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QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS...?

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ABSTRACT

In studies on the effective thermal conductivity of a powder-gas mixture, the values obtained were greatly influenced by the gaseous species. This factor has not been appreciated in quantitative differential thermal analysis techniques. The size and shape of the differential thermal analysis peak associated with a reaction involving a gas phase will be influenced by the heat transfer characteristics of that gas.

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I. INTRODUCTION

Differential thermal analysis (DTA) as a tool for mineral identification is now well established. Attempts have been made to procure quantitative thermodynamic data by this technique. The main premise of these quantitative investigations is that the differential temperature peak area is proportional to the heat change involved. To obtain peak area/heat relationships, calibration procedures are necessary. The dissociation of $CaCO_3$ was used by Wittels,[1] and later Barshad[2] employed a series of indicating compounds to calibrate for both temperature and reaction heat. In these and other such calibrations and estimations, the thermal conductivity of the sample is always assumed constant. Ellis and Mortland[3] proposed four conditions for a direct peak area/heat relationship. One of these was that the sample diffusivity must approach the diffusivity of the reference material. To fulfill this condition, the thermal conductivity of the sample should remain constant. This work presents data on the gas phase conductivity in packed powders not hitherto considered.

II. EXPERIMENTAL

A small cylindrical cell, 1-1/2 in. long, with boron nitride caps and a platinum wire heater along its axis was filled with A-14 alumina powder. The powder layer was 1/4 in. thick. The cell was suspended in a tubular furnace and the void between it and the furnace wall filled with A-14 powder. The intervening powder acted as a heat sink and insulator thus ensuring the proper thermal gradients. It also eliminates heat transfer within the system by means other than conduction. The

thickness of the powder layer above and below the cell was twice that around it. Consequently, axial heat flow from the cell heater was reduced to a minimum. Differentially connected thermocouples were located on the cell heater wall, the cell outer wall, in the powder 1/4 in. from the cell wall, and in the furnace wall itself. The assembly is shown in Fig. 1. The differential thermocouples allowed the temperature gradients across the system to be accurately measured. The furnace temperature was raised at 200°C per hour for one-half hour and then allowed to equilibrate for a further half hour. This hourly cycle was repeated until a temperature of 900°C had been reached. After each soak period the equilibrium cell wall temperature, the system temperature gradients, and the input power to the cell heater were recorded. The effective thermal conductivities of the different sections of the system were calculated. Runs were performed in helium and argon atmospheres. The effective conductivity values obtained for the gas-powder region across the cell are given in Table I. A run in vacuum produced an effective conductivity of the order of 5×10^{-4} cal/°C/cm^2/sec over the whole temperature range investigated.

III. RESULTS AND CONCLUSION

It would appear, therefore, that the thermal conductivity of a packed powder is primarily due to the gas phase within it. Sturm[4] considered that the sample conductivity is a function of the substance itself, its porosity when packed, and the particle size distribution within it. He further pointed out that the sample conductivity cannot be considered constant because of compositional changes in the solid

during thermal reactions. Saunders and Giedroyc[5] realized that the atmosphere in the sample played an important part in some reactions investigated by DTA. However, they did not consider the thermal conductivity aspect of the problem.

The results obtained in this study are further substantiated by the theory pertaining to the thermal conductivity of gases. For both monatomic and polyatomic gases, $k \propto 1/M$, where k is the thermal conductivity of the gas and M its molecular weight. In Table II conductivity values are given for some common gases along with their molecular weights.

The differential temperature recorded during a reaction in DTA is produced by the difference in thermal diffusivity which exists between the sample and the inert reference. The thermal diffusivity is directly proportional to the powder-gas conductivity ($h = \frac{k}{pc_p}$). Hence, the area of a differential temperature peak must be related to the change in diffusivity. Any reaction involving the evolution of a gas within the sample will give a DTA peak influenced by that particular gas. The use of a reaction to calibrate a DTA apparatus must evolve the same gas as produced by the reaction in question or the results will be in error. CO_2 and H_2O are often encountered in routine mineral analysis due to carbonate decomposition and mineral dehydration. The size and shape of the accompanying DTA peaks will be influenced by the thermal conductivity of these gases and this must be corrected to obtain accurate quantitative data.

IV. SUMMARY

Many attempts have been made to obtain quantitative thermodynamic data by DTA. To obtain such data it is necessary to calibrate the DTA apparatus using reactions with known thermodynamic properties. The direct application of such calibrations to obtain data on an unknown substance will lead to error due to thermal diffusivity differences between the calibrating standards and the unknown. This is especially true if a gas is involved in any of the reactions. It has been demonstrated that the thermal conductivity and therefore the diffusivity of a gas-powder mixture is influenced by the particular gas in the mixture. Calibrations involving one gas species and reactions involving another must lead to errors in quantitative data unless corrections are applied.

ACKNOWLEDGMENT

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Table I. Effective thermal conductivities in helium and argon atmospheres.

Furnace Temperature °C	Effective conductivity (cal/°C/cm^2/sec) x 10^{-4}	
	Helium atmosphere	Argon atmosphere
25	27	16
100	27	16
200	28	16
300	28	16
400	29	17
500	30	17
600	31	18
700	32	19
800	33	21
900	33	23

Table II. Molecular weight and thermal conductivities of some common gases.

Gas	Molecular weight	Thermal conductivity cal/°C/cm /sec at 20°C
Helium	4	339×10^{-6}
Methane	16	64×10^{-6}
Nitrogen	28	52×10^{-6}
Carbon monoxide	30	49×10^{-6}
Argon	40	38×10^{-6}
Carbon dioxide	46	30×10^{-6}

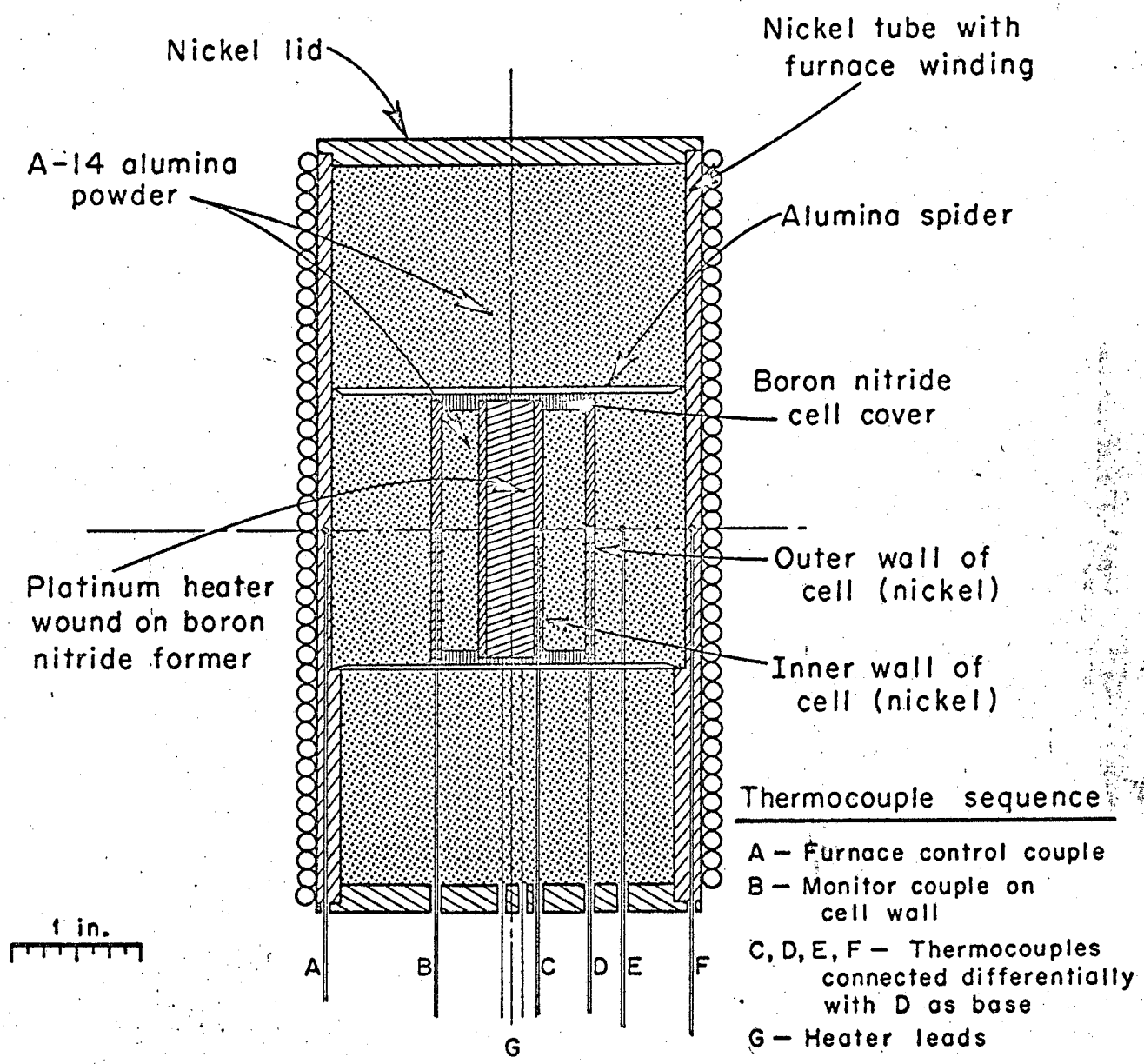

Fig. 1. Experimental complex used in determination of thermal conductivity of packed powders.

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