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A HIGH PRESSURE ELECTRICAL CONDUCTIVITY APPARATUS*

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ABSTRACT

A high pressure electrical conductivity (EC) apparatus, capable of operation at pressures from 1 to 170 atm in the temperature range from 25 to 500°C, is described. The effects of the sample holder geometry, pressure, and sample packing on the resulting EC curves are given. Operation of the apparatus is illustrated by the deaquation reactions of $BaCl_2 \cdot 2H_2O$.

INTRODUCTION

The thermal analysis technique of electrical conductivity involves the continuous measurement of the electrical conductivity of a sample as a function of temperature. This technique has been called electrical conductivity (EC)[1], amperometric thermal analysis (ATA)[2], and electrothermal analysis (ETA)[3]. Experimentally, the method consists of placing a pair of inert electrodes, with a potential applied across them, into a sample and recording the change in current as a function of temperature as the sample temperature is linearly increased .The instrumentation, which is simpler than that for TG or DTA, consists basically of the following components: A d.c. or a.c. voltage source to supply the potential across the electrodes; a heated sample container; a microammeter to detect the current flow; and a X-Y recorder to plot the temperature–current data. A liquid or solid sample may be employed for the measurements.

Initially, this technique was applied to the study of the resistance of thin metal wires[4]. An early paper has been described in which two platinum wires were embedded in a pressed, fired, ceramic disc[5] and the electrical conductivity of the material measured as a function of temperature. Many other unifunctional instruments capable of measuring the change in electrical conductivity of a solid sample as a function of temperature have been described[6–10]. Equipment for simultaneous DTA and conductivity measurements has been reported[11–13] as well as for other concurrent

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methods[2]. The technique has also been used at high temperatures to determine the transformation temperature of ZrO_2 and the solid-state reactions in the SiO_2–PbO_2 and UO_2–Al systems[14]. Studies on the melts of alkali metal acetates have been elucidated through the use of electrical conductivity methods[15]. The application of this technique to the detection of liquid water and or quadruple points in metal salt hydrate systems has also been described[1]. Numerous other applications of this method are found in the literature[16].

Although electrical conductivity measurements have been made on many chemical systems and over a wide temperature range, almost all of the data have been obtained at or below ambient atmospheric pressure. The purpose of this investigation is to describe an electrical conductivity apparatus which can be used at pressures from 1 to 170 atmospheres and in the temperature range of 25 to 500 °C.

EXPERIMENTAL

Description of apparatus

A schematic diagram of the apparatus is illustrated in Fig. 1. The apparatus consisted of a Keithley Model 160 digital recording microammeter (A), a 0–25 V regulated DC power supply (B), a Moseley Model 135 X-Y recorder (C), a 3000 psi gas supply cylinder with a regulator and gauge (D, E), a high pressure chamber (F) housing the sample holder and probe, and a temperature programmer.

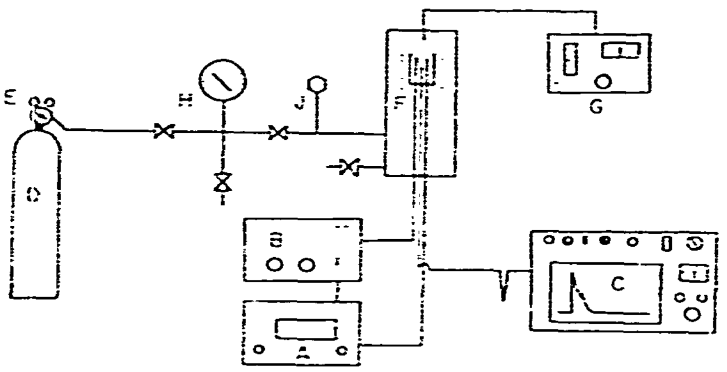
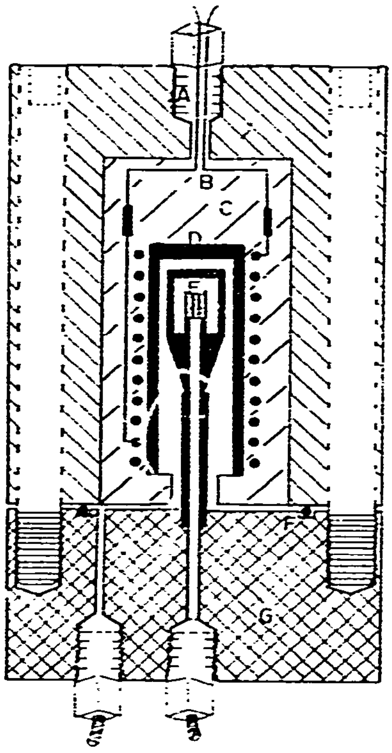


Fig. 1. High pressure electrical conductivity apparatus. A, Keithley Model 160 digital recording microammeter; B, 0–25 V regulated d.c. power supply; C, Moseley Model 135 X-Y recorder; D, 3000 psi gas supply cylinder; E, gas pressure regulator; F, high pressure chamber housing the sample holder and sample probe; G, T&T Controls Company Model No. TPC-2000 temperature programmer; H, pressure gauge; J, relief valve.

The complete pressure vessel and sample probe are shown in Fig. 2. The pressure vessel consisted of two 100 mm cylindrical pieces of type 316 stainless steel held together with six stainless steel bolts, each 13 mm in diameter. The upper portion of the vessel (A) consisted of a 22 mm id tube furnace (D) housed in a 50 mm o.d. insulated body (C). Heater wires were passed through a Conax high pressure connec-



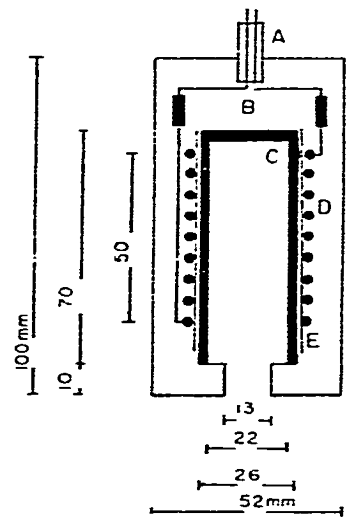


Fig. 2 (left). Schematic diagram of furnace and sample holder. A, upper portion of pressure vessel with heater wire entry through a Conax high pressure connector; B, heater connector wire; C, Marinite insulation; D, furnace; E, sample holder and thermocouple; F, Buna-N O-ring; G, base plate.

Fig. 3 (right). Schematic diagram of furnace assembly. A, ceramic insulator tube; B, marinite insulation; C, aluminum cylinder; D, heater wire element; E, asbestos paper.

tor (B) attached to the top of the chamber. The top part of the chamber was sealed to the base by means of a Buna-N O-ring (F) contained in a groove cut in the base; the base plate (G) was machined from the same bar stock as the top and was threaded to accept the high pressure gas and Conax wire connectors. The sample probe (E), which consisted of a 5 mm in diameter four-holed ceramic tube containing two platinum electrodes, a sample thermocouple, and a furnace control thermocouple, was covered by a removable machined aluminum cap to insure even heat distribution to the sample. Different types of probes were studied and they will be discussed in a later section.

A schematic diagram for the furnace is shown in Fig. 3. A cavity (C) was machined into a piece of aluminum bar stock to form a one-open-end cylinder having the indicated dimensions. The outer surface of this cylinder was covered with a 70.0 mm thick layer of asbestos paper (E). The heater element, which consisted of No. 26 gauge Nichrome V wire (D) evenly spaced over the asbeston, had a total resistance of 55 ohms. Both the tube and heater element were cemented into a cylindrical layer of Marinite insulation (B). Heater wires were connected to No. 24

gauge Nyclad copper wires which were housed in ceramic tube (A) and passed through the vessel body via a Conax high pressure connector.

Operating procedure

For all pressures the operating procedure was basically the same and consisted of the following: From 20 to 150 mg of a 100–200 mesh powdered sample, depending upon the sample holder used, was placed into the sample container and was packed until the two platinum wire electrodes were uniformly covered. The outer aluminum cap was then placed over the sample and the furnace body bolted to the base plate. The vessel was then purged with the pressurizing gas and the system pressure adjusted to a predetermined level. Once the system pressure was stabilized, the furnace heating cycle was begun and the output of the recording ammeter recorded as a function of temperature on the recorder. A furnace temperature heating rate of 5°C per min was normally employed. Due to the effect of temperature on the sample pressure, a slight purge of gas was used to maintain a constant pressure in the chamber.

RESULTS AND DISCUSSION

Effect of sample packing and container geometry

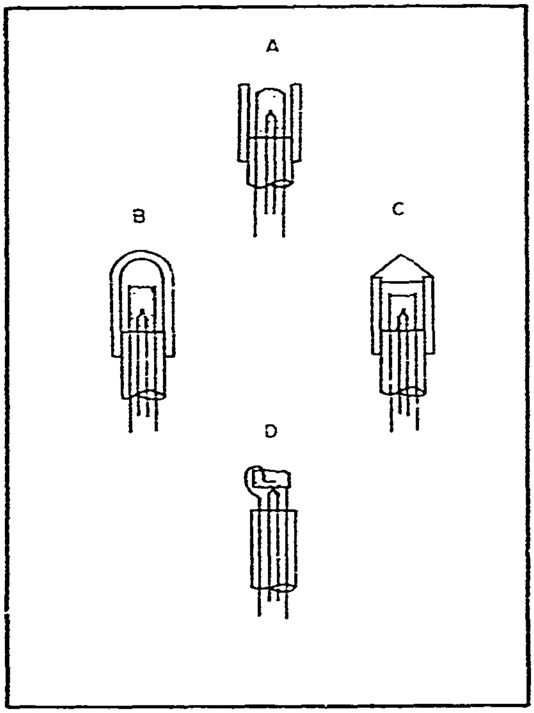
Several types of sample holders were used to investigate the effect of sample packing and sample holder geometry on the EC curves. The four sample holders, as shown in Fig. 4, were all constructed of the same diameter ceramic tubing. In holder (A), the sample is contained in a glass sleeve which surrounds the electrodes and thermocouple. Sample sizes of 50 to 300 mg and 5 to 10 mm in depth were normally used. The changes in the number and size of the peaks obtained from the dehydration of $BaCl_2 \cdot 2H_2O$ are shown in Fig. 5. The curve in Fig. 5A is for a loosely packed sample in any of the three glass enclosed sample containers. In this curve, only one peak is observed which is due to the loss of one mole of water per mole of salt in the reaction:

$$BaCl_2 \cdot 2H_2O \rightarrow BaCl_2 \cdot H_2O + H_2O$$

The presence of water as a liquid and vapor is responsible for the abrupt increase in the electrical conductivity of the sample. It should be noted that visual observation of the $BaCl_2 \cdot 2H_2O$ sample indicates that it remains in the solid state during the dehydration. Thus, the system is heterogeneous and the aqueous solution of $BaCl_2 \cdot H_2O$ which is formed is responsible for the electrical conductivity change. If the sample is moderately packed in the holder and enclosed by a glass sleeve (Fig. 5B) or a solid cap (Fig. 5C), a second peak is always observed (Fig. 5B). This second peak is due to the second dehydration reaction, or

$$BaCl_2 \cdot H_2O \rightarrow BaCl_2 + H_2O$$

The appearance of a small second curve peak is thought to be due to the effect of decreased diffusion of the evolved water vapor by the closed sample container. A



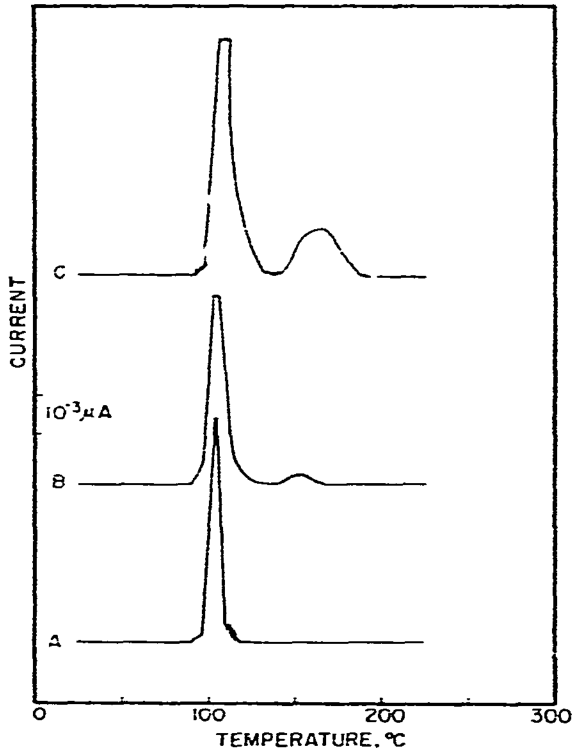


Fig. 4 (left). Types of sample holders. A, ceramic tube with open glass sleeve; B, ceramic tube with closed glass tube; C, ceramic tube with glass sleeve closed with removable aluminum cap; D, platinum pan attached to thermocouple.

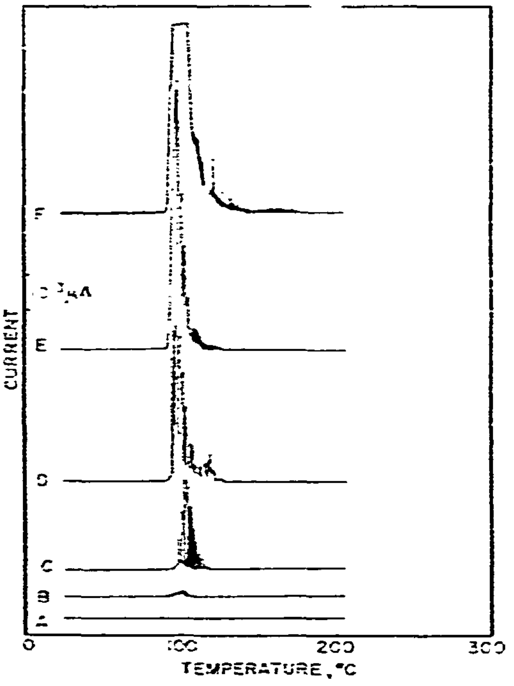
Fig. 5 (right). Electrical conductivity curves of $BaCl_2 \cdot 2H_2O$. A, open glass sleeve, sample loosely packed; B, glass sleeve closed with aluminum cap, sample moderately packed; C, glass sleeve closed with aluminum cap, sample firmly tamped.

third change in the curve is obtained by firmly tamping the sample and covering it with a closed sleeve or cap; both the height and area of the peaks in the curve (Fig. 5C) were observed to increase. The peaks were also affected by the depth of sample at constant packing; this would decrease the diffusion of vapor from the solid sample. The decreased diffusion retards the vaporization of the water and hence increases the relative amount of the conducting phase present.

Effect of system pressure

To observe the effect of pressure, the sample container in Fig. 4D was used, which consisted of a platinum cup, 2 mm in depth by 5 mm in diameter; a thermocouple was attached at the bottom. The electrode system consisted of two platinum wires, one of which was attached to the cup while the other was held inside the cup at a distance of about 0.5 mm above the bottom and parallel to it. The curves obtained from this sample holder are shown in Fig. 6. A moderately packed sample of $BaCl_2 \cdot 2H_2O$ (curve A) showed no change in conductivity during heating at one atmosphere.

As the pressure increased, a slight change in the curve near 100 °C was observed. With increasing system pressure, the magnitude of the peak height and also the area increased as did the temperature range of conductivity. The increase in the peak height and area is thought to be due to the decrease in diffusion of water vapor from the sample as the pressure is increased. A second peak was not observed because the heat transfer through the metal sample cup wall was rapid enough to vaporize the liberated water and the short diffusion path was not as effective in retarding the escape of the vapor as in the previous sample holders.



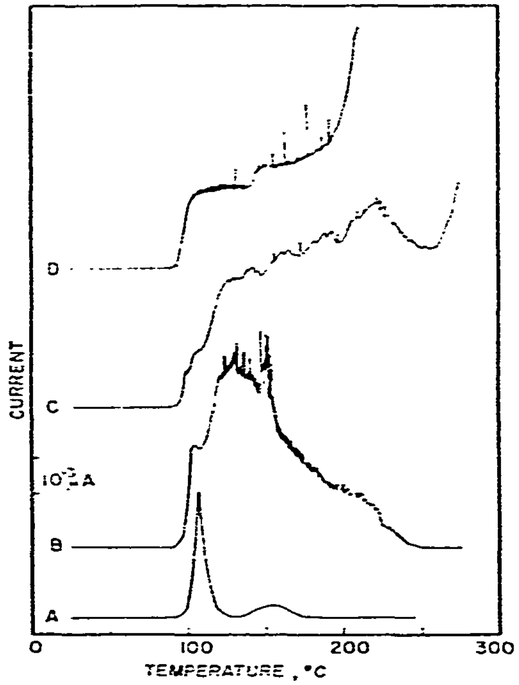


Fig. 6 (left). Effect of pressure on the electrical conductivity curves of $BaCl_2 \cdot 2H_2O$. A, 1 atm; B, 7 atm; C, 15 atm; D, 27 atm; E, 42 atm; F, 170 atm.

Fig. 7 (right). Effect of pressure on the electrical conductivity curves of $BaCl_2 \cdot 2H_2O$ contained in an enclosed glass sleeve sample container. A, 1 atm; B, 17 atm; C, 42 atm; D, 137 atm.

The combined effects of an extended diffusion path, increased sample depth, firmly packed sample, closed top, and system pressure are seen in Fig. 7. At one atmosphere of pressure, both peaks are observed because the water vapor diffusion is rapid enough to allow all of the water to escape between the two dehydration steps. As the system pressure is increased, three changes in the curves are observed. Firstly, the separation between the dehydration steps is decreased because the second reaction begins before the initial reaction is completed. Secondly, the magnitude of the electrical conductivity is increased due to the presence of water vapor from the overlapping reactions. The final difference in the curves is the shift in the peak maxima to higher temperatures; this is probably due to the presence of water vapor from the first step retarding the second reaction. The effect of gas pressure appears to increase the sample electrical conductivity by decreasing the water vapor diffusion through the sample hence increasing the relative amount of liquid phase present.

Effect of heating rate

The heating rate was also found to affect the size and shape of the EC curves at all pressures. As the heating rate is increased, the temperature at which conductivity begins and the temperature at which the maximum conductivity occurs both increase. The temperature at which the conductivity begins is not affected as much as the temperature of maximum conductivity. This is perhaps due to the fact that heat transfer to the sample and sensing thermocouple is so rapid that the reaction is initiated at essentially the same temperature. As the reaction proceeds, however, the heat transfer through the container walls and sample may not be rapid enough to maintain the reaction; this results in a shift in both the peak maximum and the final reaction temperature. The effect of heating rate on the shape of the peaks cannot be predicted due to the complicating factors of sample packing, etc.; in general, however as the heating rate is increased, the curve peaks are broadened.

CONCLUSIONS

The examples illustrated here show the operation of the apparatus and its application to the deaquation reactions of the $BaCl_2 \cdot 2H_2O$ system. The apparatus is simple to use and furnishes information which can supplement DTA or TG data. These data can often be used as an aid in the interpretation of DTA data, especially at elevated pressures.

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