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Note

Discussion of "The thermal decomposition of aluminum sulfate and hafnium sulfate"

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In a recent study by Papazian *et al.*[1] data were reported for the decomposition of $Al_2(SO_4)_3$ which showed an Arrhenius plot with a distinct knee joining two straight line portions. Comparisons were then made between the activation energies calculated from those plots and the activation energy calculated by Johnson and Gallagher[2] in a previous study.

It is the primary purpose of this note to emphasize that basic differences can exist between kinetic measurements performed by dynamic techniques and those performed by isothermal techniques. Dynamic measurements offer the immense experimental advantage of requiring only one sample and one experiment since the temperature is varied over the course of the experiment. It also allows measurements over a broader spectrum of temperatures than are experimentally accessible by isothermal techniques. A drawback to the technique which is frequently overlooked is that with a single experiment it is impossible to differentiate whether observed parameter changes have occurred as a function of changing temperature or as a function of the fraction reacted since both occur simultaneously. In comparison, isothermal experiments can follow the complete course of the reaction at various temperatures and separate these two variables.

These outlined principles bear on the interpretation of the data reported by Papazian *et al.*[1]. They have compared their data gathered by dynamic techniques with that of Johnson and Gallagher[2] gathered using isothermal techniques by superimposing the narrower temperature range of the isothermal study upon the Arrhenius plot of the dynamic study. The authors of the dynamic study then suggest that since the temperature range of the isothermal study falls over the portion of their Arrhenius plot showing a change of activation energy, the isothermal activation energy of 73 kcal/mol is an effective average of the two values 95.3 kcal/mol and [illegible]8.7 kcal/mol for their study in air. Close examination of the comparison shows that the temperature range used for the isothermal study in oxygen falls completely within the low (28.7 kcal/mol) activation energy for the dynamic study in air.

We propose that if an activation energy change exists, it is as a function of fraction reacted. Examination of data by Papazian[3] has shown that the knee in the Arrhenius plot[1] occurs at a value of α (fraction reacted) of about 0.12. Because of irregularities in the isothermal rate data of Johnson and Gallagher[2] below $\alpha = 0.15$ the data points for the calculation of the rate constant at any temperature used the α range of 0.15–0.90. Thus, the isothermal activation energy of 73 kcal/mol should be compared with the 95.3 kcal/mol obtained in the dynamic study for the latter part of the reaction ($\alpha > 0.12$).

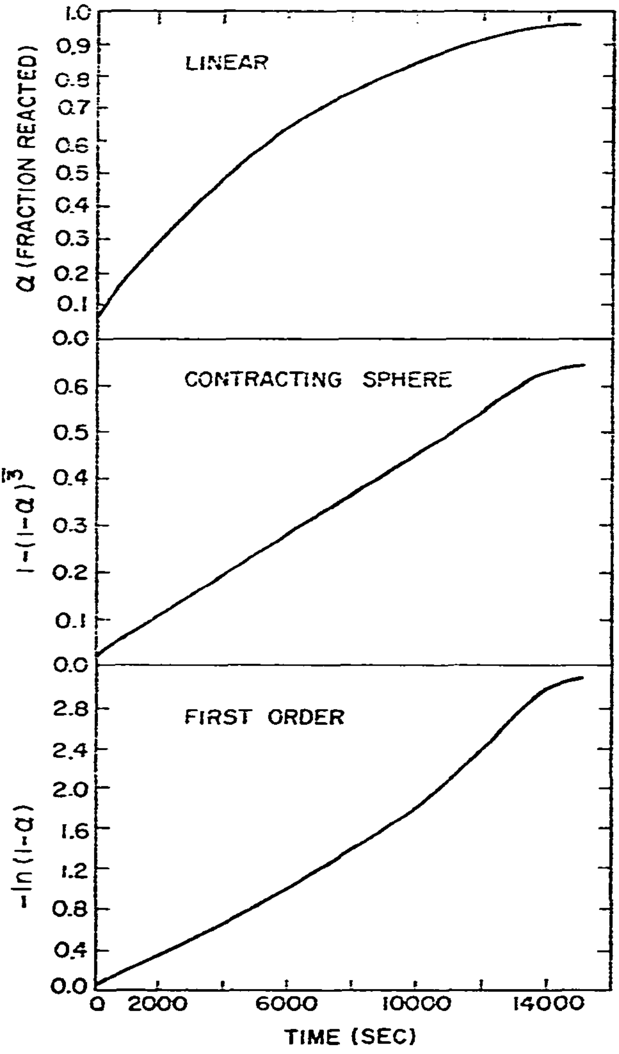

Fig. 1. Isothermal decomposition of $-50+100$ mesh $Al_2(SO_4)_3$ at 745 °C in dry O_2.

Figure 1 shows an example of the isothermal rate data plotted as fraction reacted versus time and according to both the contracting sphere and first order models. It can be seen that the curve for the contracting sphere case (best fitting model) deviates from linearity below $\alpha = 0.15$. This may be simple start-up problems in the experiments or it could be an actual mechanistic change.

Because endothermic solid state decompositions are seldom or never homogeneous in nature but rather phase boundary controlled, an argument for the formation of an intermediate phase to explain the knee in the Arrhenius plot and the plateau in the evolved gas analysis curve is questionable. Lorant's[4] proposed intermediates, $Al_2O(SO_4)_2$ and $Al_2O(SO_3)_2$ would occur at α values of 0.33 and 0.47 respectively. These intermediates are unlikely since the Arrhenius plot break occurs at $\alpha = 0.15$ and by integrating the intensity of the evolved gas analysis curves, the plateaus suggest the first reaction to cover the α range up to 0.06 using the data of Papazian *et al.*[1], or up to 0.07 using the data of Johnson and Gallagher[2]. The argument for a separate mechanism occurring for the initial decomposition which occurs at crystal surfaces is more likely. This is consistent with phase boundary controlled reactions and also predicts the mechanism change as a function of α rather than temperature.

It should be stressed that probably very little weight can be put on any value of the activation energy for this reaction. The ΔH for the decomposition of $Al_2(SO_4)_3$ to α-Al_2O_3 and SO_3 is 138 kcal/mol[5,6] at 1000 K and would be even higher if the gaseous products were O_2 and either SO or SO_2 or if the aluminum oxide were some phase other than α. In view of the fact that the enthalpy is higher than the activation energies measured by any workers suggests that the kinetic experiments are measuring a thermal transfer through the reacted layer for this endothermic reaction.

An apparent error exists in the theoretical weight loss of $Al_2(SO_4)_3$ going to Al_2O_3 as reported by Papazian *et al*[1]. The correct weight loss is 70.2% rather than 68.3%.

Papazian *et al.*[1] have also used the results of Johnson and Gallagher[2] showing an independence of activation energy on the kinetic model. It should be stressed that this holds only with isothermal measurements and as other work shows[7], the calculated activation energy can vary widely for different kinetic models if dynamic methods are used.

Papazian *et al.*[1] also present a discussion of the vapor species over $Al_2(SO_4)_3$ during decomposition and draw conclusions based, in part, upon erroneous data. In eqn (3) in ref. 1, the free energy for the dissociation of SO_3 to $SO+O_2$ is apparently incorrect and the correct values[8] are 48.4 kcal/mol at 900 K and 40.8 kcal/mol at 1100 K.

The discussion of the gas species during the decomposition[1] centers on the lack of experimental evidence for the SO_3^+ species in the residual gas analyses. Some SO_3 must exist in the system if SO_2 and O_2 are present according to the equilibrium:

$$SO_3 \rightleftarrows SO_2+\tfrac{1}{2}O_2$$

Ficalora *et al.*[9], have observed SO_3^+ with very careful experimentation. With RGA equipment used by Johnson and Gallagher[2] and by Papazian *et al.*[1] it is expected that it would be difficult or impossible to observe SO_3^+ because of a lack of sensitivity and because the ionizing voltages normally used would nearly completely crack SO_3. Also, if traces of water were present in the system, SO_3 would combine and condense.

Basically, from the type of data presented by Papazian *et al.*[1], it is not possible to determine the parent species in the mass spectrometer or the actual initial decomposition products. The argument, that SO and O_2 are the primary species based on the fact that an SO^+ peak is observed, is weak. They have corrected their SO^+ peak for the cracking of SO_2 using patterns[10] which are valid only under very stringently specified conditions. Also, SO^+ would undoubtedly be a species in the cracking of the SO_3 molecules and this correction has not been made.

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