kaolinite bands with constant absorptivities and a sample particle size of 20 microns. It is essential to conduct a grind study on any mineral mixture prior to analysis in order to establish when the required particle size reduction for each component in the mixture has been achieved. The infrared analysis should be made only after absorptivity values have become constant and particle size has been checked. We have found that particle size reduction and the high degree of blending required for such small samples used in a pellet can be achieved using a Fisher automatic grinder equipped with an agate mortar and pestle. While the particular ball mill used in this work was excellent for grinding pure minerals, it produced poorly blended mixtures, as shown from grind studies conducted on synthetic mixtures and replicate sampling.

A limitation of the application of infrared spectrometry to mineral mixtures in coal is in the analysis of pyrite in the presence of high amounts of kaolinite (2). Both of the analytical bands of pyrite are overlapped considerably by kaolinite bands and amounts of pyrite as high as 20% might be undetected when kaolinite is present to the extent of 30% or greater. For this reason, no attempt was made to analyze synthetic mixtures containing both. Work is continuing to develop a satisfactory analysis for kaolinite–pyrite mixtures when kaolinite content is high.

CONCLUSIONS

Although this method for mineral analysis was developed for bituminous coal, it would be equally applicable to coals of different rank. The calibration data have been used in this laboratory for analysis of other materials connected with the mining and utilization of coal. For example, we have determined these minerals directly in coal mine refuse samples, which often have low organic matter content. The development of the analysis demonstrates that infrared spectrometry is a valuable tool for differentiating among various polymorphic forms of naturally occurring minerals and this makes it useful for a wide variety of mineralogical problems.

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Thermal Decomposition Kinetics of Silver Carbonate as Determined by the Infrared Disk Technique

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The infrared disk technique has been used to study the thermal decomposition kinetics of silver carbonate. The technique has been improved by the design and construction of a heated cell which permits continuous in situ quantitative analysis of infrared active reactants and products. Beer's law was found to be obeyed up to a concentration of at least 10 weight per cent silver oxide in silver carbonate. The activation energy for the thermal decomposition of inactive silver carbonate was determined to be 18,000 cal/mole for the induction period and 20,000 cal/mole for the decay period. The first order rate equation:

$$\ln C_{Ag_2CO_3} = -k(t - t_{induction})$$

satisfactorily described the decay period of the thermal decomposition. The first-order rate constants can be represented by the equation:

$$k(sec^{-1}) = 1.46 \times 10^{6} \exp(-20,000/RT)$$

The value of the activation energy for the decay period agrees well with that previously found for active silver carbonate. Agreement between the experimental rate of decomposition and the rate predicted by the Polanyi-Wigner equation provides circumstantial evidence in favor of the interface mechanism for the decomposition of inactive silver carbonate.

THE INFRARED DISK TECHNIQUE has been employed infrequently in the past for studying the kinetics and mechanism of the thermal decomposition of solids. This technique is not only an alternate to thermogravimetric analysis and gas pressure methods for studying decomposition kinetics but can provide in certain instances additional information about a reaction mechanism which is not obtainable by the other methods (1-6).

One goal of this work was to determine the feasibility of the infrared disk technique for studying the decomposition of metal carbonates, specifically, silver carbonate. Silver carbonate was chosen because an understanding of its thermal decomposition kinetics is essential in the development of a silver oxide-silver carbonate system as a regenerable chemisorbent for carbon dioxide (7). Furthermore, different preparations of silver carbonate exhibit significantly different decomposition kinetics (β , β). Preparations classified as active or normal are characterized in their decomposition kinetics by a short induction period followed by an acceleration and decay

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Table I.	Analysis	for	Silver	in	Silver	Carbonate	and	Silver
		0	xide P	rep	aration	s		

Sample	Theoretical, Ag, $\%$	Experimental, Ag, %
Ag_2CO_3 Ag_2O	78.24 93.10	$\begin{array}{c} 78.33 \pm 0.06 \\ 93.01 \pm 0.05 \end{array}$

period. The most predominant characteristic of the inactive or abnormal preparations as evidenced by isothermogravimetric analysis (ITGA), has been a rapid retardation in their decomposition rates after about 10% decomposition (9). Both active and inactive silver carbonate are reported to have the same chemical composition and crystallographic structure (9). The activation energy for the decomposition of inactive silver carbonate has not been reported previously; therefore it was of interest that it be determined and compared with the known values of the activation energy for active silver carbonate. It was also found possible in this study to obtain the activation energy for the induction period which occurs in inactive silver carbonate. The activation energy for the induction period has not been reported previously for either active or inactive silver carbonate.

EXPERIMENTAL

Materials. Inactive silver carbonate, precipitated from the silver-ammonia complex, and carbonate-free silver oxide were prepared as described previously (10, 11). Samples were analyzed gravimetrically for silver by decomposing the carbonate and oxide in a muffle furnace at 440° C (Table I). Samples were stored in the absence of light, but were transferred and handled under fluorescent lighting

Pellet Preparation. Calibration pellets were prepared from Ag₂O and Ag₂CO₃ that had been ground separately in agate mortars. Appropriate amounts were weighed to an accuracy of at least 0.1% on a Cahn M-10 Electrobalance and an analytical balance, and mixed together for 1 minute on a Wig-L-Bug. One hundred milligrams of this uniformly ground and mixed powder was then pressed at 5700 kg/cm² in a cylindrical die, 13 mm in diameter. The die was evacuated 1 minute before being pressed and the evacuation was continued throughout the pressing time of 3 minutes. The average calibration pellet weight was 100.14 mg with an average deviation of ± 0.33 mg. The pellets ranged in weight from 99.33 to 101.14 mg. The average thickness of the pellets as determined with a micrometer at several different positions on each pellet was 0.14 \pm 0.01 mm. The pellets ranged in thickness from 0.127 to 0.144 mm.

Pellets of oxide-free Ag₂CO₃ for kinetic experiments were ground, pressed, and weighed under conditions similar to the calibration pellets. The average pellet weighed 100.24 ± 0.20 mg with a range from 99.65 to 101.10 mg.

Equipment and Instrumentation. The Beckman IR-9 spectrophotometer was operated in the single beam mode with the second light chopper stopped. Stopping the second chopper prevented base line drift that can be caused at elevated temperatures by pellet and furnace emission. Since the separation of adjacent infrared bands was not a problem in this work, the slit width was set at the maximum value of 6 mm. The spectrophotometer was continuously purged with dry air.

Continuous, *in situ*, quantitative analysis of infrared active reactants and products of a decomposition reaction was made

possible by a heated cell especially designed and constructed for this work. The cell was constructed of stainless steel and could be heated to 500° C with the KRS-5 cell windows maintained at room temperature by the flow of cooling water. Temperature of the cell was controlled to $\pm 0.5^{\circ}$ C or better with the aid of a West Instrument Co. Model PSCR power supply and Model JYSCR temperature controller. For the isothermal decomposition experiments, temperature control was achieved within 4 minutes or less from the time power was initially applied to the furnace windings. Temperature was measured with a chromel-alumel thermocouple located near the pellet. The estimated uncertainty in the pellet temperatures is $\pm 1.2^{\circ}$ C. Further details of the cell construction are published elsewhere (12).

Procedure for Obtaining Calibration and Kinetic Data. The pellets were located in the infrared cell which was then evacuated to 10⁻⁵ torr, pressurized to 200 torr with dry helium (stated purity 99.9%) to improve temperature response, and finally sealed by means of a high vacuum valve. Since the decomposition of Ag_2CO_3 is an endothermic reaction, helium also prevented self-cooling of the pellet during a decomposition experiment. Decreasing the helium pressure to 50 torr was found to have no significant effect on the rate of silver carbonate decomposition. For kinetic experiments, approximately 300 mg of Linde 5A molecular sieve, contained in a stainless steel boat, was located in the water-cooled region of the cell before evacuation of the furnace. The purpose of the molecular sieve was to remove carbon dioxide formed by decomposition of Ag₂CO₃, and thereby prevent possible recombination of Ag₂O and CO₂. During the calibration procedure 100% transmittance at 500 cm⁻¹ on the IR-9 was established with oxide-free samples of Ag₂CO₃. The transmittance of pellets containing known amounts of Ag₂O was then recorded as per cent transmittance of the oxide-free samples.

RESULTS AND DISCUSSION

Several preliminary experiments were performed to determine the optimum procedure for determining the rate of decomposition of Ag₂CO₃. These experiments showed that suspending small amounts of Ag₂CO₃ in spectroscopic grade potassium bromide or twice recrystallized analytical grade potassium chloride was unsuitable for studying the decomposition kinetics. Various amounts of water were adsorbed on the predried halides while the pellets were being prepared. This water was apparently not removed completely by evacuation and catalyzed the decomposition of Ag_2CO_3 (7, 8, 13). When a matrix of spectroscopic grade thallium bromide was used, there was apparently a reaction between the matrix and Ag₂CO₃ at elevated temperatures and to a lesser extent even upon standing at room temperature. This reaction was evidenced by darkening of the pellet and a decrease in its transmittance with time.

The problem of interference by the matrix was overcome by the use of undiluted pellets of Ag_2CO_3 . However, this introduced other problems which would not have been encountered with a low concentration of Ag_2CO_3 suspended in a matrix. Although Ag_2CO_3 has some strong bands in the infrared region (14), they could not be used to determine the rate of decomposition for the following reason. There is a large difference in transmittance between Ag_2CO_3 and Ag_2O , the transmittance of Ag_2O being so much lower that when more than 10% Ag_2CO_3 decomposes, the pellet is practically opaque.

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Figure 1. Calibration plot of pellet transmittance vs. silver oxide concentration in weight per cent

However, for the region of less than 10% Ag₂CO₃ decomposition, the change in carbonate band intensity due to a relatively small decrease in carbonate concentration was completely overshadowed by changes in the base line due to oxide formation.

The rate of decomposition of Ag_2CO_3 can also be determined by measuring either the Ag_2O or CO_2 band intensities since the decomposition reaction proceeds as follows:

$$Ag_2CO_3(s) \leftrightarrows Ag_2O(s) + CO_2(g)$$

[This reaction was found (8) to be free from the complications of consecutive and side reactions except for a slight amount of oxide decomposition into metallic silver which has no effect on the primary reaction.] Carbon dioxide bands cannot be monitored because of the difficulty in quantitatively purging CO₂ from the spectrophotometer. Silver oxide has a broad absorption band centered around $530 \text{ cm}^{-1}(14)$. The peak maximum could not be used because the transmittance at 530 cm⁻¹ is very low and the instrument signal-to-noise ratio becomes too small above 3% decomposition. Therefore, for studying the decomposition, 500 cm⁻¹ was chosen as a compromise because there is more transmittance through the partially decomposed pellet at 500 cm⁻¹ than at 530 cm⁻¹ and enough sensitivity to Ag₂O remains. However, the use of one wavelength-i.e., 500 cm⁻¹-instead of scanning the Ag₂O band makes it difficult to use a standard technique such as the base-line density method to obtain rate data from transmittance vs. time of heating curves. The use of the one wavelength method introduced the problem of possible base-line changes due, for example, to heat treatment of the pellet and not to Ag₂O formation. The absorbance at 500 cm^{-1} was therefore compared to the absorbance found by the base-line density method at 530 cm⁻¹ which could be used up to about 3%Ag₂O. The comparison which was made by periodically scanning the Ag₂O band during an isothermal decomposition experiment did show that the absorbance at 500 cm⁻¹ was indeed proportional to the absorbance at 530 cm⁻¹ and therefore all subsequent data were obtained at 500 cm⁻¹.

Shown in Figure 1 is the calibration curve of log transmittance *vs.* weight % Ag₂O in Ag₂CO₃. The calibration was performed to obtain a linear relationship between transmittance and Ag₂O concentration and thus to estimate the relative extent



Figure 2. Isothermal decomposition plots of silver oxide concentration vs. time of heating

of decomposition of Ag_2CO_3 during a kinetic experiment-Furthermore, the experimental kinetic data provided evidence that the calibration could be used to estimate not only the relative amount but also the absolute amount of Ag_2O during kinetic runs because of the negligible effect of temperature alone on the optical transparency of the pellets. That the temperature effect is negligible is evident from the fact that reliable values for the induction period could be obtained from the rate data and from the fact that heating Ag_2CO_3 pellets for 3 hours below the decomposition temperature (about 90° C) did not change the optical transparency significantly (less than 4% change in transmittance).

It is apparent from the linearity of the calibration plot that Beer's law does apply up to at least 10% Ag₂O in Ag₂CO₃. The slope of the curve in Figure 1 and the pellet thickness can be used to obtain the absorptivity of Ag₂O at 500 cm⁻¹ by using the following form of Beer's law:

$$\ln 1/T = A = abc$$

where A is the absorbance, T the transmittance, a the absorptivity, b the pellet thickness in mm, and c the concentration in mg of Ag₂O/mg of Ag₂CO₃. From the pellet thickness of 0.14 mm and the slope of the curve in Figure 1 [the slope was converted from (per cent Ag₂O)⁻¹ to (mg Ag₂O/mg Ag₂CO₃)⁻¹] the absorptivity calculated for Ag₂O is 260 mg Ag₂CO₃/mg Ag₂O mm. The standard deviation in the absorptivity is ± 40 mg Ag₂CO₃/mg Ag₂O mm for a 95% confidence interval.

From transmittance vs, time of heating curves and with the aid of the calibration curve, the concentration of Ag₂O vs, time of heating curves of Figure 2 were constructed. Figure 3 is a typical transmittance vs, time of heating curve. The small initial decrease in transmittance followed by an increase in transmittance (Figure 3) at the start of the decomposition experiment was typical of the kinetic runs. This was probably due to fogging of the pellet resulting from a small amount of water condensing on the colder pellet followed by desorption of the water or other adsorbed gases from the pellet. Changes in the optical transparency of pellets due to heat treatment and other solid state anomalies have been observed by others (1, 15). Since the initial decrease in trans-

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Figure 3. Representative plot of transmittance of a silver oxide-silver carbonate pellet vs, time of heating (decomposition temperature 126° C)

mittance of our pellets was always less than 8%, no detailed study of the phenomena was undertaken. However, since the transmittance did decrease initially and then increase, the concentration of Ag₂O was taken as zero up to the time when the transmittance reached a maximum after the initial decrease. This choice prevented the need for plotting the unrealistic case where the Ag₂O concentration became negative. Time zero (for kinetic data analysis) was taken when the power was first applied to the heater windings of the infrared cell.

The decomposition curves of active preparations of Ag₂CO₃ are characterized in one respect by an induction period which becomes increasingly more apparent as the decomposition temperature is lowered (8). An induction period is also present in inactive Ag₂CO₃, as evidenced by the decomposition curves (Figure 2). An induction period was not observed previously by ITGA on inactive Ag₂CO₃ (9). However, for the ITGA studies the decomposition was carried out at higher temperatures than were employed in this work (i.e., above 200° C); therefore, the induction period was probably too short to be detected. The duration of the induction period was taken as the time required for the transmittance to begin decreasing from the maximum after the initial "dip" in transmittance vs. time of heating curves (Figure 3). A semilog plot of $t_{induction}$ in minutes vs. the reciprocal of the absolute temperature was then constructed (Figure 4) and from the slope of this plot an activation energy of 18,000 cal/mole for the induction period of inactive Ag₂CO₃ was calculated. The estimated uncertainty in the activation energy is ± 3000 cal/mole.

Since the acceleratory period for the thermal decomposition of inactive Ag_2CO_3 is very short (Figure 2), no attempt was made to analyze this portion of the decomposition curve for the activation energy.

To obtain rate constants for the thermal decomposition of inactive Ag_2CO_3 during the decay period, the following first-order rate equation was employed:

$$\ln C_{Ag_2CO_3} = -k(t - t_{induction})$$

where $C_{Ag_2CO_3}$ is the weight fraction of Ag₂CO₃ in the pellet, k is the first-order rate constant in minutes⁻¹, t is the time of heating in minutes, and $t_{induction}$ is the duration of the induc-



Figure 4. Activation energy plot for induction period of decomposition of inactive silver carbonate

tion period in minutes. The fit of the first-order equation to the decomposition data for the decay period is shown in Figure 5. The first-order rate constants were obtained from the slopes of the linear equations of $\ln C_{Ag_2CO_3}$ as a function of $t - t_{\text{induction}}$ which in turn was derived from the kinetic data by the method of least squares. The first-order rate constants were then used to construct an Arrhenius activation energy plot (Figure 6). The activation energy for the decay period of the thermal decomposition of inactive Ag_2CO_3 found from the slope of the latter plot is 20,000 cal/mole. The standard deviation of the activation energy is 3600 cal/mole for a 95% confidence interval. The first-order rate constants can be represented by the equation:

$$k(\sec^{-1}) = 1.46 \times 10^6 \exp(-20,000/RT)$$

The activation energy found by Spencer and Topley (8) for the decay period of the thermal decomposition of active Ag_2CO_3 is 22,900 cal/mole. Their value was obtained by ITGA and agrees within experimental error with the value found in this study for inactive Ag₂CO₃. The agreement between the values for the decomposition of active and inactive Ag₂CO₃ indicates that the rate controlling step during the decay period is the same in both types. Furthermore, the activation energies for the induction and decay periods during the thermal decomposition of inactive Ag₂CO₃ is comparable within experimental error to the heat of decomposition of Ag₂CO₃-i.e., 19,200 cal/mole at 500° K (16). This suggests that the activation energy for the recombination of Ag₂O and CO_2 is practically without energy of activation, in agreement with Zawadski (17); and the rate controlling step in the decomposition of inactive Ag₂CO₃ during the induction or nucleation and decay periods is probably the resistance to chemical reaction and is not, for example, diffusion of CO₂ through Ag₂O during the decay period.

If it is assumed that the decomposition of Ag_2CO_3 originates on the surface of the pressed disk, and that the Ag_2O/Ag_2CO_3 interface migrates into the pellet at a constant linear rate during the decay period, then the Polanyi-Wigner equation (18)

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Figure 5. Representative plots showing correlation between experimental rate data and first order rate law for the decay period of thermal decomposition of inactive Ag_2CO_3

Concentration unit for $C_{Ag_2 \mathbb{CO}_3}$ is weight fraction

can be used to predict a reaction rate. An almost linear relationship between Ag₂O concentration and time was apparent from the higher temperature decomposition curves (e.g., see dotted line through the decomposition curve at 148° C in Figure 2). The reaction rate obtained from the slope of the dotted line was compared with the rate predicted by the Polanyi-Wigner equation in the following form:

$$dx/dt$$
 (molecules/cm²-sec) = $-\tilde{N}\nu \exp -E/RT$

In this equation, dx/dt represents the calculated reaction rate, \tilde{N} the number of molecules of Ag₂CO₃ per cm² of surface, ν the frequency of vibration in sec⁻¹, *E* the experimental activation energy for the decay period in cal/mole, and *R*, *T* have their usual significance. Letting $\nu = 10^{13} \text{ sec}^{-1}$ the calculated rate at 148° C is 9.33 $\times 10^{17}$ molecules/cm²-sec or 2.47 $\times 10^{18}$ molecules/sec for the disks with a geometrical area of 2.65 cm².

If the decomposition reaction during the decay period is assumed to occur at sites distributed at random throughout the pressed disk and not on surface sites alone (that the reaction occurs only at surface sites is assumed when using the Polanyi-Wigner equation), to obey a first-order rate law, and finally to have a normal frequency factor, then the following equation can be employed to predict a reaction rate:

$$dx/dt$$
 (molecules/sec) = $-A \exp(-E/RT) x$

where A is the frequency factor in seconds⁻¹, E is the experimental activation energy for the decay period in cal/mole, x is the concentration of Ag₂CO₃ molecules remaining in the 100-mg disk when dx/dt is evaluated, and R, T have their usual significance. If A has a normal value of 10^{13} sec⁻¹ and x equals 2.18×10^{20} molecules of Ag₂CO₃ (since only 5% decomposition was studied, x was calculated from the initial pellet weight), then the calculated reaction rate at 148° C is 8.74×10^{22} molecules/sec.

The experimental rate at 148° C calculated from the slope of the dotted line (Figure 2) is 1.51×10^{16} molecules/sec. Since the difference between the rate calculated by the Polanyi-Wigner equation and the experimental rate does not exceed two orders of magnitude and the rate calculated for the



Figure 6. Activation energy plot for decay period of thermal decomposition of inactive Ag_2CO_3

random case is six orders of magnitude greater than the experimental rate, then it may be inferred that the decomposition conforms to the Polanyi-Wigner expression—i.e., is "normal" (19). This conformity provides circumstantial evidence in favor of the interface mechanism and against, for example, spontaneous decomposition at points distributed at random throughout the crystal.

The experimental data appeared to follow a first-order rate law better than a zero-order law, especially at the lower temperatures. This does not mean that inactive Ag₂CO₃ cannot decompose by an interface mechanism for the following reasons. When only 5% decomposition is studied, it is very difficult to determine the order of reaction. This difficulty is illustrated by the fact that when our decomposition data were analyzed assuming a zero-order rate law, the decay period activation energy of 19,900 cal/mole (with \pm 3600 cal/mole uncertainty) is obtained which is almost identical with the activation energy of 20,000 cal/mole obtained when assuming a firstorder rate law. Second, the possibility that the number of surface sites is changing as the decomposition proceeds is not taken into consideration by the Polanyi-Wigner equation and therefore a decrease in the number of surface sites during decomposition will result in a decrease in the decomposition rate with time such as that shown by the low temperature decomposition experiments (Figure 2).

The uncertainty in assigning a reaction order to the decay period, when studying only 5% decomposition, would remain in the case of inactive Ag_2CO_3 even if a greater extent of reaction were studied. The difficulty in assigning a reaction order to the decay period of inactive Ag_2CO_3 arises because the reaction rate becomes very slow after approximately 10% decomposition and a different rate determining step comes into play (9). Consequently, any rate law which the decomposition data obeyed during the decay period would apply only up to 10% decomposition. Therefore, the difficulty in assigning a reaction studied would still remain.

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