

## A HIGH PRESSURE THERMOGRAVIMETRY–MAGNETIC SUSCEPTIBILITY APPARATUS

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### ABSTRACT

An apparatus is described in which the thermogravimetry and magnetic susceptibility of a compound can be obtained at pressures from 1 to 68 atm. Application of the apparatus to the thermal reduction of the cobalt(III) ion in  $K_3[Co(C_2O_4)_3] \cdot 3H_2O$  at various elevated pressures is discussed.

### INTRODUCTION

During the past few years, interest has increased in the investigation of chemical reactions at elevated pressures<sup>1–3</sup>. High pressure differential thermal analysis<sup>4–7</sup>, thermogravimetry<sup>8</sup>, and electrical conductivity<sup>20</sup> equipment have been described and employed in the study of thermal dissociation reactions. For some compounds, an oxidation–reduction reaction accompanies the dissociation reaction and this may not be detectable by TG, DTA, or electrical conductivity measurements. One convenient method of detecting such oxidation–reduction reactions in coordination compounds, if they involve changes in the number of unpaired electrons of a central metal ion, is by the use of magnetic susceptibility measurements.

A combined thermobalance–magnetic susceptibility apparatus, for measurements of reactions at atmospheric pressure, has previously been described<sup>12</sup>. The apparatus described here is capable of operation from atmospheric pressure to about 68 atm. Use of the apparatus is illustrated by the re-investigation of the solid-state thermal oxidation–reduction reaction of  $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ , a reaction which has been extensively investigated at atmospheric pressure<sup>13–18</sup>.

### EXPERIMENTAL

#### $K_3[Co(C_2O_4)_3] \cdot 3H_2O$

The compound used was the same as that previously described<sup>18</sup>.

#### *Thermobalance–magnetic susceptibility apparatus*

The thermobalance used was the balance assembly (A in Fig. 1) portion of a DuPont Model 950 Thermogravimetric Analyzer. It was mounted in a 28 cm × 15 cm o.d. × 7.5 cm i.d. cylindrical pressure vessel (B) composed of Type 316 stainless steel.

The balance housing, as shown in Figs. 1 and 2, was connected to the furnace (R) by means of a stainless steel tube (C) (13 mm o.d.  $\times$  6 cm i.d.). The furnace was non-inductively wound on a ceramic support (Nichrome wire, 20 ohms) which was insulated with Marinite and contained within the high pressure housing (D). The power

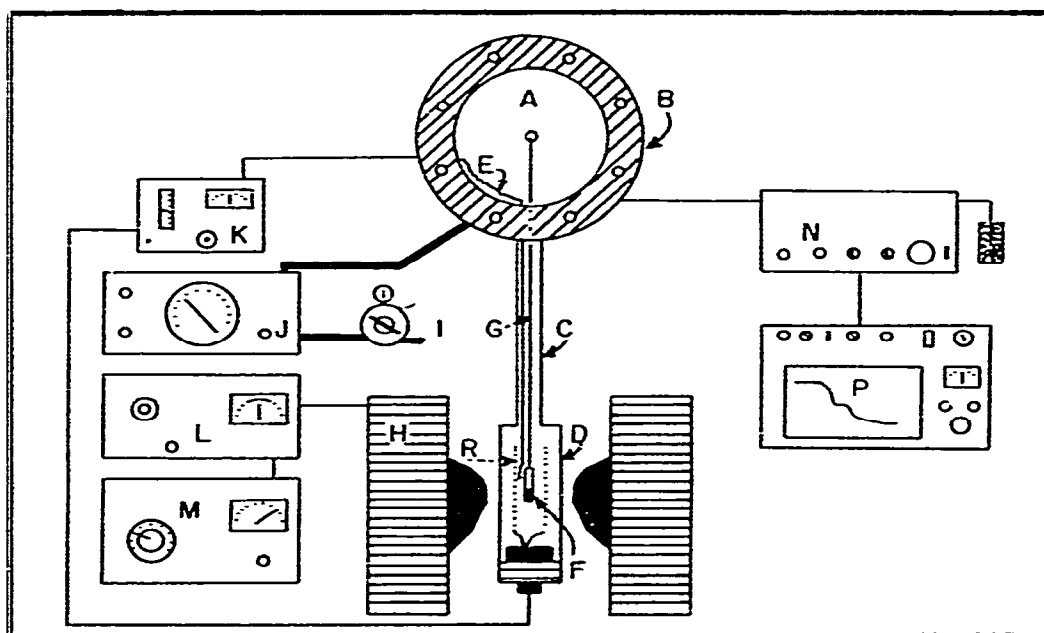


Fig. 1. Thermobalance-magnetic susceptibility apparatus (see text for figure components).

leads were brought into the high pressure chamber via a high-pressure Conax connector located at the bottom of the housing. The Chromel-Alumel thermocouple wires (E) as well as the balance control leads were connected via other Conax fittings located in the balance enclosure. The sample was contained in a Pyrex glass bucket (F), 4 mm o.d.  $\times$  2.5 mm i.d., which was attached to the quartz balance beam by means of a glass fiber (G). It was positioned so as to be in the region of maximum magnetic flux in an electromagnet (H) (Alpha Model A1 7500) fitted with Heyden pole pieces.

Nitrogen gas pressure within the system was maintained by means of a high-pressure gas regulator (I) connected to a let-down valve pressure gauge (J). The heating rate of the furnace was controlled by a T and T Controls Model 2000 temperature programmer (K). An Alpha Scientific Model AL 7500 Power Supply (M) and a Model 7500 current regulator (L) were used to control the magnet current. Electrical outputs of the balance and thermocouple were recorded on the DuPont Model 900 console (N, P) (X-Y recorder).

### Procedure

The procedure for a TG-magnetic susceptibility run was as follows. The sample, ranging in mass from 20 to 30 mg, was placed in the sample holder and the apparatus

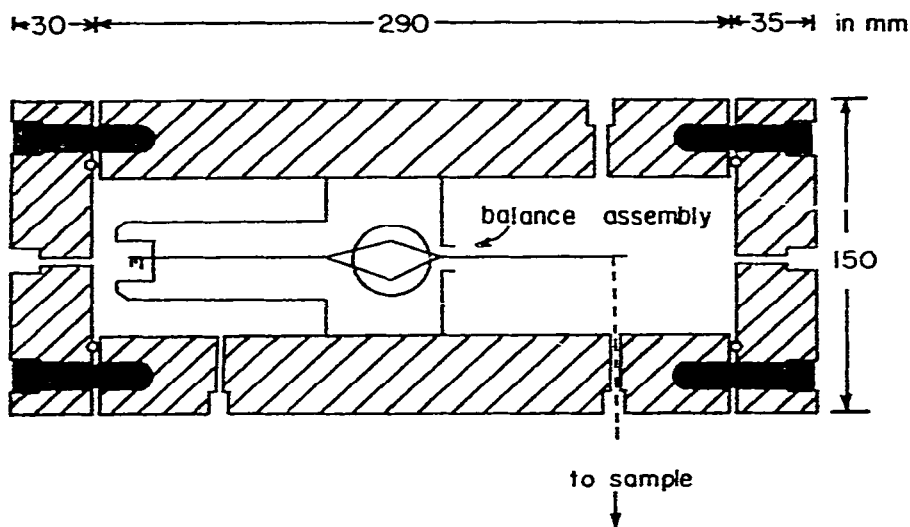


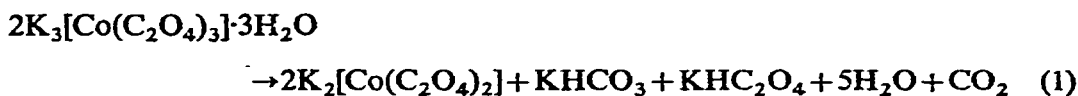
Fig. 2. Detail of high-pressure enclosure for balance assembly.

assembled and pressurized to a pressure from 1 to 68 atm. With the sample in position and the gas pressure adjusted, the furnace heating rate was programmed at  $4^{\circ}\text{C}/\text{min}$ . At various time intervals, the current to the magnet was increased momentarily from 0 to 6.0 amp. The mass-change of the sample, due to the inhomogeneous magnetic field, was thus superimposed on the TG curve. The maximum temperature of the system was  $450^{\circ}\text{C}$ , while the maximum rated pressure was 133 atm.

#### RESULTS AND DISCUSSION

The TG-magnetic susceptibility curves for  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$  at pressures from 1 to 68 atm are given in Fig. 3.

The compound undergoes concurrent deaquation and oxidation-reduction reactions at atmospheric pressures according to the following equation:



The deaquation reaction occurs over a broad temperature range, which overlaps the reduction reaction of the cobalt(III) ion, which, at atmospheric pressure, occurs at about  $125^{\circ}\text{C}$ .

The vertical lines on the TG curves in the figure indicate the mass changes due to the inhomogeneous magnetic field induced by the periodic turning on and off of the magnet power supply. In  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ , the cobalt(III) ion has zero unpaired electrons and the initial mass deflections are small and negative. On the appearance of the cobalt(II) ion in the product compound, large positive mass deflections are observed, because of the three unpaired electrons which are present in the ion. As expected, the deaquation reaction of  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$  occurs at higher temper-

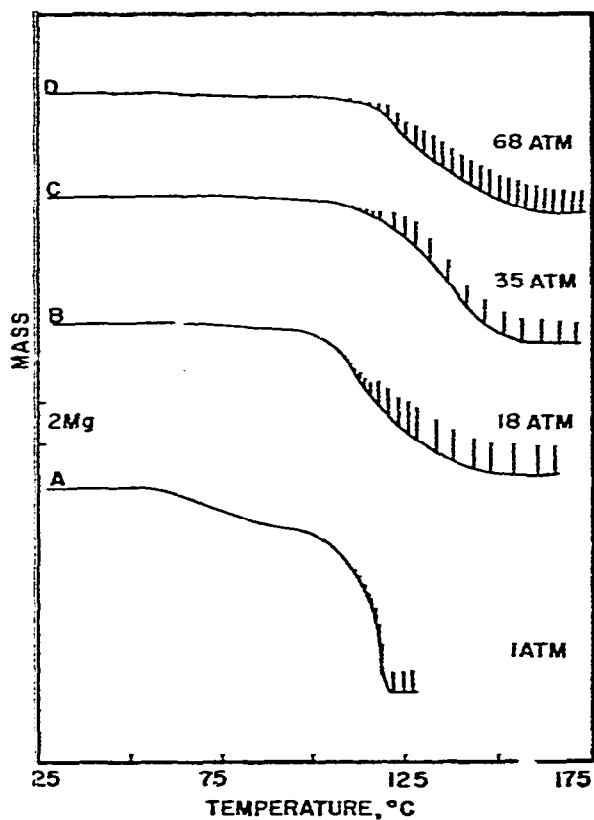


Fig. 3. TG-magnetic susceptibility curves for  $K_3[Co(C_2O_4)_3] \cdot 3H_2O$  at various pressures.

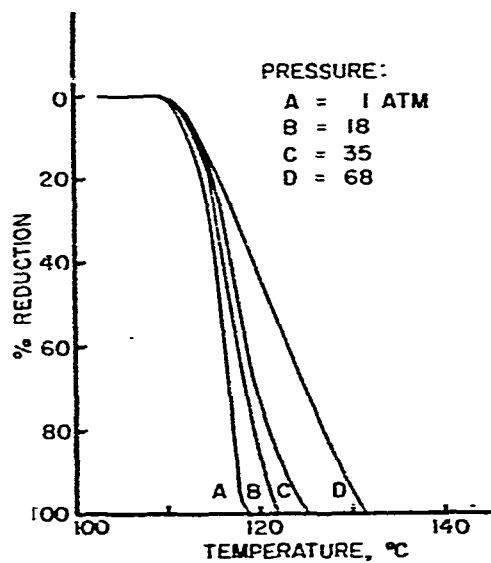


Fig. 4. The percent reduction of the cobalt(III) ion in  $K_3[Co(C_2O_4)_3] \cdot 3H_2O$  at various pressures.

atures and over a greater temperature range as the pressure is increased. The oxidation-reduction reaction of the compound is affected to a much smaller extent by the pressure, as shown by the plots of percent reduction *vs.* temperature in Fig. 4. These curves were prepared from the TG-magnetic susceptibility data in Fig. 3 in a manner which has previously been described<sup>12</sup>. As can be seen, the rate of the oxidation-reduction reaction was somewhat decreased and the reaction temperature was slightly increased as the pressure was increased. This suggests that the oxidation-reduction reaction is somewhat suppressed by the presence of the hydrate-bound water. Such suppression by the hydrate-bound water has previously been postulated<sup>19</sup> for the oxidation-reduction reaction of the corresponding manganese(III) compound,  $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$ . The evidence found in this investigation, that the presence of the hydrate-bound water suppresses the oxidation-reduction reaction of  $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ , adds only a small amount of insight into the nature of the reaction mechanism. An oxalate bridging mechanism and a free ion-radical intermediate mechanism have been postulated<sup>12</sup>. The presence of the hydrate-bound water would certainly be expected to interfere with the formation of an oxalate bridge. However, it may also inhibit the formation and/or the movement of an ion radical. Another possible explanation for the decrease in the rate of the oxidation-reduction reaction at higher pressures is connected with the rate of diffusion of the evolved carbon dioxide gas from the sample. At higher pressures, the carbon dioxide diffuses from the sample at a slower rate. Its presence may inhibit the oxidation-reduction reaction.

In conclusion, it is apparent from this investigation that the use of the high pressure TG-magnetic susceptibility apparatus described here may yield useful information concerning solid-state thermal oxidation-reduction reactions.

#### ACKNOWLEDGMENTS

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