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AN APPARATUS FOR HIGH PRESSURE THERMOGRAVIMETRY

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ABSTRACT

Construction and operation of a high pressure thermobalance usable to 300 psig and a temperature of 350 °C is described. Utilization of a modified commercially-available balance mechanism and associated circuitry provided an apparatus which is easily constructed and has satisfactory performance characteristics. Thermograms are presented to show typical operation and performance of the apparatus using aniline to demonstrate retardation of evaporation and copper sulfate pentahydrate to show relatively unchanged decomposition rates with increased pressure.

INTRODUCTION

In our laboratory we have found thermogravimetric analysis (TGA) especially suited for the study of kinetics of decomposition and vaporization of liquids or solids where information about the rate of reaction over a range of temperature is required. It has been possible to identify vaporization, determine kinetic data constants, and obtain information about mechanisms of decomposition.

In using the thermobalance to study rates of decomposition, a problem could arise in that the compound under study may undergo evaporation either before or during the decomposition reaction. Consequently, any method of controlling the rate of vaporization would extend the usefulness of the balance by making it possible to either increase the vaporization rate of the products or decrease the rate of vaporization of the compound being studied. Two methods to reduce the rate of evaporation are immediately apparent, the use of high molecular weight inert gases and/or operation of the apparatus at high pressures. The apparatus described in this report was constructed so that high pressure thermogravimetry could be used to selectively control the vaporization of samples.

A search of the literature when this work was begun produced only two references to the construction of high pressure thermobalances[1,2]. In 1968 Feldkirchner and Johnson[3] published information on such an apparatus and referenced work performed by McKewan[4].

None of the apparatus described was suitable for our purposes. Each instrument appeared to require considerable effort and facilities to construct so that duplication was not attempted. A DuPont Model 950, Thermogravimetric Analyzer, already in our laboratory, was available for modification into a pressure balance. This required only the fabrication of a suitable pressure vessel large enough to contain the balance mechanism and provide easy access for calibration and loading of samples.

Description of the apparatus

The apparatus consists of a modified Balance Assembly portion of a DuPont Model 950 Thermogravimetric Analyzer mounted in a pressure vessel. The pressure vessel was constructed of a piece of 6-inch diameter, Schedule 40, carbon steel pipe with smooth-finished welded neck flanges at both ends; the overall internal length is 18 inches. The ends of the vessel are closed with smooth-finished blind flanges; the flanges were standard 300-lb pressure rated, 6-inch pipe size. The pressure seal is afforded by silicone "O" rings set into the face of the blind flanges. Power Lead Pressure Seals, manufactured by Conax Corporation, are used for all electrical connections between the pressure balance and the associated controlling and measuring circuitry. These are attached through the rear blind flange which need not be removed during routine operation of the apparatus. The front flange is removable and provides access to the balance mechanism for adjustment and loading of test samples. A Pop Safety valve set at 350 psig is mounted on this flange. Fig. 1 shows an

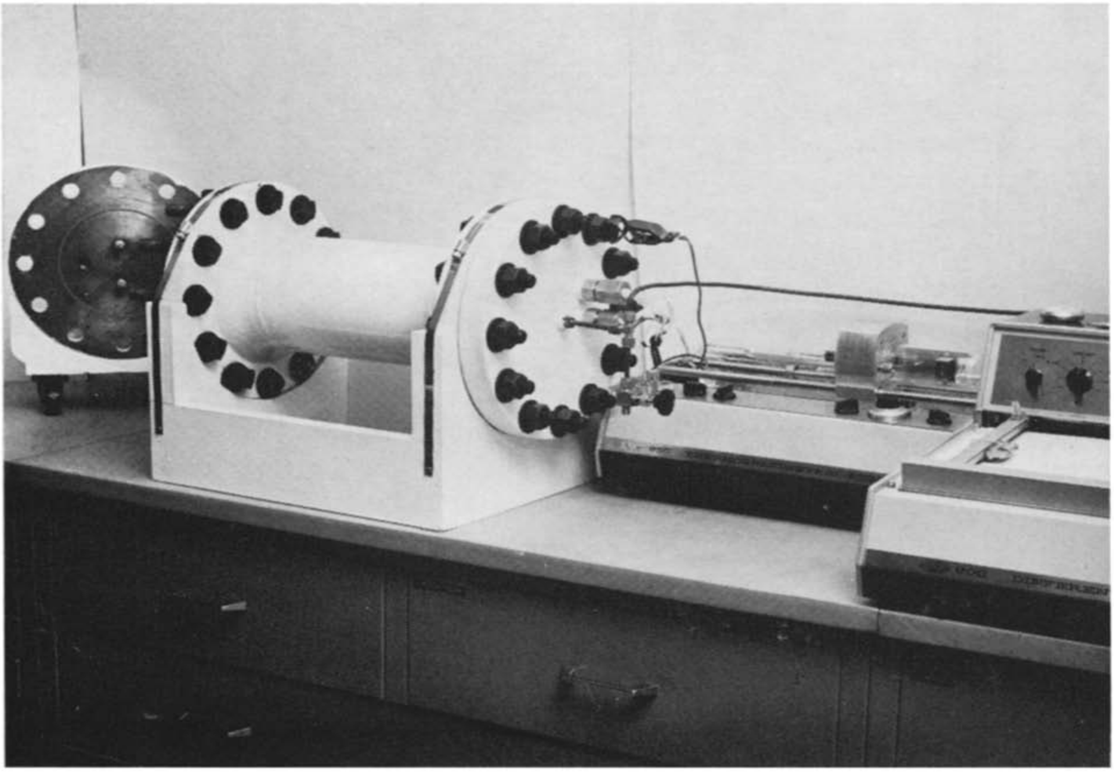

Fig. 1. The high pressure thermobalance and associated circuitry.

overall view of the apparatus. A DuPont Model 900 DTA unit and Model 950 TGA unit (bypassing the balance mechanism) are used for electrical control of the pressure balance. This affords all the convenience and accuracy associated with the commercial apparatus and greatly reduces construction time and complexity of operation.

A cylinder of prepurified nitrogen (not shown in Fig. 1) is connected to the pressure vessel through a dual-stage pressure regulator; one-quarter inch O.D. copper tubing was used for the connecting lines. A precision test gauge reading 600 psig full scale was mounted next to the pressure regulator to measure pressure in the system. The gauge, which has 0.25% accuracy, was manufactured by Marshalltown Manufacturing, Inc. of Marshalltown, Iowa.

Performance of the thermobalance

Operation of the thermobalance at pressures above atmospheric follows closely the procedure set forth in the manual for the DuPont Thermogravimetric Analyzer[5]. Fig. 2(a) displays the apparatus with the sample pan (in the Pyrex furnace tube) extended for loading. Fig. 2(b) shows the balance mechanism and furnace in the operating position.

After loading the sample and positioning the balance mechanism, the end flange is put in place and secured with twelve bolts. The sealing procedure is relatively rapid and no leak has been observed even after repeated seating and removal of the flange. When the vessel is sealed, the appropriate gas is slowly admitted to the system until the desired test pressure is reached.

During initial testing buoyancy effects were noted, both during pressurization and upon increasing temperature. These effects have previously been discussed[1,3,6,7]. In the case of all test samples, organic compounds or inert materials (glass beads), there was first an apparent weight loss upon pressurization of the system and then a slow apparent weight gain as the temperature was programmed upwards.

Trial and error methods were used to find counterweights of suitable size and density to eliminate the apparent weight loss on pressurization. Success was achieved with relatively little effort. Attempts to modify the balance to eliminate the change in buoyancy upon heating met with mixed success. It was found, however, that the apparent weight gain was consistent and reproducible for identical experimental conditions. Therefore, a series of correction curves was constructed for specific pressures and heating rates; the method used was similar to that described by Rabatin and Card[1]. The correction curve was obtained by running a thermally inert material (glass beads) at the test pressure over the temperature range of interest. Any apparent weight changes observed were therefore due to effects of pressure and temperature on the balance mechanism; subtracting the apparent weight changes from the vaporization curve eliminated the buoyancy effect from the experimental data.

The upper temperature limit of the modified balance is about 350°C. Above this temperature convection currents in the furnace tube cause severe fluctuations in the recorded weight due to movement of the sample pan. Attempts to reduce these fluctuations by placing baffles around the sample pan were not successful.

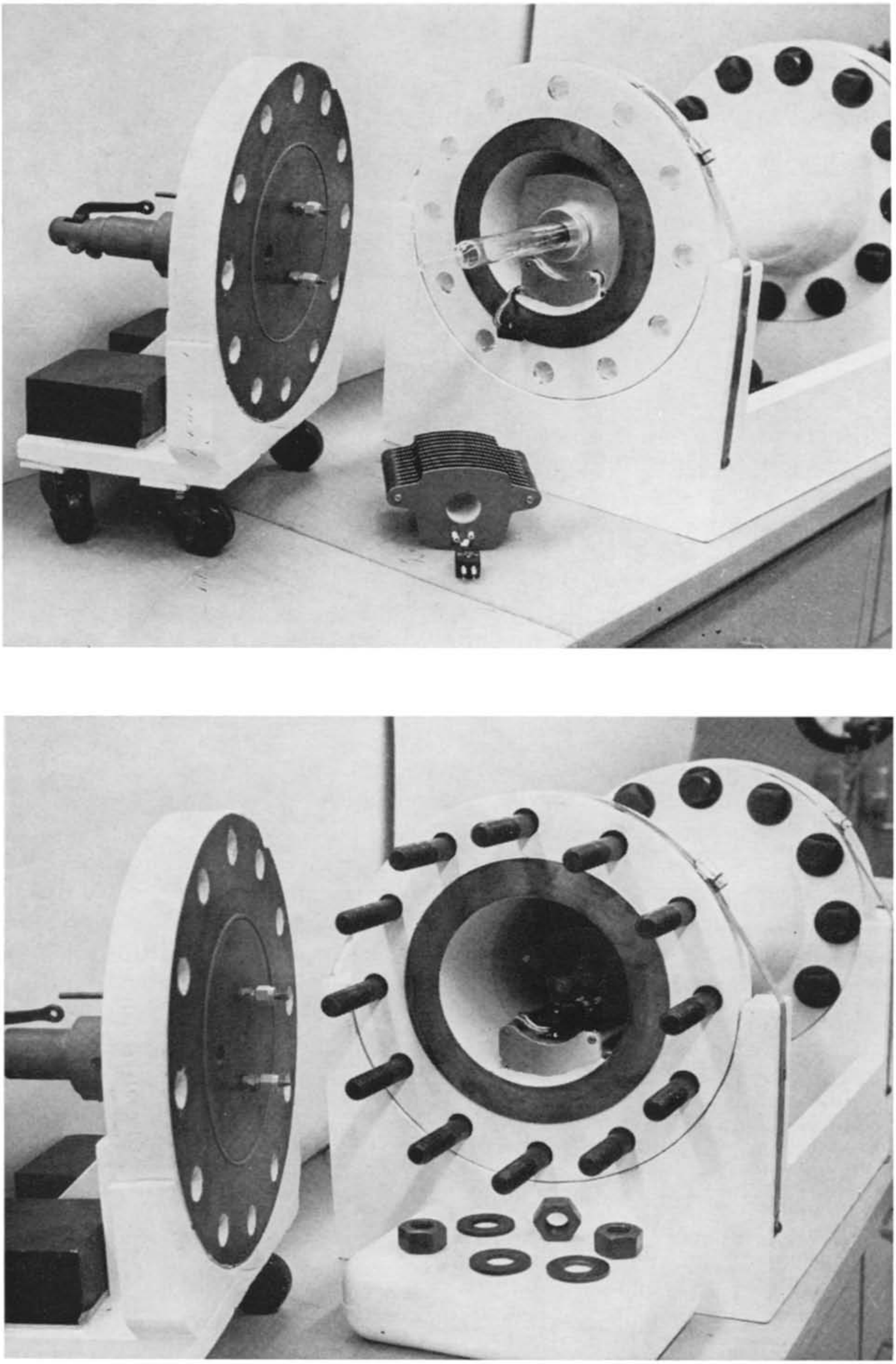

Fig. 2. The pressure vessel. (a) Balance mechanism extended for sample loading, (b) balance mechanism and furnace in operating position.

RESULTS

In order to test the operation of the apparatus, TGA runs were made to follow typical vaporization and decomposition reactions. Fig. 3 presents thermograms for the vaporization of aniline at atmospheric and pressure at 300 psig. At atmospheric pressure, a 10 mg sample programmed at a heating rate of 3 °C/min had completely vaporized when the temperature reached 105 °C (curve A). A similar sample, run at 300 psig reached 155 °C before vaporization was complete (curves B and C) indicating that significant retardation of evaporation had occurred.

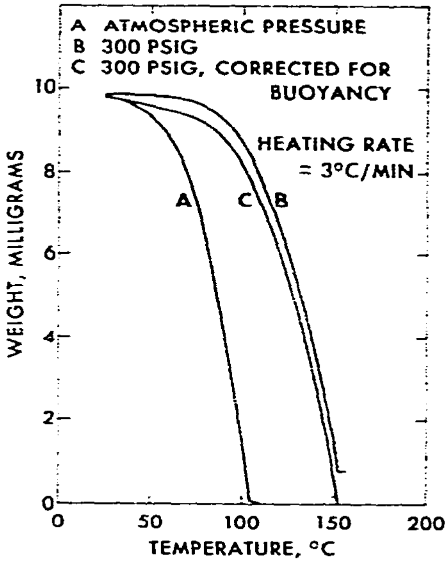

Fig. 3. TGA curves for the vaporization of aniline at atmospheric pressure and 300 psig.

Fig. 4 presents curves for the decomposition of copper sulfate pentahydrate to

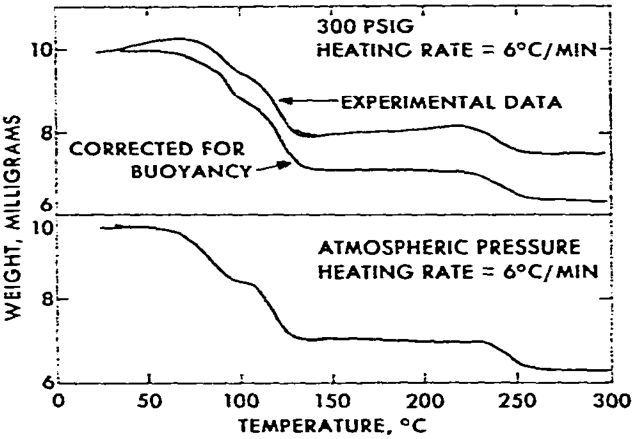

Fig. 4. TGA curves for the dehydration of $CuSO_4 \cdot 5H_2O$ at 300 psig and at atmospheric pressure.

form anhydrous copper sulfate. The curve obtained at atmospheric pressure is typical of many runs made with this material. Loss of two molecules of water is complete when the programmed temperature has reached 110 °C: two additional molecules of water have been removed at 130 °C. The last water molecule is more tightly bound to the copper sulfate and a temperature of 260 °C is reached before the anhydrous material is obtained. The weight loss at 300 °C is 35.2 weight % which is in agreement with the theoretical value of 35.5%.

The weight loss curve obtained at 300 psig (corrected for buoyancy effects) is similar to that obtained at atmospheric pressure except at temperatures below 100 °C. The initial decomposition step of copper pentahydrate results in a solution of water and copper trihydrate[8,9]. Evaporation of the water is retarded at 300 psig and this is shown in Fig. 4 as a reduction in evaporation rate. Weight losses associated with removal of the remaining water are unaffected by pressure and the decomposition reaction is rate controlling. The weight loss observed at 300 psig was 35.8%, in agreement with the theoretical value.

The use of trade names in this paper does not constitute an official endorsement or approval of the use of such commercial hardware or software by the United States Government. This paper may not be cited for purposes of advertisement.

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