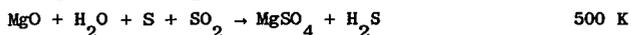


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A number of thermochemical cycles for producing hydrogen from water are based on sulfate systems (1). A simple cycle, for example, is:



The predicted efficiency for conversion of primary heat into chemical energy in the form of hydrogen by such a cycle is very sensitive to the quality of the thermodynamic data used in evaluating each step. Errors of several kcal in a reaction enthalpy, for example, can effect a change of several percentage points in a calculated efficiency (2, 3). A close inspection of available data shows that the thermodynamics of some sulfate cycle steps are not known with sufficient accuracy to rank the cycles properly. Additionally, it is doubtful that many of the steps proceed as written because of side reactions, condensed phase interactions, kinetic limitations, and so on.

We are studying the high temperature chemistry of metal sulfate decomposition processes on a program funded by the National Science Foundation. This decomposition step, typified by the reaction $\text{MSO}_4(\text{s}) \rightarrow \text{MO}(\text{s}) + \text{SO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$, is common to all sulfate cycles, as exemplified in the cycle referred to earlier. However, the thermochemistry of many metal sulfates is not well established, and directly measured decomposition pressures are often inconsistent or incomplete. Both of these sources of error are stressed in reviews of sulfate decomposition equilibria (4, 5). Information about the kinetics of these decompositions is also crucial to the development of efficient cycles; again the available data are fragmentary (4). The objective of our program is to provide some of the fundamental thermochemical and kinetic data required in the overall evaluation of sulfate cycles.

At this stage, detailed studies of the vaporization-decomposition of MgSO_4 and CaSO_4 have been carried out by means of the combined torsion and gravimetric Knudsen effusion method. With this method, one measures simultaneously the recoil force and the weight loss associated with the molecular effusion process, and can thereby evaluate both the vapor pressure and vapor molecular weight of the substance being studied. A description of the torsion method and its application to various vaporization studies is given in previous publications (6-8). In addition, the vaporization of MgSO_4 was also studied by high temperature mass spectrometry, using an instrument and technique described in earlier work (9, 10). Alumina effusion cells were used in all of the present studies. Results obtained on MgSO_4 and CaSO_4 are described separately below.

Torsion-gravimetric effusion measurements were made with four cells of orifice diameter 0.6, 1.0, 1.5, and 2.00 mm covering a range of 980 to 1060 K. A substantial variation of decomposition pressure with effective orifice area (product of orifice area and transmission factor) was observed, indicating an appreciable kinetic barrier for the vaporization-decomposition process.

Additionally, the measured vapor molecular weight, M^* , showed an interesting variation with temperature and orifice area. M^* derived from the combined torsion-weight loss data is really a weight average molecular weight, and would have values of 54.6 and 80.1 for the overall vaporization processes $\text{MgSO}_4(s) = \text{MgO}(s) + \text{SO}_2(g) + 1/2\text{O}_2(g)$ and $\text{MgSO}_4(s) = \text{MgO}(s) + \text{SO}_3(g)$, respectively. With the larger orifices at the lower end of the temperature range, M^* values of 78-80 were measured, indicating the vapor to be comprised almost entirely of SO_3 under those conditions. Vapor molecular weights determined with the 0.6 and 1.0 mm diameter orifice cells were somewhat lower, varying from 55 to 65 [$P(\text{SO}_3)/P(\text{SO}_2) = 0.02$ to 0.92], a clear indication that vapor composition is approaching the $\text{SO}_2 + 1/2\text{O}_2$ stoichiometry as orifice size decreases, and as temperature and residence time of gaseous species in the cell increase. Since a free energy calculation shows that at equilibrium the ratio $P(\text{SO}_3)/P(\text{SO}_2) < 100$ under our conditions, it is obvious that the vaporization process is kinetically limited to a substantial degree. It is a matter of both practical and fundamental importance to determine the nature of this kinetic barrier.

As a check on the vapor molecular weights, the composition of the effusing vapor over $\text{MgSO}_4(s)$ was determined by high temperature mass spectrometry, using an alumina cell with 1.5 mm diameter orifice. Over the range 940 to 1080 K, the ratio $P(\text{SO}_3)/P(\text{SO}_2)$ was found to have the relatively constant value of 19 ± 1 . In agreement with the above molecular weight measurements. The mass spectrometric data thus reinforce the concept of a kinetically limited vaporization process. It appears that under dynamic conditions, the initial vaporization step involves the evolution of an SO_3 molecule, rather than the equilibrium mixture of SO_2 and O_2 on the surface. There are several factors which could influence the kinetics of the final conversion to SO_2 and O_2 , including the thickness of the residual MgO layer on the sample, possible catalytic effects of the sample surface and/or cell walls, and the temperature.

A thermodynamic analysis of the results reveals other interesting information. Figure 1 is a plot of our measured total pressures for the MgSO_4 decomposition, obtained by the torsion method with the 0.6 and 1.0 mm diameter orifices. The solid line in Figure 1 is the pressure derived from these data by an extrapolation to zero orifice area using the Whitman-Motzfeldt relation $P = P_e(1 + BCa)$ where P and P_e are equilibrium and observed pressures, C and a are orifice area and Clausing factor, and B is a constant for a particular cell design. It would be especially instructive to compare the extrapolated pressures with calculated equilibrium pressures for the process $\text{MgSO}_4(s) = \text{MgO}(s) + \text{SO}_2(g) + 1/2\text{O}_2(g)$, since measured M^* values are approaching the $\text{SO}_2 + \text{O}_2$ composition at the temperature shown. However, the heat of formation and heat content of MgSO_4 are not sufficiently well established for a meaningful thermodynamic calculation of equilibrium pressures. Shown, instead, in Figure 1 are equilibrium pressures extrapolated from the higher temperature decomposition measurements of Dewing and Richardson (11) and from the selected data of Kellogg (4). Our derived pressures extrapolated to zero orifice area are an order of magnitude or more lower than the best literature results for the equilibrium decomposition process,

further evidence of a severe kinetic limitation. Much remains to be done to clarify the situation, but a tentative explanation envisions SO_3 as the primary vaporizing species, with subsequent decomposition to SO_2 and O_2 by wall, surface or gas phase collisions, the extent of which is highly dependent on residence time. A measured M^* close to 55 would not necessarily signify total equilibration within the cell, but could be the result of a large concentration gradient between sample surface and effusion orifice. In this sense, the observed pressure would be dominated by the evolution of SO_3 .

It appears that the pressure data obtained with the larger effusion orifices, where vapor molecular weights of 80 ± 2 indicate the vapor to be composed largely of SO_3 , can be interpreted to yield the SO_3 equilibrium decomposition pressure for the process $\text{MgSO}_4(\text{s}) = \text{MgO}(\text{s}) + \text{SO}_3(\text{g})$, which can be used in turn to derive a value for the enthalpy of formation of $\text{MgSO}_4(\text{s})$. Our preliminary analysis yields $\Delta H_{298}^{\circ}(\text{MgSO}_4) = -311 \pm 1 \text{ kcal/mol}$, and indicates the JANAF Table (12) value to be in error by about 10 kcal/mol.

B. CaSO_4

Because of the complex results observed for MgSO_4 , it seemed worthwhile to test the applicability of the effusion method and the Whitman-Motzfeldt model to a sulfate decomposition process for which all the relevant thermodynamic data are reasonably well established. CaSO_4 is highly satisfactory in this regard, and to our knowledge, there are no previous effusion measurements reported.

To date, torsion pressure data and vapor molecular weights have been obtained over the range 1140 to 1240 K with effusion cells of 0.6 and 1.0 mm diameter orifice area. A plot of the observed pressure data is shown in Figure 2. With both cells, M^* values of 54 ± 2 were determined, independent of temperature, clearly indicating the effusing vapor to have the stoichiometry $\text{SO}_2 + 1/2\text{O}_2$. Also shown as the solid line on Figure 2 is the pressure derived from a zero orifice size extrapolation and its comparison with the selected equilibrium data of Kellogg (8) and equilibrium pressures calculated from thermochemical data for the process $\text{CaSO}_4(\text{c}) = \text{CaO}(\text{c}) + \text{SO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$.

It is evident that the extrapolated effusion pressures agree closely with the best available equilibrium data, providing a satisfactory test of the experimental technique and data treatment model. The observed orifice size effect does signify an appreciable kinetic barrier, but in this instance it would appear that the barrier does not include a slow $\text{SO}_3 \rightarrow \text{SO}_2$ conversion step on the surface or on the walls. In contrast to the results for MgSO_4 , this behavior of CaSO_4 may be due to enhanced catalytic properties of the CaSO_4 - CaO surface, or to a simple temperature effect. (The CaSO_4 measurements were made at temperatures about 200 degrees higher than for MgSO_4 .)

C. Mechanism of Decomposition

Although the experimental and data analysis phases of the work on MgSO_4 and CaSO_4 are not yet complete, we present here some preliminary thoughts about the mechanism of sulfate decomposition.

The effusion results obtained to date can be interpreted to indicate that the first step in the decomposition of MgSO_4 is:

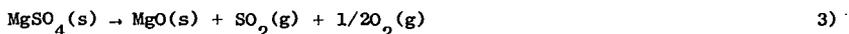


even though the thermodynamically favored reaction is decomposition to $\text{SO}_2 + \text{O}_2$. Reaction 1) is then followed by further decomposition



only if the SO_3 has sufficient residence time in the effusion cell. In other words, reaction 2) is catalyzed by processes occurring inside the effusion cell, and the longer SO_3 residence times associated with the smaller orifices lead to the observed decrease in the ratio $P(\text{SO}_3)/P(\text{SO}_2)$.

The results are in accord with the literature. Hulbert (13) studied the kinetics of decomposition of MgSO_4 between 920° and 1080°C , and found that the results could be represented by a contracting-sphere rate equation, which implies that the rate is controlled by the surface area of unreacted MgSO_4 . That is, the rate per unit surface area is constant, but the amount of surface decreases as the particles decompose. The activation energy was 74.5 kcal per mole, which is close to the enthalpy change for reaction 1), 72 ± 5 kcal/mole, implying that reaction 1) is rate-limiting. The effect of sample size was interpreted as indicating that increased SO_3 pressure decreased the rate. That is, further evidence that reaction 1) is rate limiting. Pechkovski (14, 15) found that, in a stream of flowing gas at temperatures of 750 to 1050°C , the rate of decomposition of MgSO_4 was independent of the partial pressure of O_2 . That result also indicated reaction 1) was the rate limiting step rather than the thermodynamically more favored reaction 3)



for which the rate would be inhibited by oxygen. Knopf and Staude (16) quenched a gas stream that had passed over heated MgSO_4 and identified SO_3 as a product, which indicates that reaction 2) was slower than reaction 1) in their experiments.

On the other hand, our results show that in the decomposition of CaSO_4 the products are SO_2 and O_2 , independent of temperature and orifice size. Searcy⁴ and his students have studied the decomposition of BaSO_4 (17) and SrSO_4 (18). They found the decomposition products to be SO_2 and O_2 , and their torsion effusion results for BaSO_4 were in agreement with equilibrium pressures calculated from thermodynamic data for the reaction analogous to reaction 3).

Searcy's group has also measured the rate of evaporation of BaSO_4 under free surface conditions. Under those conditions, the apparent pressures are about 1% of the equilibrium values. They remark that their explanation, in terms of active surface sites, is not entirely satisfactory.

We feel that the behavior of MgSO_4 compared to the sulfates of Ca, Ba, and Sr can be explained by a different model, as follows. The rate determining step is presumed to be the surface desorption of SO_3 for all these sulfates. The metal oxide formed by the decomposition is left on the surface as a porous layer which does not impede the desorption of SO_3 . However, as the SO_3 diffuses through the oxide layer it is converted to SO_2 and O_2 . In effect, the porous oxide layer catalyzes the conversion of SO_3 to SO_2 and O_2 . Catalysis by the MgO layer is presumed to be much less effective than that by CaO , SrO or BaO ; therefore, the

apparent products of the reaction are SO_3 for MgSO_4 and SO_2 and O_2 for the other sulfates.

The reason that MgO is less catalytic may be simply that the temperature is lower for MgO than the other oxides by several hundred degrees. The decomposition of SO_3 is a thermally activated reaction (19) (activation energy, 40 kcal per mole). There is also some evidence that the decomposition of MgSO_4 is catalyzed by oxides, i.e., Fe_2O_3 , Cr_2O_3 and CuO (14, 15).

These initial studies indicate that the experimental method can be used to generate thermodynamic data needed in cycle analysis, and also that the kinetics of the decomposition process may present some practical problems. In particular, the conversion of SO_3 to $\text{SO}_2 + \text{O}_2$ may be a rate limiting step in low temperature sulfate decompositions. Further studies of the thermodynamics and kinetics of sulfate decompositions are in progress.

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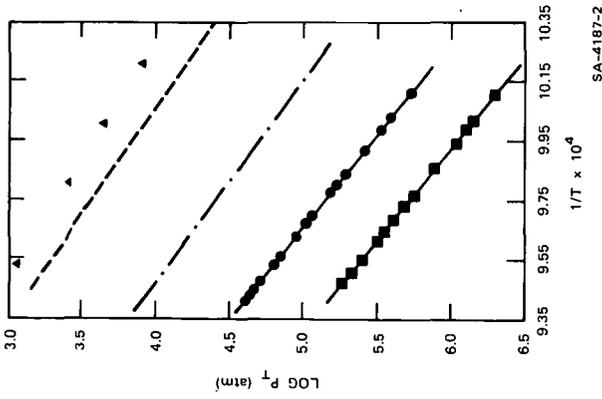


FIGURE 1 VAPOR PRESSURE OF
MAGNESIUM SULFATE;

- Cell 3
- Cell 4
- ▲ Dewing and Richardson
- Data
- · - · - Extrapolation to Zero
- Orifice Area
- - - Kellogg's Data

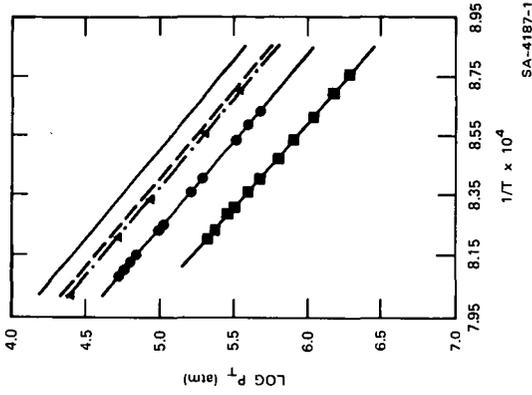


FIGURE 2 VAPOR PRESSURE OF
CALCIUM SULFATE;

- Cell 3
- Cell 4
- ▲ Dewing and Richardson
- Data
- · - · - Extrapolation to Zero
- Orifice Area
- - - Kellogg's Data
- Kelley's Data