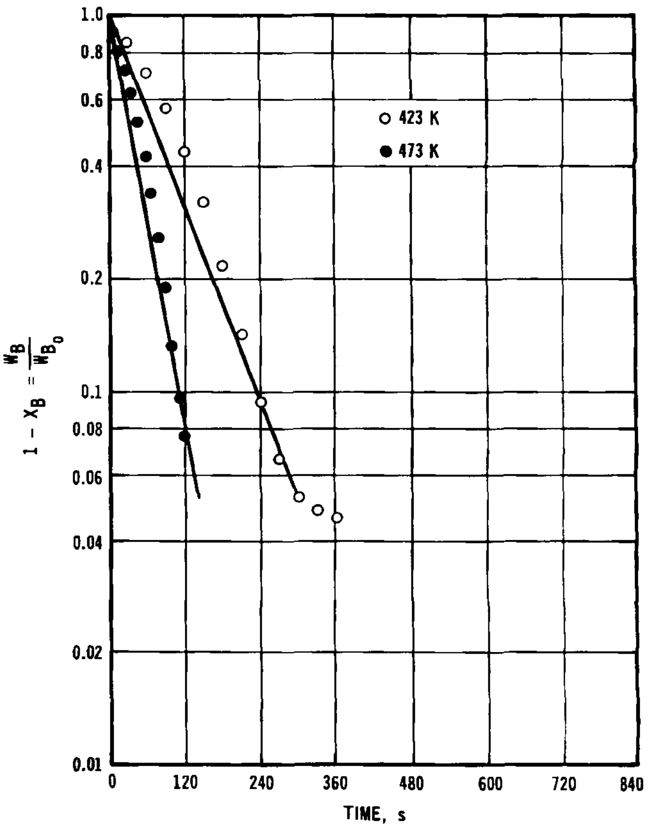

**Figure 5. First-order plot for decomposition of $NaHCO_3$ particles at 423 and 473 K.**
Particle dia. = $1.25 \times 10^{-4}$ m.

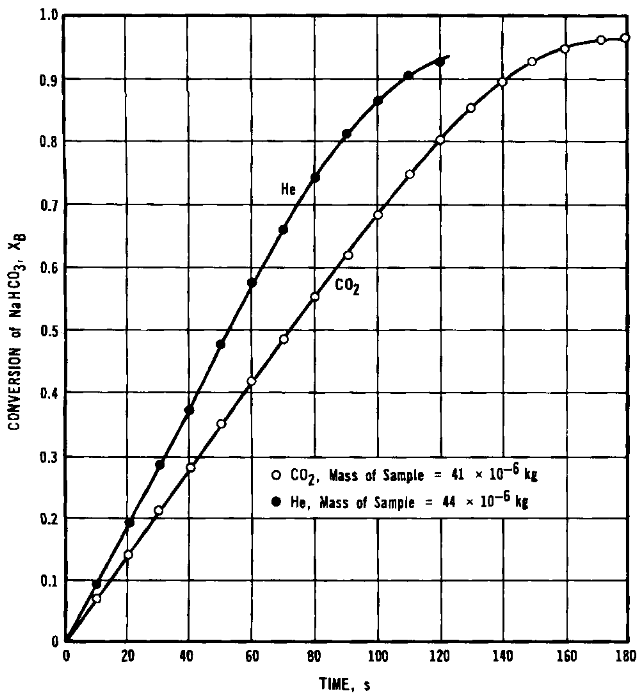

**Figure 6. Conversion-time curve at 473 K for decomposition of NaHCO$_3$ particles in CO$_2$ and in He.**

**Table 3. Decomposition Rate Constants**

| Temp. K | Rate Constant, $k_d$, s$^{-1}$ Constant Temp. Method | Temp. Increase Method |
|---|---|---|
| 373 | 0.00060 | 0.00070 |
| 393 | 0.0027 | 0.0039 |
| 423 | 0.0097 | 0.035 |
| 473 | 0.021 | 0.761 |

**Table 4. Decomposition Rate Constants by Method of Suzuki et al. (1978)**

| Heating Rate K/s | $T_{1/2}$ K | $\Delta T$ K | $E$ kJ/mol | $k_o$ $s^{-1}$ |
|---|---|---|---|---|
| 0.1 | 397.7 | 35.7 | 103 | $1.44 \times 10^{11}$ |
| 0.1 | 396.5 | 35.4 | 101 | $1.40 \times 10^{11}$ |
| 0.3 | 400.3 | 37 | 102 | $1.40 \times 10^{11}$ |
| 0.3 | 401 | 38 | 100 | $1.48 \times 10^{11}$ |

Our constant temperature data plotted according to Eq. 2 are shown for the four temperatures in Figures 4 and 5. The deviation from a straight line at 423 and 473 K, Figure 5, in the low conversion region is because the particle temperature is less than the thermocouple reading, as discussed earlier. This deviation disappears at 373 and 393 K, Figure 4. All the data deviate in the direction of a reduced rate at high conversions. This deviation could be due to the presence of a large amount of $Na_2CO_3$ product with a small amount of undercomposed $NaHCO_3$. While the mechanism is not clear, such a situation could hinder the elimination of $CO_2$ and $H_2O$ products from within the particle and reduce the decomposition rate. To test this hypothesis, decomposition runs were made with pure $CO_2$ as the gas stream flowing through the TGA. The conversion-time data are compared with those using helium for a run at 473 K in Figure 6 and show that the decomposition rate is considerably less in $CO_2$. Since complete decomposition is achieved with $CO_2$ there is no equilibrium limitation. Also the reaction can occur within the solid as well as on the surface between $NaHCO_3$ and gas.

The rate constants from the constant-temperature data can be evaluated from the slopes of the straight-line sections of the curves in Figures 4 and 5. The values are shown in the second column of Table 3.

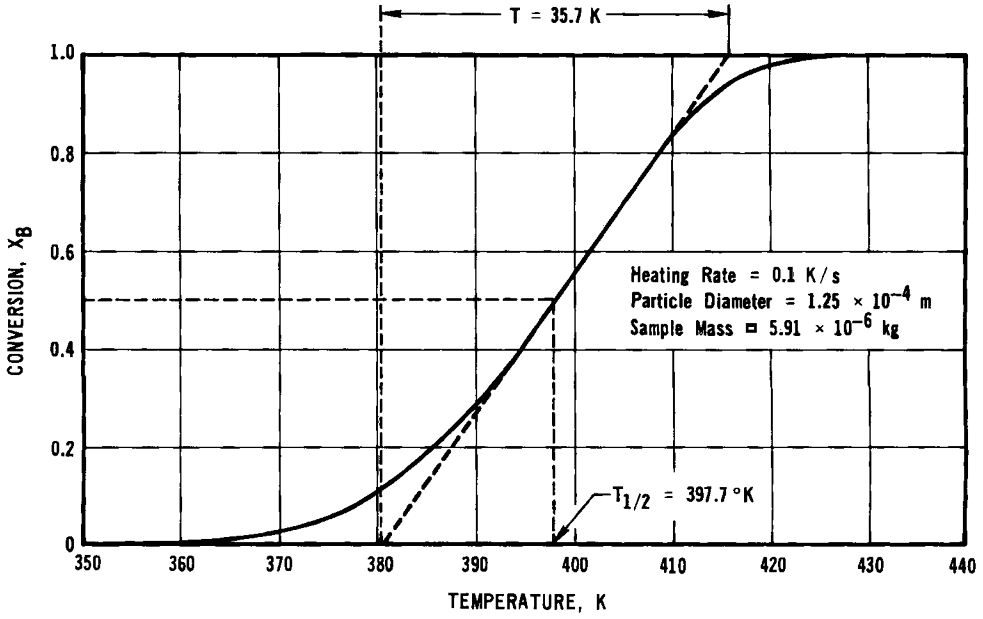

**Figure 7. NaHCO$_3$ decomposition, temperature-increasing run.**

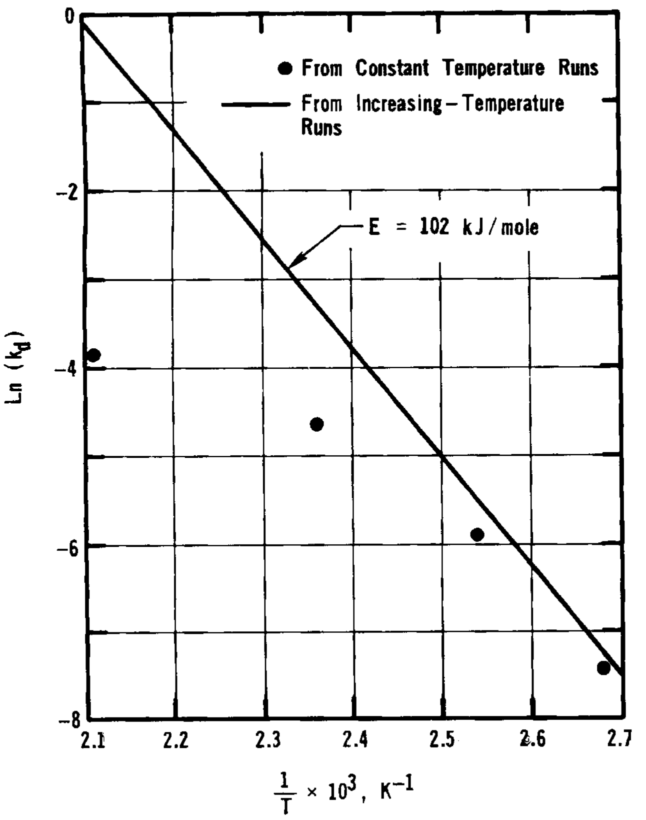

**Figure 8. Arrhenius plot of rate constant $k_d$ for $NaHCO_3$ decomposition.**

Rate constants were also calculated from the data for the rising-temperature runs. The method of Suzuki et al. (1978), which requires the temperature $T_{1/2}$, and slope $\Delta T$, at 50% conversion, was used to calculate the preexponential factor $k_o$ and the activation energy $E$. Conversion vs. temperature data, including the geometric construction for the Suzuki method, are shown in Figure 7 for a typical run. Two runs were made for a 0.1 K/s rate of temperature rise and two for a 0.3 K/s rate. The results, given in Table 4, for $k_o$ and $E$ are in good agreement. Finally, rate constants $k_d$ were calculated using these $k_o$ and $E$ values in the Arrhenius equation

$$k_d = k_o \exp(-E/R_g T) \tag{3}$$

These rate constants are shown in the third column of Table 3.

Figure 8 shows as points the rate constants from the constant-temperature measurements. The line is for rate constants calculated using the average values of 102 kJ/mol and $1.43 \times 10^{11} s^{-1}$ for $E$ and $k_o$ obtained by the temperature-increasing method. The two methods give results in reasonable agreement at low temperatures, but the constant-temperature $k_d$ values are much lower at the higher temperatures. This deviation is caused by the temperature difference between the particles and the thermocouple in the TGA. Further evidence for this explanation is that the higher temperature data deviate from the straight line relation required by the Arrhenius equation. For a fast reaction with a large heat of reaction, the temperature-increasing method is more suitable than constant-temperature experiments for obtaining intrinsic rate constants at high temperature levels.

Subramanian et al. (1972), reported an activation energy of 84 to 96 kJ/mol determined by differential thermal analysis.

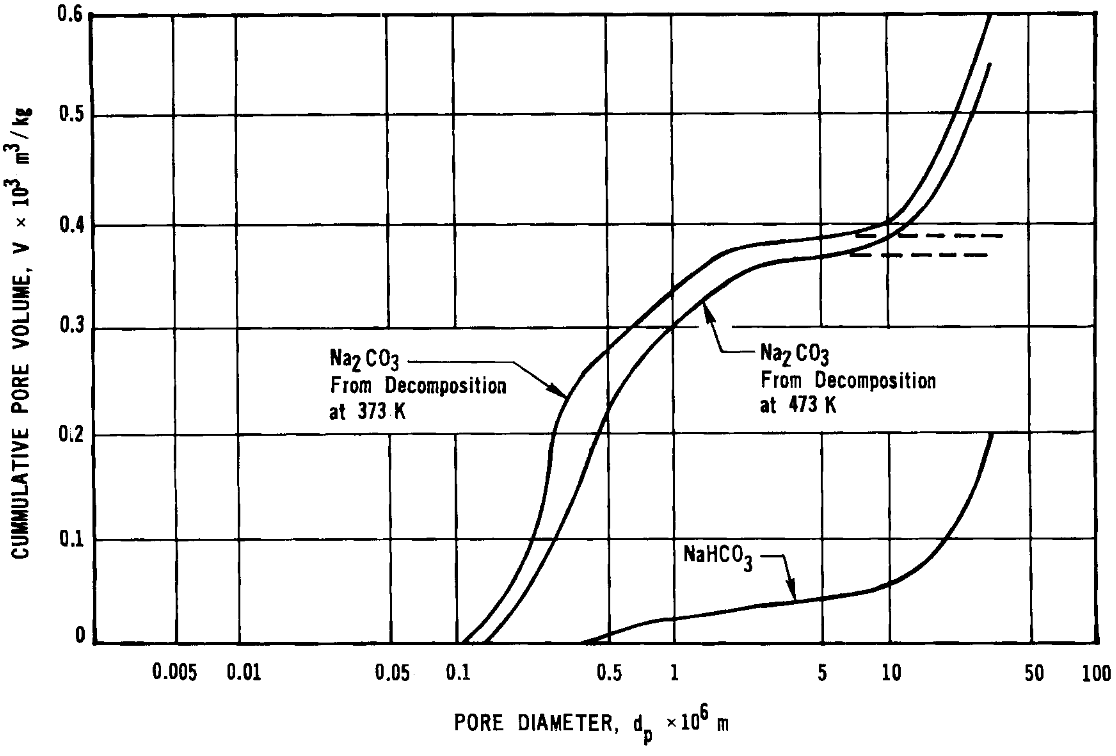

**Figure 9. Pore volume vs. pore diameter for $NaHCO_3$ particles before and after decomposition to $Na_2CO_3$.**
Particle dia. = $1.25 \times 10^{-4}$ m.

Van Dooren (1983), using differential scanning calorimetry, obtained values of $E$ from 99.1 to 111 kJ/mol. These results are in approximate agreement with our data. From constant-temperature measurements in air, Ifrim and Calistru (1974) found activation energies from 34 to 64 kJ/mol. These much lower results could be affected by the heat transfer limitation shown by our experiments at higher temperature.

## Pore-Volume Distribution of $NaHCO_3$ and $Na_2CO_3$

Figure 9 displays the cumulative pore volume vs. pore diameter data for $Na_2CO_3$ particles (avg. particle dia. = $1.25 \times 10^{-4}$ m), obtained by decomposition of $NaHCO_3$ at 373 and at 473 K. The large increase in pore volume as a result of thermal decomposition is striking. Microscopic examination (40× magnification) showed the $NaHCO_3$ particles to be composed of a dense assembly of flakelike grains. After decomposition to $Na_2CO_3$ the grains become smaller, more spherical in shape, and with much more intergrain space. The surface of the grains after decomposition was less smooth than before and contained numerous indentations.

The particles decomposed at 373 K had a little more pore volume, $0.39 \times 10^{-3}$ m³/kg, than those decomposed at 473 K ($0.37 \times 10^{-3}$ m³/kg). The large increase in volume for pores greater than $10^{-6}$ m dia. is likely to represent the volume between the particles of the sample rather than intraparticle pore volume. The distribution curves shown in Figure 10 indicate that the $Na_2CO_3$ particles obtained by decomposition at 373 K have more pore volume in the smaller pores than do particles decomposed at 473 K. Average pore diameters and surface areas, the latter obtained assuming an assembly of parallel noninterconnected pores, can be calculated from the equations

$$\bar{d}_p = \frac{\int_o^{V_t} (d_p)\, dV}{V_t} \tag{4}$$

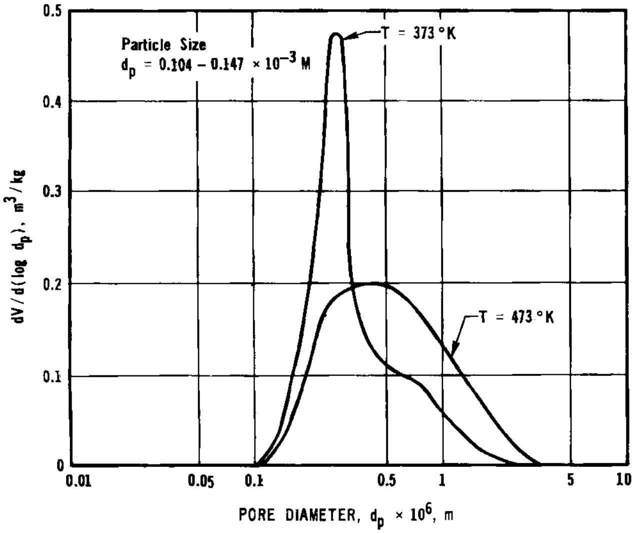

**Figure 10. Pore-volume distribution of $Na_2CO_3$ particles at 373 K and 473 K.**
Particle dia. = $1.25 \times 10^{-4}$ m.

and

$$S = \frac{4V_t}{\bar{d}_p} \tag{5}$$

Using the data of Figure 9 in Eqs. 4 and 5, the values for the particles decomposed at 373 K are $\bar{d}_p = 0.48 \times 10^{-6}$ m and $S = 3.3 \times 10^3$ m²/kg, while for particles decomposed at 473 K, $\bar{d}_p = 0.57 \times 10^{-6}$ m and $S = 2.6 \times 10^3$ m²/kg. The higher surface area of the $Na_2CO_3$ particles prepared at 373 K is expected to lead to a greater activity for reaction with $SO_2$.

## Acknowledgment

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## *Notation*

$d_p$ = pore diameter, m
$E$ = activation energy for decomposition of $NaHCO_3$, kJ/mol
$k_d$ = first-order rate constant for decomposition of $NaHCO_3$, $s^{-1}$
$k_o$ = preexponential factor for decomposition of $NaHCO_3$, Eq. 3, $s^{-1}$
$M_i$ = molecular weight of species $i$; $i = B = NaHCO_3$, $i = CO_2$, $i = H_2$
$R_g$ = gas constant, kJ/mol
$S$ = surface area per unit mass of $Na_2CO_3$ particle at $t = 0$, m²/kg
$t$ = time, s
$T$ = temperature, K
$T_{1/2}, \Delta T$ = temperature in temperature-increasing runs, Figure 7
$V$ = pore volume, m³/kg
$V_t$ = total pore volume, m³/kg
$W_B$ = mass of $NaHCO_3$-$Na_2CO_3$ particles at any time, kg
$W_{B_0}$ = mass of $NaHCO_3$ sample at $t = 0$, kg
$x_B$ = conversion of $NaHCO_3$

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