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A CONVENIENT AC ELECTRICAL CONDUCTIVITY (EC) APPARATUS

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ABSTRACT

A convenient AC electrical conductivity apparatus is described. The sample, which is in the form of a pressed disk, is placed between two platinum plates located in a small cylindrical furnace. A 1-10V, 100 Hz potential is applied to the sample and the resulting current, in μA, is recorded on an X–Y recorder as a function of temperature. An EC curve of the dehydration of $BaCl_2 \cdot 2H_2O$ to $BaCl_2 \cdot H_2O$ is presented to illustrate the operation of the apparatus.

INTRODUCTION

The electrical conductivity (EC) of solid samples is a recognized thermal analysis technique[1] and is widely used in this laboratory. A simple EC apparatus has been described[2] which was used to detect quadruple points in metal salt hydrate systems. Later, this apparatus was modified for high pressure studies up to 170 atm[3] and also for simultaneous EC–DTA measurements[4, 5]. All of the above instruments used a DC applied potential (usually 1–5V) and employed powdered samples.

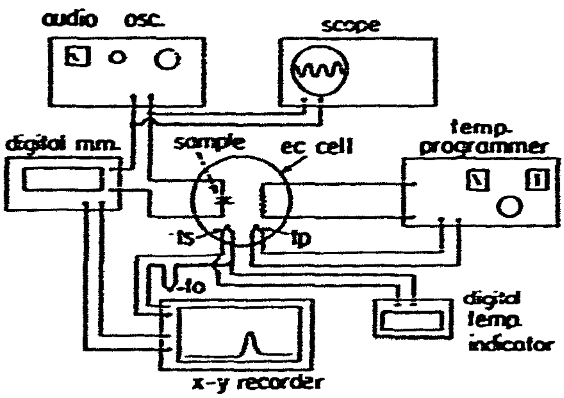
We wish to describe here a new apparatus which uses an AC applied potential (1–10V) at a frequency of 100 Hz and in which the sample is in the form of a pressed disk. The disk type of sample configuration has been very useful for the study of certain decomposition and solid-state reactions[6–8]. Up to now, the technique of DSC or DTA was used to investigate the various reactions in the disk matrices. However, with the apparatus described here, EC measurements can readily be made on disks of the pure substances or mixtures with a matrix material such as KBr, KI or KCl.

EXPERIMENTAL PART

EC apparatus

The components used in the EC apparatus are shown schematically in Fig. 1.

The apparatus consists of the EC cell, a linear temperature programmer (Theall Model TP-2000), an audio oscillator (Heath Model IG-1B), a digital multimeter (Keithley Model 171), an X–Y recorder (Hewlett-Packard Model 7035B), an oscillo-



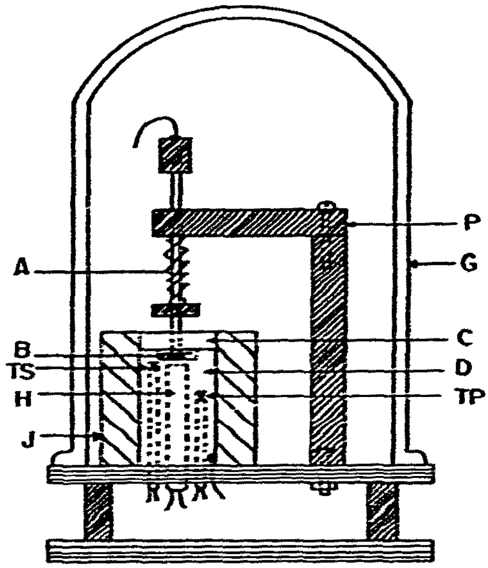


Fig. 1. Schematic diagram of the EC apparatus.

Fig. 2. Schematic diagram of the EC cell. (A) Spring; (B) sample; (C) sample cover; (D) furnace block; (G) bell-jar glass enclosure; (H) heater cartridge; (J) furnace block insulation; (Tp) programmer thermocouple; (Ts) sample thermocouple.

scope (B & K Model 1470), and a digital temperature indicator (Doric Model DS-500). The 100 Hz signal from the audio oscillator is passed through the sample and then to the digital multimeter. The output from the latter is recorded on the Y-axis of the recorder. The sample temperature, as detected by thermocouples Ts and To, is recorded on the X-axis and is also observed on the digital temperature indicator. Temperature rise of the EC cell furnace is controlled in a linear manner, usually 5°C min^{-1} by the temperature programmer and the feedback thermocouple Tp.

A schematic diagram of the EC cell is illustrated in Fig. 2.

The furnace block, which is constructed of aluminum and is 6.0 cm high by 4.0 cm in diameter, is heated by a 80W 120V heater cartridge. The sample, in the form of a pressed disk, is placed between two platinum foil disks, one of which is grounded to the furnace block and the other attached to a 3.0 mm in diameter ceramic insulator tube by means of a platinum wire. Firm pressure is assured between the platinum disks and the sample by a light spring attached to the ceramic insulator tube. The two thermocouples must not touch the furnace block otherwise the induced 100 Hz signal will block the X-axis channel of the recorder. A glass bell-jar is placed over the furnace and sample block so that the EC measurements can be made in an inert (N_2) atmosphere if so desired.

Sample preparation

About 50 mg of sample is placed in a laboratory built die and compressed at an applied pressure of 2000 lb $in.^{-2}$ in a hydraulic press. The resulting disk is 5.0 mm in diameter by 1.0 mm in height. No difficulty was found in making rigid disks of most of the compounds that were studied. If difficulty is experienced, the sample may be placed in a KBr matrix which does form a rigid disk.

Procedure

The pressed sample disk is placed in position on the lower platinum foil disk. The upper spring loaded platinum foil disk is then placed in firm contact with the sample, the furnace cover placed in position, and the glass bell-jar lowered around the entire furnace and sample holder. A 100 Hz audio signal at about 0.5–1.0V is applied to the sample and the current through the circuit detected by the digital multimeter set on the 0–10 μA scale. Other scale settings, frequencies, and applied voltages may be used depending upon the nature of the sample studied. The output from the multimeter is recorded on the 0–1V scale of the Y-axis of the recorder. The voltage output from the Ts thermocouple is recorded on the X-axis using the 2mV in.$^{-1}$ scale of the recorder.

RESULTS AND DISCUSSION

An EC curve for the dehydration of $BaCl_2 \cdot 2H_2O$ is shown in Fig. 3.

This compound, which has been the subject of several investigations[2, 3, 9], contains a quadruple point during the initial dehydration reaction,

$$BaCl_2 \cdot 2H_2O(c) \rightarrow BaCl_2 \cdot H_2O(c) + H_2O(l)$$
$$H_2O(l) \rightarrow H_2O(g)$$

The liquid water forms a saturated solution of $BaCl_2$ which is the conducting phase, even in a disk of the pure compound. The increase in conductivity begins at about 50°C, depending upon the range of the DMM and the heating rate. After a

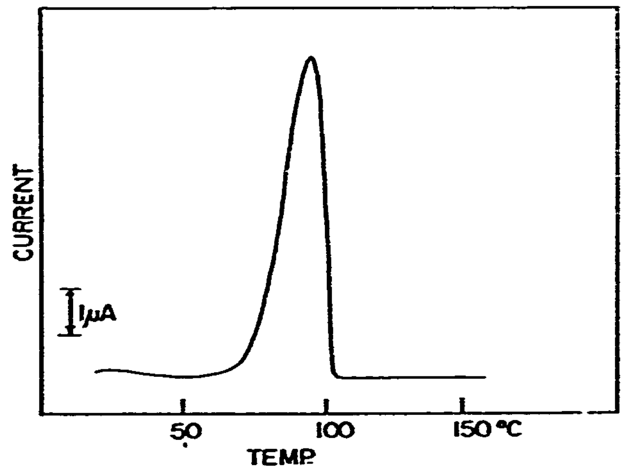


Fig. 3. EC curve of a $BaCl_2 \cdot 2H_2O$ disk. Conditions are a heating rate of 5°C min^{-1} and 100 Hz at 1.0 V applied AC potential.

maximum at about 100°C, the peak decreases rapidly, resulting in a baseline which gives no evidence of additional peaks during the dehydration of the 1-hydrate, $BaCl_2 \cdot H_2O$.

This apparatus is currently being used to study the phase transitions and thermal decomposition reactions of ammonium salts. These investigations will be reported at a later date.

ACKNOWLEDGMENT

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