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EVOLVED GAS DETECTION TECHNIQUES

II. VOLUME–TEMPERATURE

W. W. WENDLANDT
Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)
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ABSTRACT

A simple constant pressure-variable volume evolved gas detection apparatus is described. It consists of a glass system in which the pressure change activates a motor-driven variable-volume gas syringe. A slidewire and contact on the syringe plunger permits the recording of the change in volume of the system. Use of the apparatus is illustrated by the thermal dissociation reactions of $KHCO_3$, HgO, $CaC_2O_4 \cdot H_2O$, BaO_2, and Cd, Cu, Co, Ni and Mg carbonates.

INTRODUCTION

In the first paper of this series[1], an evolved gas detection technique was described in which the pressure change (at constant volume) in a system was monitored as a function of temperature (*P–T*). It is frequently necessary, however, to study the thermal dissociation of a compound in an atmosphere of the dissociation products at constant pressure, rather than at constant volume. The most widely used constant pressure evolved gas detection system is that using a thermal conductivity or other type of detector[2,3]. The evolved gases from the chemical reaction are removed from the reaction zone by means of a carrier gas such as nitrogen, helium, air, and so on. The atmosphere surrounding the sample is, by necessity, a dynamic one consisting of the carrier gas with momentary contact of the sample with the evolved gaseous product(s).

A convenient constant pressure system is one containing a variable-volume motor-driven gas syringe. Such an approach is simple to use and requires a minimum of instrumentation. It is the purpose of this short report to describe such an apparatus and to illustrate its use by studying the thermal dissociation of several well known chemical systems.

EXPERIMENTAL

Apparatus

The constant pressure evolved gas apparatus is shown in Fig. 1. It consists of (a) a furnace; (b) sample holder, furnace tube and glass connecting system; (c) motor-

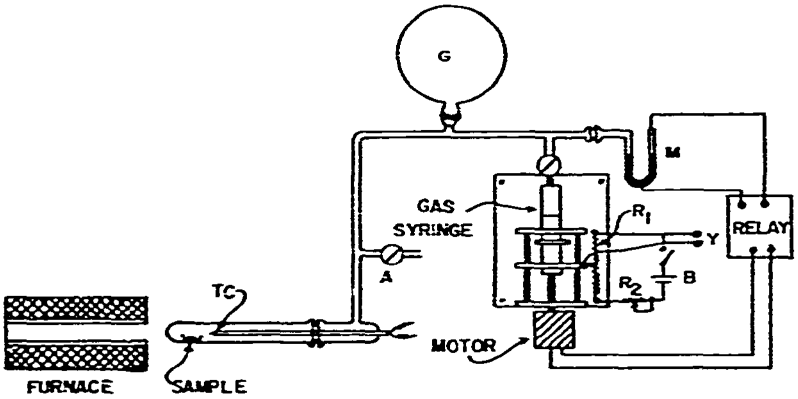

Fig. 1. Constant pressure apparatus. TC = Thermocouple; A = vent valve; G = gas bulb; M = mercury filled "U" tube and pressure detector; R_1 = 90 Ω slidewire; R_2 = 1000 Ω ten-turn potentiometer; B = 1.35 V mercury battery; Y = connection to Y-axis of X–Y recorder.

driven gas syringe; and (d) pressure detection device. Parts (a) and (b) have previously been described for use in the variable pressure apparatus[1]. The motor-driven gas syringe consisted of a 100-ml glass syringe connected by means of a screw-drive to a small reversible electric motor, in which the drive rate of the motor was about 20 ml min^{-1}, in either the decreasing or increasing volume mode. The position of the plunger, and hence the volume of the syringe, was detected by a slidewire, R_1, and a movable contact mounted on the plunger. This slidewire was fabricated from the resistance element of a 10-turn precision potentiometer and had a total resistance of about 90 Ω. The remainder of the slidewire circuit consisted of a 1.35-V mercury battery, switch, and a potentiometer, R_2, (1000 Ω). Output voltage of the circuit at Y was fed to the Y-axis of a Hewlett–Packard X–Y recorder.

Pressure change in the system was detected by a small "U" tube mercury manometer, M. Electrical contact between the mercury and a stationary wire electrode activated a relay which controlled the reversible motor-drive of the gas syringe. The usual mode of operation of the manometer and syringe was of increasing volume although the reverse mode could be employed.

The furnace programmer, sample container, and so on, were the same as previously described[1].

Procedure

A sample was weighed out into the nickel boat, loaded into the furnace tube, and assembled to the glass system. Stopcock A was closed, the relay system energized, and the recorder pen adjusted on the X- and Y-axes. The furnace was placed into position and the furnace temperature programmer activated. A plot of volume increase versus temperature was then recorded on the X–Y recorder. Full scale deflection on the volume axis was 70 ml (10 ml in.^{-1}) while the furnace temperature was recorded on the X-axis. Furnace heating rates employed ranged from 5 to 20°C min^{-1}.

RESULTS AND DISCUSSION

Effect of apparatus and sample variables

The effect of furnace heating rate on the recorded V–T curves is illustrated in Fig. 2. Using the thermal dissociation of $KHCO_3$ as the test compound, the effect of heating rate and sample size were recorded. This compound dissociates according to the well known reaction:

$$2KHCO_3(s) \rightarrow K_2CO_3(s) + H_2O(g) + CO_2(g)$$

The initial volume increase in the system is caused by the thermal expansion of the ambient gas (air). No correction was applied to the curves for this effect, which is illustrated for the temperature range from 25 to 650°C in Fig. 2.

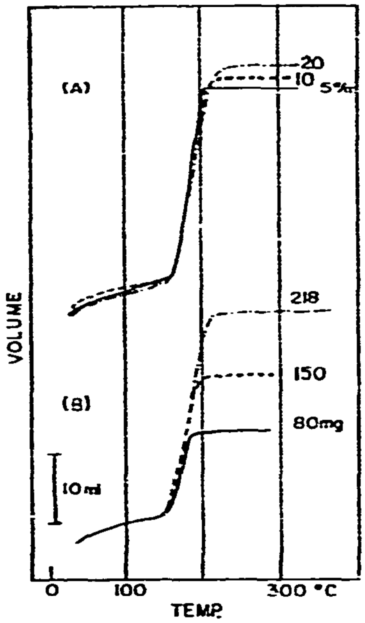

Fig. 2. Effect of heating rate (A) and of sample size (B) on the V–T curves for $KHCO_3$.

As can be seen by the curves in Fig. 1, the heating rate has little effect on the initial dissociation temperatures (T_i) although it does change the final dissociation temperatures (T_f) to some extent. The T_i value found was about 165°C while T_f values were 205° (5°C min^{-1}), 215° (10°C min^{-1}) and 240°C (20°C min^{-1}). There was, naturally, an increase in the reaction interval ($T_f - T_i$) with increase in heating rate.

The effect of sample size on the T_i and T_f values is illustrated in Fig. 2B. As in the case of the heating rate, the T_i values did not change appreciably but there was a slight increase in the T_f values with sample size; T_f values found were 185°C (80 mg), 200°C (150 mg) and 205°C (218 mg). There was, of course, a larger volume change associated with the increase in sample size.

Inorganic compounds

The *V–T* curves of some representative inorganic compounds are given in Figs. 3 and 4.

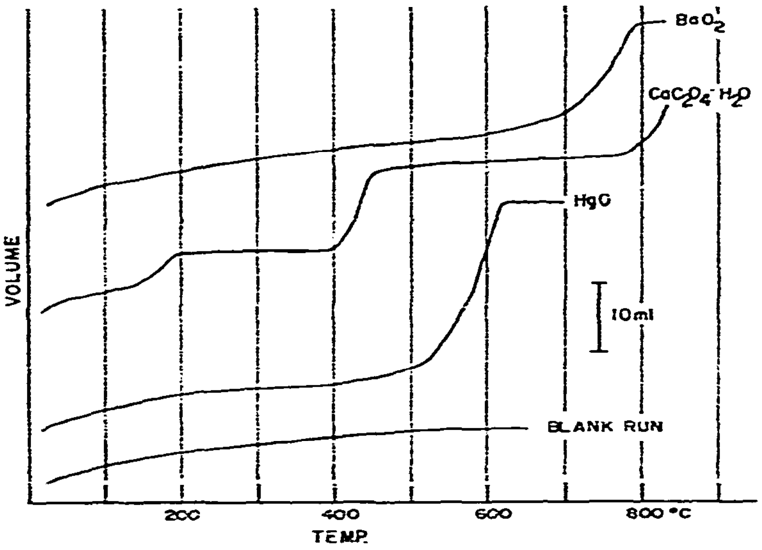

Fig. 3. *V–T* curves of some inorganic compounds. Heating rate of 10°C min^{-1}.

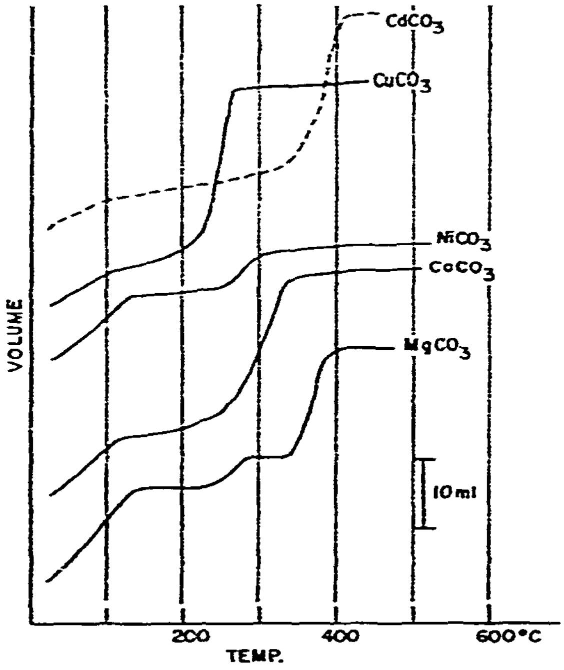

Fig. 4. *V–T* curves of some inorganic compounds. Heating rate of 10°C min^{-1}.

The curves in these two figures represent typical *V–T* curves for various types of inorganic compounds. The dissociation reactions for these compounds are all well known and involve reactions of

Type I: $\text{Solid}_1 \rightarrow \text{Solid}_2 + \text{Gas}_1$

or Type II: $\text{Solid}_1 \rightarrow \text{Gas}_1 + \text{Gas}_2$

Reactions of Type I are illustrated by all of the compounds studied except for mercury(II) oxide. The latter is a Type II compound which dissociates into mercury and oxygen, a reaction which begins at about 400 °C, with rapid dissociation in the temperature range of 500 to 615 °C.

Reactions of Type I are illustrated by the remaining compounds. The well known dissociation reactions of $CaC_2O_4 \cdot H_2O$ are illustrated in the *V–T* curve in Fig. 3. Hydrate water evolution occurs between 90 and 190 °C; loss of CO between 390 and 450 °C; and evolution of CO_2 starts at about 770 °C.

The gradual evolution of oxygen from barium peroxide, BaO_2, is illustrated by the curve for this compound in Fig. 3. Oxygen is evolved, according to the reaction:

$$BaO_2(s) \rightarrow BaO(s) + \tfrac{1}{2}O_2(g)$$

A reaction interval of 550 to 790 °C was observed.

V–T curves of a number of metal carbonates are illustrated in Fig. 4. Single-stage dissociation reactions of Type I are illustrated by $CuCO_3$, $CdCO_3$, and $CoCO_3$ while multi-stage reactions are exhibited by $MgCO_3$ and $NiCO_3$. The composition of the intermediate compounds was not determined.

ACKNOWLEDGMENT

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