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Roche, S.L.

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THERMAL DECOMPOSITION OF MAGNESIUM AND CALCIUM
SULFATES

Susan L. Roche
(Ph.D. thesis)

April 1982

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Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Materials Science and Mineral Engineering
University of California
Berkeley, CA 94720

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Susan L. Roche

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Mineral Engineering
University of California, Berkeley, California 94720

ABSTRACT

The effect of catalyst on the thermal decomposition of MgSO_4 and CaSO_4 in vacuum was studied as a function of time in Knudsen cells and for MgSO_4 , in open crucibles in vacuum in a Thermal Gravimetric Apparatus. Platinum and Fe_2O_3 were used as catalysts. The CaSO_4 decomposition rate was approximately doubled when Fe_2O_3 was present in a Knudsen cell. Platinum did not catalyze the CaSO_4 decomposition reaction. The initial decomposition rate for MgSO_4 was approximately 5 times greater than when additives were present in Knudsen cells but only about 1.5 times greater when decomposition was done in an open crucible.

To determine whether or not the equilibrium pressures of SO_2 , O_2 , and SO_3 are approached in the powder bed when MgSO_4 is heated in vacuum, the effect of sample size (powder bed depth) and temperature on the initial decomposition flux from open crucibles was studied. At 1123 K the initial decomposition flux is approximately bed depth independent. This bed depth independence indicates that a metastable equilibrium is established when SO_3 chemisorption pressures are 10^{-1} or 10^{-3} times the equilibrium values calculated from alternate sources of thermochemical data. The maximum value for the enthalpy of the metastable equilibrium, $\text{MgSO}_4(\text{s}) = \text{MgO}(\text{s}) + \text{SO}_3(\text{g})$, was calculated to

be 77.7 Kcal/mole. At 1023 K the initial flux is approximately linearly dependent on bed depth. This linear dependence indicates that at lower temperatures, the decomposition reaction approaches complete irreversibility. The molar flux of SO_3 per cm^2 of total MgSO_4 surface area is either 5.5×10^{-8} or 5.5×10^{-6} times the flux that would be obtained for a thermodynamically reversible reaction, depending on choice of thermochemical data. The minimum value for the activation enthalpy for the irreversible process is 58.4 Kcal/mole.

It is shown that because the contracting sphere model and similar models which are commonly used to analyze decomposition reactions neglect the possible establishment of equilibrium in a sample powder bed, the apparent agreement of data with such models may often be fortuitous.

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Introduction

Metal sulfate decomposition reactions have been under recent investigation for a variety of potential applications. They have been suggested as possible oxygen producing steps in thermochemical hydrogen generation cycles¹, for the possible storage of solar thermal energy², and are used to produce various sulfides and oxides in the ceramic industry.

The gaseous decomposition products are not the same for all metal sulfates. For sulfates that decompose at relatively low temperatures the principal gaseous decomposition product is SO_3 . For sulfates like MgSO_4 and CaSO_4 , which decompose only at higher temperatures, the expected principal reaction at equilibrium is

However, evolution of the SO_2 and O_2 from the sulfate ion in the lattice may be kinetically hindered so that the gaseous SO_2 and O_2 may evolve through an intermediate SO_3 molecule. Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, is reported to decompose to a mixture of $\text{SO}_2(\text{g})$, $\text{SO}_3(\text{g})$, $\text{O}_2(\text{g})$, and $\text{Al}_2\text{O}_3(\text{s})$ ³. The decomposition rate appears to be accelerated by the addition of various metal oxides⁴. Strontium and barium sulfates (SrSO_4 and BaSO_4) reportedly decompose to $\text{SO}_2(\text{g})$, $\text{O}_2(\text{g})$ and the metal oxide^{5,6} as does CaSO_4 while the gaseous decomposition products from MgSO_4 depend on the effusion orifice area⁷. Unfortunately, the above experiments and others⁸ were not conducted under similar conditions so they must be considered individually.

Attention in the present study is centered on MgSO_4 decomposition after measurements were also made on CaSO_4 decomposition.

In 1954 Pechkovsky studied the decomposition of MgSO_4 in flowing oxygen, air, or dry nitrogen.⁹ He concluded that MgSO_4 decomposed by the two step path

As the oxygen concentration in the flowing gas decreases, the fraction of SO_3 in the product gas decreases although the overall rate of decomposition is unchanged with decreasing oxygen concentration in the flowing gas. Addition of small amounts of Fe_2O_3 and CuO increase the rate of decomposition, but SiO_2 additions do not.

A metal oxide could react with MgO

where $n\text{MgO} \cdot m\text{MeO}$ is a silicate, ferrite, etc. of magnesium. But Pechkovsky concludes that the increased decomposition rate of MgSO_4 with CuO and Fe_2O_3 additives is not a consequence of reaction (4) but results from the catalytically increased rate of reaction (3). The experimental evidence that supports this conclusion is 1) very small amounts of additive (5 weight percent) accelerate MgSO_4 decomposition; 2) decomposition is accelerated considerably in the presence of Fe_2O_3 and CuO , which are catalysts for reaction (3), and practically no

acceleration occurs in the presence of SiO_2 which does not catalyze SO_3 decomposition; 3) when Fe_2O_3 or CuO are present the rate of MgSO_4 decomposition increases considerably with a decrease in oxygen concentration in the gas passing over the sulfate. When MgSO_4 is decomposed in flowing gases the gaseous products are continuously removed from the reaction zone and there is insufficient time for equilibrium according to (3) to be reached. With catalytically active substances present, reaction (3) is accelerated and approaches equilibrium which, Pechkovsky argued, results in an increase of the total rate of MgSO_4 decomposition. Similarly, if an additive that increases the rate of (3) is present there is an increase in the total rate of decomposition if the concentration of oxygen in the flowing gas is decreased. According to Pechkovsky, this explains why a decrease in the oxygen concentration in the gas passed over pure MgSO_4 has little effect on the decomposition rate, although the ratio of product gases changes.

This explanation seems contradictory; if an increase in (3) through catalysis increases the decomposition rate, a decrease in the fraction of SO_3 in the product gas with a decrease in the concentration of oxygen in the flowing gas seems to indicate an increase in (3) which would then increase the decomposition rate. The additives may, in fact, be affecting both (2) and (3).

The effect of sample size and degree of pelletization on the kinetics of MgSO_4 decomposition in air was studied by Hulbert¹⁰. Since the molar volume of the solid product is less than that of the MgSO_4 , a discontinuous solid product layer is left on the surface and diffusion

through the solid MgO cannot be rate limiting. Hulbert concluded that the kinetics of the decomposition reaction best fit a contracting sphere model which assumes that nucleation takes place rapidly and that the rate of the reaction is proportional to the surface area of unreacted material. The apparent activation energy for decomposition, independent of processing pressure, is 74.5 Kcal/mole which compares well to the heat of dissociation of MgSO_4 of 67.5 ± 7.0 Kcal/mole that Hulbert reports. The rate constant for the reaction depends on the sample mass, which suggests the existence of a reversible reaction which limits the kinetics of the forward process. Local concentrations of $\text{SO}_3(\text{g})$ may accumulate at the reaction zones if the SO_3 is not able to escape through the powder compacts quickly.

Hulbert concludes that the activation enthalpy of 74.5 Kcal/mole is too high for diffusion of gas through pores in the powder compacts to be rate controlling. This argument is not valid because the apparent activation enthalpy agrees with the reported heat of decomposition to within its ± 7 kcal uncertainty. This result is predicted for effusion controlled decomposition rates.¹¹ But Hulbert's rates of weight loss are inversely proportional to sample size, which suggests that a certain internal pressure of SO_3 is quickly developed throughout the sample and is maintained until the final stages of the reaction. If effusion through the porous MgO layer on each MgSO_4 particle limited the decomposition rate, the rate would decrease more rapidly with time of decomposition. Probably the decomposition rates are limited by the rate of gas phase diffusion of SO_3 away from the powder bed. This step of decomposition is often rate limiting¹² unless decomposition is carried out in vacuum or in a rapidly flowing stream

of gas.¹³ Because sample dimensions are not provided by Hulbert, net fluxes from his powder beds cannot be calculated.

Recent investigations of the decomposition of CaSO_4 and MgSO_4 in vacuum have been performed by Lau, Cubiccioti and Hildenbrand⁷. Torsion effusion and simultaneous weight loss were used to measure the decomposition pressures and vapor molecular weights. They report that the initial step in the decomposition process is the evolution of an SO_3 molecule from the lattice. The SO_3 molecule subsequently decomposes to SO_2 and O_2 on the sample and cell surfaces. By varying the effusion orifice area (the effusing vapor species are orifice size dependent) Lau et al. determined that both steps are kinetically hindered. When MgSO_4 is decomposed in a sample cell with an orifice diameter of ~ 1.5 mm or larger, SO_3 is the principal gaseous product. When the orifice diameter is ~ 1 mm or less the primary gaseous decomposition products are SO_2 and O_2 . With the addition of a small amount of Fe_2O_3 the gaseous decomposition products become SO_2 and O_2 with all the orifices used.

Lau et al. conclude that because for small orifices the uncatalyzed decomposition products are SO_2 and O_2 only, the conversion of SO_3 to SO_2 and O_2 on the surfaces is slow, and the gaseous decomposition products approach equilibrium only when the residence time in the Knudsen cell is increased and the desorbed SO_3 converts to SO_2 and O_2 by wall collisions and/or collision with the product MgO layer. The Fe_2O_3 surface is reported to act as a catalyst only on the decomposition of SO_3 to SO_2 and O_2 through a cyclic oxidation-reduction process.

The decomposition products of CaSO_4 are not orifice size dependent⁷. Lau et al.'s data show the gaseous decomposition products are SO_2 and O_2 , indicating that SO_3 decomposition is not kinetically hindered in CaSO_4 decomposition. If a catalyst is acting only on the decomposition of SO_3 , an increase in the decomposition rate of CaSO_4 would not be expected.

Further studies by Knittle, Lau and Hildenbrand on MgSO_4 with other catalysts¹⁴ indicate that there is no dependence on the particle size of the catalyst. The authors conclude that the initial step of decomposition, evolution of SO_3 from the lattice, is not catalyzed.

Similar, but less detailed, Knudsen-weight loss studies have been conducted on CaSO_4 and MgSO_4 by Jagannathan, Powell and Wyatt¹⁵. Their data on decomposition pressures indicate a slight dependence on cell material. Pressures recorded from platinum cells are slightly higher than pressures recorded from spinel cells with platinum lids.

Calculations have shown, however, that the pressures reported by Lau et al. in the MgSO_4 effusion cell studies could not be obtained if only gaseous SO_3 decomposition were being affected by the catalyst¹⁶. To increase the gaseous mass flux beyond that characteristic of the SO_3 equilibrium pressure requires catalysis of some reaction step prior to desorption of SO_3 from the reactant or solid reaction product surface.

This situation raises the question of whether the catalyst remains effective after the product oxide particles form and separate the solid catalyst from the metal sulfate interface. Previously, only the effect of catalysts on the initial rates of MgSO_4 decomposition in vacuum have been reported. In this study the effect of catalysts on

MgSO_4 and CaSO_4 decomposition rates were measured as functions of time in Knudsen effusion cells and, for MgSO_4 , in open crucibles to answer this question. Past studies of MgSO_4 and CaSO_4 decomposition have provided little information on the morphology of product oxides and none on the influence of the catalysts on that morphology or on the distribution of catalyst particles and product particles after reaction. X-ray diffraction, BET measurements, and scanning electron microscopy were employed to obtain such information, which might provide clues to the means by which the catalysts influenced the decomposition rates.

Catalysts proved to have relatively little effect on rates of open crucible decompositions. In the open crucible study of MgSO_4 decompositions attention, therefore, was centered on a second important question: whether or not equilibrium was approached in the powder beds when they are heated in vacuum.

A recent study of calcite decomposition showed that samples of different bed depths yield the same initial total decomposition fluxes, which indicated that a metastable equilibrium is set up in the beds at CO_2 pressures only $\sim 10^{-3}$ times the pressures of the equilibrium decomposition reaction.¹⁷ This is an interesting observation. Review articles¹⁸⁻²⁰ do not mention other examples of this behavior in vacuum, but the lack of examples may simply reflect the fact that rates of decomposition reactions are commonly reported in terms of weight losses per unit time or of fraction of reaction completed per unit time. Sample dimensions are often not specified and flux densities of the gaseous product that leaves the powder bed, from which the effective

product gas pressure at the surface of the bed could be calculated, are not reported. If MgSO_4 powder decomposition shows behavior like that of calcite, the establishment of metastable equilibrium gas pressures in powder beds probably can be expected to be a common occurrence for decomposition reactions in vacuum.

Experimental Procedure

Figure 1 is a schematic drawing of the weight loss apparatus. An alumina tube (inside diameter 6 cm) served as the experimental vacuum chamber. Two furnaces were used (at different times) to heat the experimental chamber; one with Pt 40% Rh windings and a Eurotherm temperature controller and another with Kanthal windings and an Athena temperature controller. A zone, 5 cm long, which was isothermal to ± 2 K, was located in the furnace to insure that the sample cell would be at a constant temperature. The sample crucible was held in an alumina pan and suspended by a platinum wire on a quartz rod connected to the microbalance. The sample cells were made of 99.5% Al_2O_3 . The inside diameter was 6.8 mm, the cell depth was 3 cm. The Knudsen lid had a 0.52 mm diameter orifice and was 1 mm thick.

The sample chamber was evacuated with a mechanical roughing pump and a water cooled diffusion pump. A background pressure of 3×10^{-2} Pa was obtained before each experiment. During heating the product gases were continuously pumped out of the chamber, and the gage reading typically ranged from 4×10^{-2} to 5×10^{-1} Pa.

Chromel-Alumel and Pt-Pt 10% Rh thermocouples were used to measure the temperature of the sample chamber and to control the furnaces. Temperatures were monitored by a digital display unit. Temperatures in the crucible were calibrated by measuring the fluxes of copper, tin and sodium chloride at various temperatures. Appendix I shows the temperature calibration plots of $\ln(\text{flux})$ as a function of $1/T$. The equilibrium vaporization data has also been plotted on the same figures. From a least squares analysis of the experimental data

the enthalpy of vaporization is calculated. For example, experimentally $\Delta H_v = 70$ kcal/mole was found for copper in the temperature range 1420 to 1640 K. This agrees well with the accepted value, 75 kcal/mole, when a correction factor of 9 degrees is added to each of the experimental datum.

A Cahn 1000 microbalance was used to continuously monitor the weight change of the sample. This equipment has been described previously¹⁷. The microbalance has a selection of full scale ranges. The 10 milligram full scale range was most often used with the 1 milligram full scale range being employed for measurements of very low fluxes and the 100 milligram full scale range for high fluxes. The microbalance was equipped with an automatic range expander so that rebalancing during the experiment was not necessary. A Linear strip chart recorder was used to record the weight loss as a function of time.

Samples

Mallinckrodt Analytical Reagent grade $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystals were used to provide MgSO_4 for the experiments (see Appendix II for characteristics). The samples were heated at 423 K in vacuum until the sample weight no longer changed with time. An additional small weight loss which mass spectrometer analysis showed to be CO_2 was noted around 610 K. Surface area measurements were made using the BET method. The method and apparatus for measuring surface areas have been described elsewhere.²¹ Optical and scanning electron microscope observations showed $\sim 90\%$ of the $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ powder particles had external dimensions of ~ 2 mm by $\sim (0.5 \text{ mm})^2$.

The water in the crystal was not bound very tightly. Attempts to measure the surface area and observe the $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ particles in the SEM (under vacuum) changed their appearance from transparent to white and reduced each particle size. These phenomena were also observed when the crystals were purposely baked to remove the water. It was not possible, therefore, to accurately measure the surface area of the initial $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystals.

The powder samples were also analyzed by x-ray diffraction before and after vacuum decomposition. The sample was placed in an aluminum holder and irradiated in a Picker x-ray diffractometer using $\text{Fe K}\alpha$ radiation, 14mA, 40 kV, 2° $2\theta/\text{min}$, $\tau = 3$ sec and 200 cps scans were made from $2\theta = 20^\circ$ to 120° , which covers the major peaks.

Mallinckrodt Analytical reagent grade $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ powder was used to provide the CaSO_4 used (see Appendix II).

For catalysts, -100 mesh platinum powder from Apache Chemicals Inc. and -325 mesh platinum black from Wesgo were used as well as Allied Chemical Reagent grade Fe_2O_3 powder (see Appendix II).

Initially dynamic weight loss runs were performed. The sample cell was loaded with 0.069 g of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or 0.106 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and placed in the vacuum chamber. The sample depth was approximately 3 mm. The powders were loosely packed. The packing density of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was $9.7 \times 10^5 \text{ g/m}^3$, compared to a theoretical density of $1.68 \times 10^6 \text{ g/m}^3$. The packing density for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was $6.3 \times 10^5 \text{ g/m}^3$, compared to a theoretical density of $2.32 \times 10^6 \text{ g/m}^3$. The packing density of $9.7 \times 10^5 \text{ g/m}^3$ for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ yields a porosity of $\sim 73 \%$. After the

TGA apparatus was balanced and the chamber evacuated, the chamber was heated to 423 K and held for several hours to remove water from the sample and desorb gases from the chamber walls.

When no further weight loss occurred at 423 K and the vacuum level was below 7×10^{-2} Pa, the furnace was ramped at 5 degrees/minute to the desired temperature and the weight loss was measured as a function of temperature. Dynamic experiments were also done for $\text{MgSO}_4 + 2.8$ mole percent (m/o) Fe_2O_3 (Fig. 2), $\text{MgSO}_4 + 2.8$ m/o Pt, $\text{CaSO}_4 + 2.8$ m/o Fe_2O_3 and $\text{CaSO}_4 + 2.8$ m/o Pt. These experiments were done maintaining a constant amount of MgSO_4 and CaSO_4 . The sample depth did not vary from those of the uncatalyzed experiments. From these experiments an experimental range for isothermal runs was picked.

The isothermal runs were set up in the same manner as the dynamic runs, but, instead of ramping the furnace to the desired temperature, it was heated as quickly as possible (in ~ 10 to 12 minutes) to the isothermal decomposition temperature. After reaching the desired temperature the sample was allowed to decompose in vacuum until no further weight loss was observed. A mass balance was used to confirm the weight loss at 100 ± 2 % of theoretical decomposition.

The samples were carefully weighed before being loaded in the microbalance. A constant $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ weight was used (within 0.2%) for each experiment.

The catalysts were mechanically mixed with the samples and were all added in an amount to insure that they were 2.8 m/o of the sample. The platinum black and Fe_2O_3 coated the particle surfaces evenly. The coarser platinum powder did not adhere to the sulfate surfaces at all so it was more difficult to insure a good mixture.

Isothermal experiments were carried out in an open crucible (diameter = 6.8 mm) and with an orifice (diameter = 0.52 mm). Some open crucible experiments were done with different size samples to determine if sample bed depth affected the decomposition rate.

When an experiment was completed the sample was removed from the decomposition chamber and immediately put in a BET sample holder and heated at 400 K for one hour. The surface area of the fully decomposed sample was measured, and scanning electron microscope observations and x-ray diffraction analyses were done on the samples.

MgSO_4 in a thick powder bed was approximately half decomposed isothermally at 1123 K in a large (1.5 cm diameter by 3 cm depth) open crucible. Surface areas of samples from the top and bottom of the bed were measured. Initially, the MgSO_4 samples have surface area of $\sim 7 \text{ m}^2/\text{g}$ while after total decomposition the product MgO has surface area of $\sim 20 \text{ m}^2/\text{g}$. The top samples from the $\sim$ half decomposed MgSO_4 measured $\sim 11.2 \text{ m}^2/\text{g}$ and the bottom measured $\sim 10.5 \text{ m}^2/\text{g}$. These results indicate that the sample decomposes uniformly throughout the depth of the bed.

Most of the experiments were conducted twice. The results were always reproducible, consequently there is a high level of confidence in the data.

Mass spectrometric measurements of MgSO_4 and CaSO_4 decomposition products were made using a quadrupole mass spectrometer attached to a TGA apparatus and in a magnetic sector mass spectrometer (in which ionized particles are deflected by a magnetic field through a 60° arc from the sample source to the instrument detector). To

determine if any H_2O was coming from the sample the H_2O peak was monitored during heat up and at the decomposition temperatures because of previous problems discovered in this area with $\text{Al}_2(\text{SO}_4)_3$.³ No water was detectable at the decomposition temperatures. An interesting feature of the mass spectrum during heat up was a fairly large amount of CO_2 at around 623 K. This may account for the $\sim 1\%$ weight loss noticed on the TGA apparatus between 423 K and the decomposition temperature. There is, however, no CO_2 observed coming from the sample at the decomposition temperatures.

Results

Initially dynamic weight loss experiments were run on MgSO_4 , $\text{MgSO}_4 + 2.8$ mole percent (m/o) Fe_2O_3 , CaSO_4 and $\text{CaSO}_4 + 2.8$ m/o Fe_2O_3 . The data are taken as weight lost (mg) as a function of temperature (K) while the furnace temperature is ramped at a constant rate (Figure 2). The dynamic runs were used to pick a temperature range in which to conduct isothermal experiments. The 10 milligram full scale range was the most sensitive range that could be used reliably and repeatedly on the microbalance. This was also a factor in the choice of the isothermal experiment temperatures.

The isothermal Knudsen effusion experiments on $\text{MgSO}_4 +$ catalysts were run at 1023 K, 1072 K, 1123 K, and 1173 K. Pure MgSO_4 was decomposed at these and additional temperatures. The data are plotted as weight lost vs. time. Figure 3 gives the data for MgSO_4 decomposition at 1123 K in Knudsen conditions. The rate of weight loss is constant until the sample is nearly 100 % decomposed. Similar behavior is observed at all temperatures. The rate of weight loss is not constant with time for $\text{MgSO}_4 +$ additives. A typical plot is shown in Figure 4. All of the additives used produce similar weight loss data, i.e. a fast initial rate with slowing rate to completion.

Time measurement was begun when the sample reached the decomposition temperature. Between 423 K and the isothermal decomposition temperature ~ 1 % of the sample weight was lost, presumably as CO_2 . There was an additional weight loss (the amount depended on the decomposition temperature) from MgSO_4 decomposition prior to attaining the desired isothermal decomposition temperature.

"Initial" fluxes were measured by using the weight loss data from ~the first 10 minutes of the reaction starting from time zero (the time at which the desired temperature was reached). The zero weight loss point was taken to be the weight of the sample after the water was removed at 423 K.

Since the rate of weight loss is not constant with time for MgSO_4 + additives, initial fluxes and fluxes at ~ 50 % decomposed were plotted vs. $1/T$ (Figures 5 and 6) to calculate the apparent enthalpies for the decomposition reaction

(reported in Table I).

In all cases not only the initial fluxes but also the fluxes at 50 % decomposed are higher for the MgSO_4 + additive than for pure MgSO_4 . The additives affect the decomposition rate even after they are separated by MgO from the MgSO_4 .

Open crucible experiments on MgSO_4 and MgSO_4 + catalysts were conducted isothermally at 1073 K, 1123 K, and 1173 K. In all cases, in an open crucible, the rate of weight loss was not constant; a fast initial weight loss with continual rate decrease to completion was observed, e.g. Figure 7. Again, initial fluxes and fluxes after the reaction was 50 % completed were used to calculate pressures and thermodynamic quantities.

In Figure 8 the initial fluxes from MgSO_4 and from MgSO_4 + catalysts from open crucible decomposition are plotted vs. $1/T$. Although the effect is not as dramatic as for Knudsen conditions, the initial fluxes for MgSO_4 + catalysts are in all cases higher than for

pure MgSO_4 . The same is true when the reactions are 50 % completed. Figure 9 is the plot of the fluxes at 50 % decomposed for MgSO_4 and MgSO_4 + catalysts.

An experiment run in a Nuclide 60⁰ magnetic sector mass spectrometer at 1085 K yielded approximately equal amounts of SO_2 and SO_3 (~52 % SO_3 , ~48 % SO_2) from MgSO_4 decomposed in an open crucible. Electrons with energy of 15 eV were used to ionize the product species. Extensive studies have been conducted and comparable results were obtained in this instrument when pure SO_3 was used as a source.²² Additional mass spectrometric measurements were made in a quadrupole mass spectrometer connected to a TGA apparatus on MgSO_4 + 2.8 m/o platinum black and MgSO_4 + 2.8 m/o Fe_2O_3 in an open crucible. Various electron energies were used at 1023 K. The primary gaseous decomposition products for these reactions are SO_2 and O_2 (Table II).²³

Knudsen experiments were conducted on CaSO_4 , CaSO_4 + 2.8 m/o Pt, and CaSO_4 + 2.8 m/o Fe_2O_3 at 1313 K. When Fe_2O_3 is added to CaSO_4 the decomposition rate increases by about a factor of 2 (Figure 10). However when platinum is added the reaction rate is unchanged (Figure 11).

A mixture of Fe_2O_3 and Fe_3O_4 ($\text{Fe}_2\text{O}_3 \cdot \text{FeO}$) was added to MgSO_4 which was then decomposed at 1123 K in an open crucible to determine if reduction of SO_3 by Fe^{++} , which might be present at very low concentrations in the Fe_2O_3 phase, is the source of the catalytic activity of Fe_2O_3 . The pressure of O_2 from Fe_2O_3 at the decomposition temperatures is $< 10^{-12}$ atm; the pressure of O_2 from Fe_3O_4 in this temperature range is $< 10^{-13}$ atm. The initial decomposition rate was reduced by about 14 % with respect to the initial rate of MgSO_4 + Fe_2O_3 .

with a substitution of approximately 18 % Fe^{++} ions from Fe_3O_4 . This result indicates that reduction of SO_3 by Fe^{++} is not the source of the catalytic activity of Fe_2O_3 .

To determine if sample size affects decomposition rates MgSO_4 , MgSO_4 + platinum black, and MgSO_4 + Fe_2O_3 were decomposed in Langmuir cells at 1123 K. Samples of varying size, "full" (0.106 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), "1/2 full" (0.053 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and "1/3 full" (0.035 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) were decomposed. The samples with the catalysts had the same set of MgSO_4 contents. The initial decomposition rates for MgSO_4 + additives did not appear to change much (Figure 12).

Further studies on the effect of bed depth on rates of decomposition of MgSO_4 in the absence of catalysts were conducted to determine whether or not equilibrium decomposition pressures are established in the powder beds. In these experiments sample of "1/3 full" (0.035 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), "full" (0.106 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and "3 x full" (0.318 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) were decomposed at various temperatures. Plots of initial flux vs. bed depth are shown in Figure 13. The initial flux increases with increasing bed depth, but as the temperature gets higher the variation of flux with bed depth decreases. The initial fluxes for each size sample vs. $1/T$ are plotted in Figure 14.

Surface area measurements were made using the BET method on samples before and after decomposition (Table III). The catalysts were mechanically mixed with the reactants. Platinum black and Fe_2O_3 coated the exterior surfaces of the sulfate particles well, the platinum powder did not. After decomposition the oxide product appeared to be very evenly coated when using platinum black and Fe_2O_3 . The greater

increase in surface areas for samples with catalysts is undoubtedly a consequence of the catalysts and their continued presence on the surface.

Analysis of the samples before and after decomposition was done with an x-ray diffractometer (detection limit $\sim 1\%$). The only species observed were those expected, e.g. MgSO_4 , MgO , Fe_2O_3 , and platinum. No mixed oxides were observed.

No difference in appearance of the surface of the product particles was noticed in scanning electron micrographs between samples decomposed in Knudsen cells vs. open crucibles. The apparent particle shapes did not change although the initial particle dimensions seemed to be about halved after decomposition. Figure 15 shows $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystals. The water was easily lost and Figures 16 and 17 show the fairly rough, cracked surface of MgSO_4 . MgO resulting from MgSO_4 decomposition regained a smoother surface (Figure 18). Figures 19 and 20 are of $\text{MgSO}_4 + 2.8 \text{ m/o platinum black}$ and $\text{MgO} + 2.8 \text{ m/o platinum black}$. It is seen that the platinum particles are well distributed over the surface. Similar results with x-ray maps (resolution limit $2 \times 10^{-6} \text{ m}$) are shown for MgSO_4 and MgO with Fe_2O_3 (Figure 21 to 24). Because the iron oxide particles are relatively uniformly distributed on the MgSO_4 it is impossible to determine if there has been significant redistribution on the part of the Fe_2O_3 . The mixture of Fe_2O_3 and Fe_3O_4 that was used as a catalyst did not cover the surface as well and it was possible to find apparently clear areas on the product oxide particles. X-ray analysis of a clear spot shows a small amount of iron present which indicates that it has moved on the surface (Figure 25 and 26).

When CaO from CaSO_4 , $\text{CaSO}_4 + 2.8 \text{ m/o Fe}_2\text{O}_3$ and $\text{CaSO}_4 + 2.8 \text{ m/o Pt}$ was observed an interesting feature appeared. The surface of the CaO particles from CaSO_4 and $\text{CaSO}_4 + \text{Pt}$ were practically indistinguishable (Figure 27 and 28). Although x-ray analysis on $\text{CaSO}_4 + \text{Fe}_2\text{O}_3$ indicated that the iron was, like platinum, not well dispersed (Figure 29 to 31), the morphology of the CaO resulting from decomposition had a significant difference. The crystals appeared to have joined; they have a glassy appearance (Figure 32). An x-ray analysis of the sample indicated that there was a small amount of iron present everywhere.

An interesting feature noticed only on the MgO particles that were decomposed with Fe_2O_3 present is a scalloped surface which apparently may have formed below the original Fe_2O_3 coated crystal surface by conchoidal fracture (Figure 33 to 35). This type of surface was noted in every sample observed, although not on every crystal. The Fe_2O_3 probably diffused over the crystal surface and followed the reaction interface along the product oxide pores.

Some MgO crystals that were decomposed with Fe_2O_3 and platinum black were carefully broken to observe the interior of the crystal. X-ray analysis was done and there was no indication of the presence of iron or platinum inside the crystal. This observation is not enough to prove that the catalysts are not following the reaction interface, however, because the levels of catalyst in the interior of the crystal may be too low to detect.

Discussion

When CaSO_4 is decomposed without any additives in a Knudsen cell, the thermodynamically favored products, SO_2 and O_2 , readily approach their equilibrium concentrations.⁷ In this circumstance it is not surprising that Fe_2O_3 increased the rate of CaSO_4 decomposition by only a factor of ~ 2 and platinum had no measurable effect (Figures 10 and 11). The catalytic studies, accordingly, were concentrated on MgSO_4 , for which larger effects were obtained.

For comparison with the data of reference 7 a plot of initial pressure vs. $1/T$ for MgSO_4 and MgSO_4 + additives decomposed in a Knudsen cell is shown in Figure 36. Pressures were calculated using the Hertz-Knudsen-Langmuir equation

$$P = J(2\pi MRT)^{1/2} \quad (6)$$

For these calculations the principal vapor species were assumed to be SO_2 and O_2 . Lau et al.⁷ found these species under similar conditions and they were observed in the mass spectrometer experiments.^{22,23} The general agreement of these data with those of reference 7 is satisfactory. Similar orifice areas were used in the two studies, but differences in fluxes can be expected from differences in sample size or in the processing conditions used to produce the anhydrous MgSO_4 .

Lau et al. found that MgSO_4 decomposes to MgO and SO_3 gas when a large ($> \sim 1.5$ mm) Knudsen orifice is used.⁷ The expected equilibrium vapor mixture of SO_2 and O_2 gas is obtained only when smaller ($< \sim 1$ mm) orifices are used.⁷ There is known⁹ to be an energy barrier to the

reaction

Lau et al.⁷ assumed that when a catalyst is added the SO_2 and O_2 pressures from MgSO_4 are increased by an effect on reaction 7. But calculations by Meschi and Searcy¹⁶ show that a catalyst which influenced only the gas phase reaction 7, could not, as found by Lau, increase the total product gas pressure to $> 10^2$ times the equilibrium pressure of SO_3 for the reaction

A catalyst may convert $> 99\%$ of the SO_3 to SO_2 and O_2 , but if SO_3 gas is an intermediate in formation of the SO_2 and O_2 , the maximum molar flux density, which is generated by MgSO_4 decomposition can never be greater than

$$J_{\max} = P_{\text{SO}_3}^{\text{eq}} (2\pi \text{MRT})^{-1/2}$$

where $P_{\text{SO}_3}^{\text{eq}}$ is the equilibrium decomposition pressure for the reaction.

To increase the decomposition rate above the rate $J_{\max}$, the catalyst must increase the net flux of gaseous product that leaves the MgSO_4 surface.

After decomposition has begun, the catalyst and MgSO_4 are separated by a porous MgO layer. When Fe_2O_3 is used as the catalyst, O_2 from the Fe_2O_3 could diffuse through the gas phase to the MgSO_4 , but

O_2 gas phase transport is unlikely with platinum. Continued catalysis by platinum after an MgO layer has formed requires condensed phase diffusion of the catalyst or an SO_3 -containing particle, eg SO_3 itself or the $SO_4^{=}$ ion and a counter current of $O^{=}$ ion. As it will be shown later that catalysis by O_2 gas at the reaction interface is unlikely, similar diffusion must occur for catalysis by Fe_2O_3 .

If the catalyst diffuses on the surface of the MgO to the $MgSO_4$ surface the catalysis of the decomposition of SO_3 there to SO_2 and O_2 could produce the observed results. Alternately, condensed phase or surface diffusion of SO_3 through the MgO to the catalyst could occur with decomposition occurring there.

Figure 37 compares calculated initial pressures for $MgSO_4$ and for $MgSO_4$ with catalysts from open crucible experiments to the equilibrium SO_3 pressure. It is assumed for these calculations that the principal gaseous species for $MgSO_4$ decomposition is SO_3 and the principal gaseous species for $MgSO_4$ + additives are SO_2 and O_2 .⁷ These gaseous molecules were those found in mass spectrometer experiments.^{22,23}

In both Knudsen cells and open crucibles the fluxes from the $MgSO_4$ + additive samples are higher than the fluxes for pure $MgSO_4$ initially and throughout ~90% of the decomposition reaction (Figures 5, 6, 8 and 9) These data prove that catalysis occurs throughout the reaction and not just in the initial stages of decomposition. The results from attempts to determine if platinum or iron is present in the interior of a product MgO particle are inconclusive. Greater amounts of catalyst and higher resolving powers are needed to

distinguish the additives inside the product.

It has been suggested that Fe_2O_3 catalysis of SO_3 conversion to SO_2 and O_2 may be associated with the ability of the transition metal ions to provide a cyclic oxidation-reduction couple or to allow oxygen transfer processes to occur via oxygen vacancies in the defect structure.⁷ It is unlikely that the low O_2 partial pressure established by Fe_2O_3 ($P_{\text{O}_2} \sim 10^{-12}$ atm) plays a significant role in the catalysis. Furthermore, O_2 is an oxidizing agent. The slow step is probably the reduction of SO_4^- or adsorbed SO_3 to SO_2 .

Fe_3O_4 is thermodynamically a stronger reducing agent than Fe_2O_3 . But when in the present study a portion of the Fe_2O_3 catalyst is replaced by Fe_3O_4 , a comparable decrease in initial decomposition flux is observed. This result indicates that reduction of SO_3 by Fe^{++} is probably not the source of the catalytic activity of Fe_2O_3 . Probably, Fe_2O_3 is an effective catalyst for the decomposition of SO_3 gas and MgSO_4 because bonding to the Fe_2O_3 surface weakens one or more S-O bonds of SO_3 or of SO_4^- . Platinum probably has a similar effect.

Catalysts usually have greater effects on rates when reactions are far from equilibrium, but Knutsen, Searcy and Beruto¹⁷ observed that LiCl is a better catalyst for CaCO_3 decomposition in Knudsen conditions than Langmuir conditions. Such results imply a pressure dependent decomposition mechanism change.

Sulfate decomposition may also have a pressure dependent mechanism for the SO_3 to SO_2 and O_2 conversion. The effect of the catalysts on MgSO_4 decomposition is much less in open crucibles where SO_3 pressures are low than in Knudsen cells, where SO_3 pressures (and activities) are higher. The rate limiting process, therefore, may

depend not on the encounter of 1 SO_3 with the catalyst, but of 2 SO_3 .

Table I compares apparent heats of decomposition of MgSO_4 and MgSO_4 + catalysts calculated from the slopes of the $\log(\text{initial flux})$ vs. $1/T$ plots (Figure 5) to heats of decomposition calculated from calorimetric data.²⁴ In all cases of Knudsen decomposition for MgSO_4 and MgSO_4 + additives, SO_2 and O_2 are the decomposition products. In each case ΔH^* is greater than ΔH^0 indicating that a high activation enthalpy barrier limits the rate of formation of the gaseous products. For pure MgSO_4 the initial value of ΔH^* is greater than ΔH^0 by ~ 33 kcal/mole. For MgSO_4 + additives the initial values of ΔH^* are 4 to 9 kcal/mole greater than ΔH^0 .

When the data for pure MgSO_4 decomposition in open crucibles and Knudsen cells are compared it is important to note that the reported gaseous products are different. Lau et al.'s conclusions⁷ and mass spectrometric measurements^{22,23} indicate that in open crucibles SO_3 would be the primary gaseous product while with Knudsen cells the products are SO_2 and O_2 ,⁷ so a comparison of ΔH for the two reactions is a more complicated matter.

The gaseous product from open crucible decomposition of pure MgSO_4 is SO_3 . In this case ΔH^* is greater than ΔH^0 for decomposition to SO_3 gas by ~ 7 kcal/mole. For open crucible decomposition of MgSO_4 + Fe_2O_3 , the gaseous products are SO_2 and O_2 . Probably the catalysts increase the flux of SO_2 and O_2 primarily by decreasing ΔH^* below the

value for the uncatalyzed sample, but that value could not be measured.

For 50 % decomposed samples, the value of ΔH^* for the uncatalyzed decomposition is essentially unchanged from the initial value, but values of ΔH^* measured for the catalyzed decomposition are 15 to 29 kcal/mole greater than ΔH^0 . These data show that the catalysis becomes less effective in reducing the apparent enthalpy barrier to decomposition when the product MgO layer increases the separation between the catalyst and the MgSO_4 . Presumably diffusion of catalyst to the MgSO_4 surface or SO_3 to the catalyst is too slow to maintain a constant rate of SO_2 and O_2 formation as the MgO layer thickens.

The most fundamental question about decomposition reactions in a powder bed is the question of whether the equilibrium decomposition pressure is approached in the bed or, if not, how far the pressure deviates from equilibrium. This question is not usually evaluated in studies of decomposition reactions.¹⁸⁻²⁰ The paper by Hulbert¹⁰ is exceptional in that it provides information on the influence of sample weight on the decomposition rate. These data would provide a quantitative test for whether or not an equilibrium is established in the powder bed if he had provided information on sample external surface area.

Hulbert finds that his data fit an equation of the form

$$\log k = -A \log W - B$$

where k has units of minutes, W of weight in grams and A proves experimentally to have a value of 1. Hulbert argues that if a fraction

"of the reaction interface is effectively blocked for the decomposition process by the presence of an internal pressure (P_1) of SO_3 such that

$$\theta = \Delta P_1^C = BW^A$$

then it follows that the rate constant ought to be an inverse function of (θ)

$$k = \frac{1}{BW^A}$$

from which ($\log k = A \log W - B$) follows immediately."

An important experimental finding, on which Hulbert does not comment, is that A has the value 1. He does not describe the geometry of his container or the nature of its loading. Probably he increased the sample weight by raising the level of a powder bed in a container of constant cross section. If so, a unit value of A in his expression implies a flux density leaving his powder bed that is independent of mass.

This is the expected result; in an inert gas, gas phase diffusion of the gaseous products away from the bed is usually rate limiting, and equilibrium decomposition pressures will be approached in the bed.^{12,13}

Searcy and Beruto²⁵ showed that the ratio of the flux of gas that leaves a decomposing single crystal in vacuum to the flux calculated from the equilibrium pressure by means of the Hertz-Knudsen-

Langmuir equation provides a quantitative measure of the deviation of the decomposition rate from the maximum possible rate for the reaction. Knutsen, Searcy and Beruto recently applied the same relation to determine whether or not the flux in a powder bed of calcite approaches the equilibrium value in vacuum.¹⁷ The somewhat surprising result was that the molar flux density of CO₂ from the bed (or equivalently the weight loss per unit time) was independent of bed depth, but was $< 10^{-3}$ times the flux that corresponds to the equilibrium decomposition pressure if calcite were in equilibrium with CaO in its standard state. This result implies that a highly metastable equilibrium is established. The nature of this metastable equilibrium is under investigation.²⁶

The mass spectrometer measurements in the present study showed that in the absence of a catalyst the gaseous product from decomposition of a powder bed of MgSO₄ in an open crucible in vacuum is SO₃ rather than the thermodynamically more favored products, SO₂ and O₂. The experiments carried out in a cell of constant cross section with samples of different weights provided tests of the approach to equilibrium at 1023 K to 1123 K for the reaction

(Figure 13).

The apparent heats of decomposition measured in open crucibles were essentially unchanged as the reaction proceeded to 50 % decomposition if no catalyst was present but increased for the catalyzed reaction (Figures 7 and 8; Table I). This suggests that as the MgO grows, surface or condensed phase diffusion becomes the rate limiting

step in the reaction. If either condensed phase or gaseous diffusion through the MgO is rate limiting, the reaction should follow a parabolic rate law, that is a plot of weight loss vs. $(\text{time})^{1/2}$ should be a straight line. The transition in a $t^{1/2}$ plot between the interface controlled initial rate would be from an initial regime in which the slope decreases with $t^{1/2}$ to a linear regime in which the slope is constant as $t^{1/2}$ increases.

Figures 38 and 39 show the type of curve that results when the data from MgSO_4 and $\text{MgSO}_4 + 2.8 \text{ m/o Fe}_2\text{O}_3$ at 1123 K and 1073 K are plotted vs. $t^{1/2}$. For much of the reaction the slopes are approximately constant, but the initial slopes increase with $t^{1/2}$. The change in apparent heats, therefore, probably do not reflect a transition from an interface controlled reaction to a diffusion controlled reaction. The analysis presented below shows that increasing the temperature or increasing the particle size changes initial reaction fluxes from fluxes characteristic of the slowest reaction step to fluxes characteristic of an equilibrium in the powder bed. It seems likely that the decreases in flux with extent of reaction at constant temperature which have just been discussed reflects a transition from the equilibrium regime or a near equilibrium regime to a regime in which the flux is limited by the slowest reaction step.

The question of whether fluxes measured in decomposition reactions reflect equilibrium at the surfaces of the reactants or some irreversible step was not answered, or even usually asked until the study of Beruto and Searcy on decomposition of calcite single crystals. (The analyses of gas-solid reaction kinetics described, for example by

Szekely, Evans and Sohn¹⁹ could be used for this purpose, but apparently has not.) Recently Knutsen, Searcy and Beruto extended the analysis to demonstrate that a metastable equilibrium is established between calcite powder and the CO_2 generated from it at ~ 1000 K in vacuum. Below, a similar analysis is applied to demonstrate that the conditions employed for open crucible measurements with MgSO_4 in the present study range between an irreversible regime and a metastable equilibrium regime. It is shown that conventional methods of analysis of decomposition reactions do not reveal this important fact.

Increasing MgSO_4 sample mass (and therefore depth at constant cross section) in an open crucible decreases the decomposition flux per unit mass (Figure 13). The samples were all loosely packed ($\sim 70\%$ porosity), and the sample was in vacuum so the product gas pressure could approach a constant value in the powder bed only if reaction of the gas with the powder approached equilibrium.

At 1123 K, the fact that the flux is approximately mass independent indicates that an apparent equilibrium is established. The value calculated for the apparent equilibrium pressure of $\text{MgSO}_4 \rightarrow \text{MgO} + \text{SO}_3$ is 3.6×10^{-6} atm, while from JANAF data the equilibrium pressure for the reactant and product solid in their standard states is calculated to be 2.3×10^{-3} atm, and Lau et al. find equilibrium pressures from extrapolation of Knudsen data which agree with thermochemical data of Kellogg²⁷. Those data yield 3.6×10^{-5} atm for the equilibrium pressure at 1123 K. The apparent equilibrium pressure measured in the powder bed is only 10^{-3} times the higher calculated pressure and 10^{-1} times the other calculated pressure. The factor of 10 difference between the present measurements and those of

reference 7 is greater than expected experimental error. A metastable equilibrium must be established in the powder bed, perhaps because its MgO is produced in a state of high internal strain and high surface energy.

The lower the temperatures at which decomposition of different weights of powder were carried out, the greater the dependence of weight loss per unit time on sample weight (Figure 13). At the lowest experimental temperature, 1023 K, the decomposition flux varied strongly with sample size and approached a linear dependence of flux on sample mass for the smallest sample mass studied (Figure 40). A perfectly linear dependence would indicate a negligible probability of back reaction of SO_3 molecules that have desorbed from the MgSO_4 . When back reaction is negligible, the measured flux density per total surface area of the MgSO_4 powder, J_L is the flux density characteristic of the slowest step of the decomposition at the MgSO_4 surface. The ratio, α , of this flux density to the flux calculated from the equilibrium decomposition pressure by means of the Hertz-Knudsen-Langmuir equation is the measure of irreversibility identified by Beruto and Searcy. From the initial rate at 1023 K, α is calculated to be 5.5×10^{-8} if the JANAF thermochemical data are accepted or 5.5×10^{-6} if the equilibrium pressures calculated by Lau et al. are accepted.

This analysis shows then that in the temperature range in which weight losses were obtained in our study the reaction approaches a metastable equilibrium state when the highest temperature and largest samples are used and approaches complete irreversibility when the lowest temperature and smallest sample is used. Plots of $\log J$ (or $\log$ (weight

loss)) versus $1/T$ for constant sample sizes give reasonably straight lines (Figure 14), but when the temperature is in this transition region between control by a slow reaction step and by equilibrium in the bed, it is not possible to get meaningful activation enthalpies. The apparent ΔH calculated from the slope of the plot with the largest samples gives a maximum value for the enthalpy of the metastable equilibrium reaction, and the slope from the smallest sample gives a minimum value for the apparent activation enthalpy of the reaction.

It is common practice to fit decomposition reactions to equations that assume reaction proceeds along an advancing interface which moves toward the center of the sample. For example, Hulbert analyzed his $MgSO_4$ decomposition data by means of the contracting sphere model and got good agreement until reaction was 80 % or more complete.¹⁰ As noted in the introduction, his powder beds probably reached equilibrium SO_3 pressures and the decomposition rates were probably limited by the rates at which SO_3 diffused away from the samples. The demonstration that equilibrium is approached in a one gram powder bed in vacuum makes this interpretation probable.

Searcy and Beruto¹¹ showed that if a decomposition reaction generates an equilibrium pressure, growth of a porous barrier on one particle should decrease the flux according to

$$J \cong \frac{aJ_{eq}}{1+a}, \quad \text{or } J \text{ as } f(\text{time})$$

where a is the average pore cross section and l is average pore length. Because this influence of a porous barrier on a reversible decomposition

is neglected in derivations of the decreasing sphere model, that model is only appropriate for a decomposition in a powder bed where the reaction has been shown to be irreversible.

Probably the good fit obtained by Hulbert to that model is a fortuitous consequence of transition from an equilibrium regime to a regime of increasing deviation from equilibrium as the reaction proceeds. Similar criticisms can be made of other decomposition reaction analyses that fail to address the fundamental questions of whether equilibrium or non-equilibrium processes are being measured and of how far the fluxes measured differ from those possible if the thermodynamically favored equilibrium are established.

Conclusions

Since the effect of the addition of Fe_2O_3 and platinum to CaSO_4 did not produce much increase in decomposition rate (~ 2 times increase with Fe_2O_3 , no change with platinum), the majority of experiments were conducted on MgSO_4 decomposition.

The initial decomposition rate for MgSO_4 was increased by ~ 5 times with Fe_2O_3 or platinum present in a Knudsen cell. The resulting gaseous products were SO_2 and O_2 .

The initial decomposition rate for MgSO_4 decomposition in an open crucible was only increased by ~ 1.5 times when additives were present. The gaseous reaction products changed, however. The gaseous product from pure MgSO_4 decomposition in an open crucible was SO_3 . When catalysts were present the gaseous products were SO_2 and O_2 .

Although a solid, porous MgO product layer was built up on the MgSO_4 during decomposition, catalysis continued throughout the reaction. Either an SO_3 -containing molecule must diffuse to the catalyst on the surface or the catalyst must diffuse to the reaction interface. Attempts to determine if any catalyst was present inside product MgO particles were inconclusive.

To determine if equilibrium is approached in the powder bed when pure MgSO_4 is decomposed in vacuum, the effect of sample bed depth and temperature on the decomposition flux from open crucibles was studied. The initial decomposition flux is almost bed depth independent at 1123 K. A metastable equilibrium is established with an SO_3 pressure of 10^{-3} times the equilibrium value. The enthalpy of the

metastable equilibrium is ≤ 77.7 Kcal/mole.

The initial decomposition flux varies approximately linearly with bed depth at 1023 K. This dependence indicates an irreversible process. The ratio of the flux density to the maximum possible flux density is 5.5×10^{-8} or 5.5×10^{-6} depending on choice of thermochemical data. The apparent activation enthalpy for the irreversible process is ≥ 58.4 Kcal/mole.

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Table I. Apparent Heats of Decomposition

SAMPLE MATERIAL	H (Kcal/mole) (initial flux)	H (Kcal/mole) (50 % decomposed)
KNUDSEN		
$\text{MgSO}_4 + \text{Fe}_2\text{O}_3$	87.30 ± 1.55	98.12 ± 2.84
$\text{MgSO}_4 + \text{Pt}$	91.97 ± 1.46	108.24 ± 2.23
$\text{MgSO}_4 + \text{Pt black}$	89.67 ± 0.30	111.69 ± 0.93
MgSO_4	114.56 ± 0.28	116.24 ± 1.47
OPEN CRUCIBLE		
$\text{MgSO}_4 + \text{Fe}_2\text{O}_3$	70.89 ± 1.13	91.11 ± 1.73
$\text{MgSO}_4 + \text{Pt}$	83.00 ± 1.41	91.43 ± 1.22
$\text{MgSO}_4 + \text{Pt black}$	95.42 ± 0.85	120.00 ± 1.81
MgSO_4^*	67.44 ± 1.58	69.36 ± 0.80

*Heat calculated for $\text{MgSO}_4 \rightarrow \text{MgO(s)} + \text{SO}_3(\text{g})$ for which

$\Delta H^0 = 60.14 \text{ Kcal/mole}^{24}$. All other entries calculated for

$\text{MgSO}_4 \rightarrow \text{MgO(s)} + \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ for which

$\Delta H^0 = 83.37 \text{ Kcal/mole}^{24}$.

Table II. Mass Spectrometer Line Intensities, $T = 1023$ K

SAMPLE MATERIAL	eV	$I_{SO_2^+}$	$I_{SO_3^+}$	$I_{O_2^+}$	$I_{SO_3^+}/I_{SO_2^+}$
MgSO ₄ + Pt black	14	4.5	0.1	0.2	0.022
	20	24	0.2	-	0.0083
	30	26	3.2	-	0.0025
MgSO ₄ + Fe ₂ O ₃	14	20	1	22	0.05
	20	47	0.5	15	0.01

Table III. Magnesium Oxide Surface Areas

SAMPLE MATERIAL		SURFACE AREAS (m ² /g)	
Unreacted			
MgSO ₄		~ 7	
MgSO ₄ + Fe ₂ O ₃		~ 12	
MgSO ₄ + Pt black		~ 13	
Reacted			
	T (K)	Knudsen	Open Crucible
MgO + Fe ₂ O ₃	1173	~ 47	~ 53
	1123	~ 43	~ 54
	1073	~ 40	~ 58
MgO + Pt	1173	~ 36	~ 59
	1123	~ 33	~ 54
	1073	~ 34	
MgO + Pt black	1173	~ 36	~ 55
	1123	~ 39	
	1073	~ 34	~ 51
MgO	1173	~ 18	~ 46
	1123	~ 22	~ 45

Figure Captions

- Figure 1. TGA apparatus.
- Figure 2. Dynamic weight loss vs. temperature for MgSO_4 and $\text{MgSO}_4 + 2.8 \text{ m/o Fe}_2\text{O}_3$ in a Knudsen cell.
- Figure 3. Weight lost vs. time for MgSO_4 in a Knudsen cell at 1123 K.
- Figure 4. Weight lost vs. time for MgSO_4 and $\text{MgSO}_4 + 2.8 \text{ m/o Pt}$ in a Knudsen cell at 1123 K.
- Figure 5. Initial flux vs. $1/T$ for MgSO_4 and $\text{MgSO}_4 + \text{additives}$ in a Knudsen cell.
- Figure 6. Flux at 50 % decomposed vs. $1/T$ for MgSO_4 and $\text{MgSO}_4 + \text{additives}$ in a Knudsen cell.
- Figure 7. Weight lost vs. time for MgSO_4 and $\text{MgSO}_4 + 2.8 \text{ m/o Fe}_2\text{O}_3$ in an open crucible at 1123 K.
- Figure 8. Initial flux vs. $1/T$ for MgSO_4 and $\text{MgSO}_4 + \text{additives}$ in an open crucible.
- Figure 9. Flux at 50 % decomposed vs. $1/T$ for MgSO_4 and $\text{MgSO}_4 + \text{additives}$ in an open crucible.
- Figure 10. Weight lost vs. time for CaSO_4 and $\text{CaSO}_4 + 2.8 \text{ m/o Fe}_2\text{O}_3$ in a Knudsen cell at 1363 K.
- Figure 11. Weight lost vs. time for CaSO_4 and $\text{CaSO}_4 + 2.8 \text{ m/o platinum}$ in a Knudsen cell at 1363 K.
- Figure 12. Weight lost vs. time for $\text{MgSO}_4 + 2.8 \text{ m/o platinum black}$ in an open crucible varying bed depth at 1123 K.
- Figure 13. Initial flux vs. bed depth and temperature for MgSO_4 in an open crucible.

- Figure 14. Initial flux vs. $1/T$ for MgSO_4 with various bed depths in an open crucible.
- Figure 15. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ powder particles. 40X.
- Figure 16. MgSO_4 particle surface. 1000X.
- Figure 17. MgSO_4 powder particles. 40X.
- Figure 18. MgO particle surface. 4000X.
- Figure 19. MgSO_4 + 2.8 m/o platinum black. 1000X.
- Figure 20. MgO + 2.8 m/o platinum black. 1000X.
- Figure 21. MgSO_4 + 2.8 m/o Fe_2O_3 . 1000X.
- Figure 22. X-ray map indicating location of iron on MgSO_4 in Figure 21.
- Figure 23. MgO + 2.8 m/o Fe_2O_3 . 1000X.
- Figure 24. X-ray map indicating location of iron on MgO in Figure 23.
- Figure 25. MgO + 2.57 m/o $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ mixture. 1000X.
- Figure 26. X-ray spectrum from clear area indicated on Figure 25.
- Figure 27. CaO from CaSO_4 decomposition. 4000X.
- Figure 28. CaO + 2.8 m/o platinum. 4000X.
- Figure 29. CaSO_4 + 2.8 m/o Fe_2O_3 . 1000X.
- Figure 30. X-ray map indicating location of iron on CaSO_4 in Figure 29.
- Figure 31. Fe_2O_3 particle with CaSO_4 . 1000X.
- Figure 32. CaO + 2.8 m/o Fe_2O_3 . 4000X.
- Figure 33. MgO + 2.8 m/o Fe_2O_3 . 200X.
- Figure 34. MgO + 2.8 m/o Fe_2O_3 . 200X.
- Figure 35. MgO + 2.8 m/o Fe_2O_3 . 1000X.
- Figure 36. Initial pressure vs. $1/T$ for MgSO_4 and MgSO_4 + additives in a Knudsen cell compared to reference 7.
- Figure 37. Initial pressure vs. $1/T$ for MgSO_4 and MgSO_4 + additives in an open crucible compared to equilibrium SO_3 pressure.

Figure 38. Weight lost vs. $(\text{time})^{1/2}$ for MgSO_4 and $\text{MgSO}_4 + 2.8$ m/o Fe_2O_3 at 1123 K.

Figure 39. Weight lost vs. $(\text{time})^{1/2}$ for MgSO_4 and $\text{MgSO}_4 + 2.8$ m/o Fe_2O_3 at 1073 K.

Figure 40. Initial flux. vs. bed depth for MgSO_4 at 1023 K.

Figure 41. Temperature calibration of furnace with NaCl.

Figure 42. Temperature calibration of furnace with Cu.

Figure 43. Temperature calibration of furnace with Sn.

Figure 1

XBL 8110-6739

XBL 8110-6747

Figure 2

Figure 3

XBL 8110 - 6754

XBL 8110-6734

Figure 4

XBL8110-6749

Figure 5

XBL 8110-6750

Figure 6

XBL 8110-6743

Figure 7

XBL 8110-6741

Figure 8

Figure 9

XBL8110-6742

XBL 8110-6752

Figure 10

Figure 11

XBL 8110-6753

Figure 12

XBL 8110-6755

Figure 13

XBL8110-6744

Figure 14

XBL 8110-6740

25 mm

Figure 15

10 μ m

Figure 16

XBB810-10066A

Figure 17

Figure 18

XBB810-10060A

10 μm

Figure 19

10 μm

Figure 20

XBB810-10059A

10 μm

Figure 21

10 μm

Figure 22

XBB810-10050A

10 μm

Figure 23

10 μm

Figure 24

XBB810-10056A

Figure 25

Figure 26

XBB810-10047A

2.5 μm

Figure 27

2.5 μm

Figure 28

XBB810-10063A

10 μm

Figure 29

10 μm

Figure 30

XBB810-10049A

10 μm

Figure 31

2.5 μm

Figure 32 XBB810-10061A

50 μm
XBB810-10067A

Figure 33

50 μm

Figure 34

10 μm

Figure 35

XBB810-10058A

Figure 37

XBL8110-6746

Figure 38

XBL 8110-6738

Figure 39

XBL 8110-6907

XBL8110-6906

Figure 40

APPENDIX I

Figure 41

XBL 8110-6756

Figure 42

XBL 8110-6757

Figure 43

XBL8110-6758

APPENDIX II

Mallinckrodt Analytical Reagent $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Maximum Limit of Impurities (%)

NH_4	.002
As	.0002
Ca	.02
Cl	.0005
Fe	.0005
Mn	.0005
NO_3	.002
K	.005
Na	.005
Sr	.005
Heavy Metals	.0005
Insoluble Matter	.005

Mallinckrodt Analytical Reagent $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Maximum Limit of Impurities (%)

Cl	.002
Fe	.002
NO_3	.005
Mg and alkali salts	.20
Heavy Metals	.002
Insoluble Matter	.05

Allied Chemical Reagent Fe_2O_3

Maximum Limit of Impurities (%)

SO_4	.20
Cu	.005
Zn	.005
Insoluble in HCl	.20
Sulfates	.10

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720