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EXPERIMENTAL RESULTS AND THEORETICAL CONSIDERATIONS ON THERMOGRAVIMETRIC DECOMPOSITION REACTIONS OF CHEMICAL COMPOUNDS UNDER HIGH VACUUM

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ABSTRACT

Investigations on thermogravimetric decomposition reactions under high vacuum have demonstrated that special attention should be paid to such factors as the sample size, the crucible form, the thickness of the layer in the crucible, the particle size of the probe material, etc. It is shown how the various influences can be eliminated by observing certain starting or test conditions. In addition to experiments on these specific influences, a comparison has been made of the degradation speeds of single crystals and crystal powders of chemical compounds.

Results, which are complementary to the thermogravimetric measurements can be obtained with qualitative or quantitative determination of the gaseous decomposition products by mass spectrometric analysis. From these measurements the course of decomposition is followed by recording the partial pressure at the various individual masses. This method is particularly suitable for the study of thermal degradations which produce more than one decomposition product in the same step.

INTRODUCTION

The thermal analysis results show that thermogravimetric investigations become even more important when they are carried out under vacuum[1]. The fields of application range from simple thermal decomposition to the measurement of the kinetics of chemical reactions, including the conditioning of samples before carrying out reactions in a special gas atmosphere, for instance the removal of adsorbed layers such as water, CO_2, etc. which could interfere with the process under examination. Especially in the thermogravimetric decomposition of a chemical compound the sample size is dependent on the quantity of the resulting gaseous decomposition products. An idea of the correct sample size can generally be obtained from the performance of the pumping system which is combined with the balance. A short pressure increase during such measurements cannot be avoided, it must not, however, exceed the admissible pressure of the diffusion pumps. This means that samples for thermal decomposition in high vacuum should be limited to a few milligrams. So as to avoid secondary reactions, in particular sorption effects during decomposition reactions, the layer of the substance in the crucible must be kept as thin as possible.

This requires, even for small samples, plate-type crucibles. The layer thickness of the substance should not exceed 0.5 to 1 mm[13]. Only in the case of thin layers is a steady warm-up possible because in the range of 25–650 °C the heat transmission takes place mainly via the crucible. The selection of the heating rate is in many cases dependent on the purpose of an investigation; it is recommended, however, to use small heating rates (see Figs. 1A and 1B).

For studying the kinetics of a decomposition, probes with different particle size were used. Figures 1A and 1B show the dehydration of whewellite powder ($CaC_2O_4 \cdot H_2O$, 150 mesh) and of a single crystal (1 × 1 × 2 mm) of whewellite under identical conditions which were a sample mass of 6 mg, heating rates of 2 and 8 °C/min and an initial pressure of 10^{-5} mm Hg. In this example the pronounced difference in the reactions shows the significance of the particle size and the heating rate.

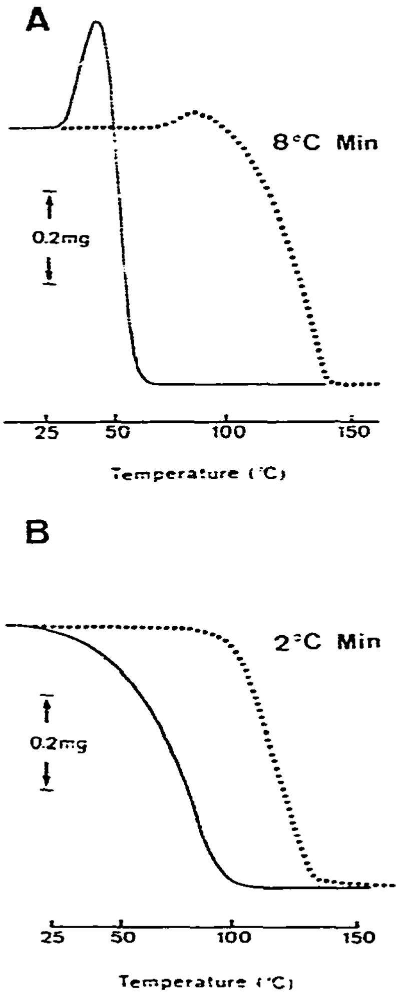

Fig. 1. Dehydration of whewellite ($CaC_2O_4 \cdot H_2O$): ———, powdered material (particle size 150 mesh); ······, single crystal (ca. 1 × 1 × 2 mm). All sample weights 6 mg. A, Heating rate: 8 °C/min. B, Heating rate: 2 °C/min.

Several types of errors, including buoyancy effects, radiometric effects and thermomolecular flow, can influence vacuum thermogravimetry. Some of these have been discussed in different volumes of vacuum microbalance techniques[3-5]. One effect which occurs during the thermal decomposition in vacuum will be discussed here.

Figure 2A shows as an example the decomposition of calcium oxalate. During heating up an increase in weight up to a certain maximum can at first be seen, after

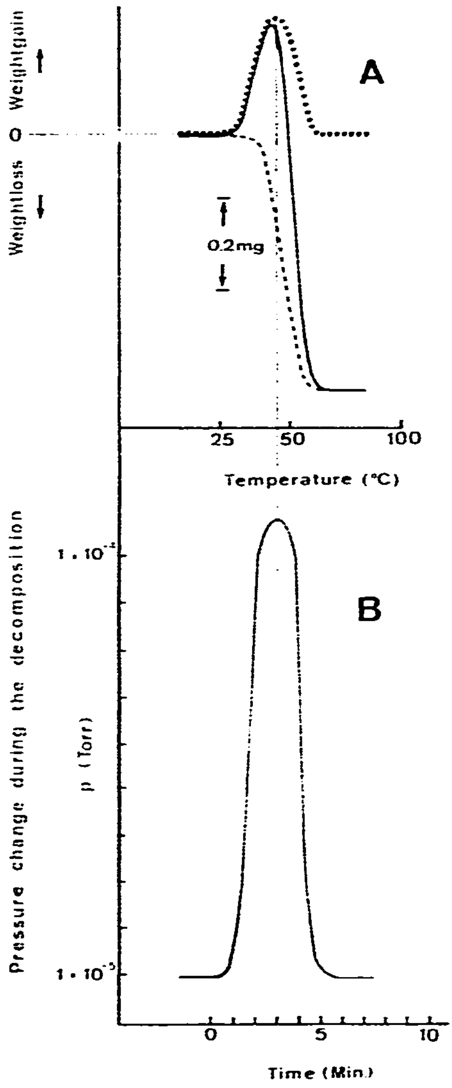

Fig. 2. Dehydration of whewellite ($CaC_2O_4 \cdot H_2O$). A, ———, Weight change during the reaction taking place on the balance pan (plate-type crucible); ······, weight change during the reaction taking place beside the balance pan (ring); – – – – –, curve diagrammatically determined from the measured curves. B, Pressure change simultaneously measured during dehydration of calcium oxalates.

which the actual weight decrease takes place (full line). So as to be able to define this effect more precisely, a second test with the whewellite (same sample size and under the same conditions) has been carried out; the substance, however, has been weighed on a ring (see Fig. 3) beside the empty crucible, the same weight increase has been measured; after decomposition the weight curve came back to its starting position (dotted line). This means that only a small part of this effect (>0.5%) can be attributed to a recoil of the molecules leaving the balance pan, but practically the whole effect is due to a re-impact.

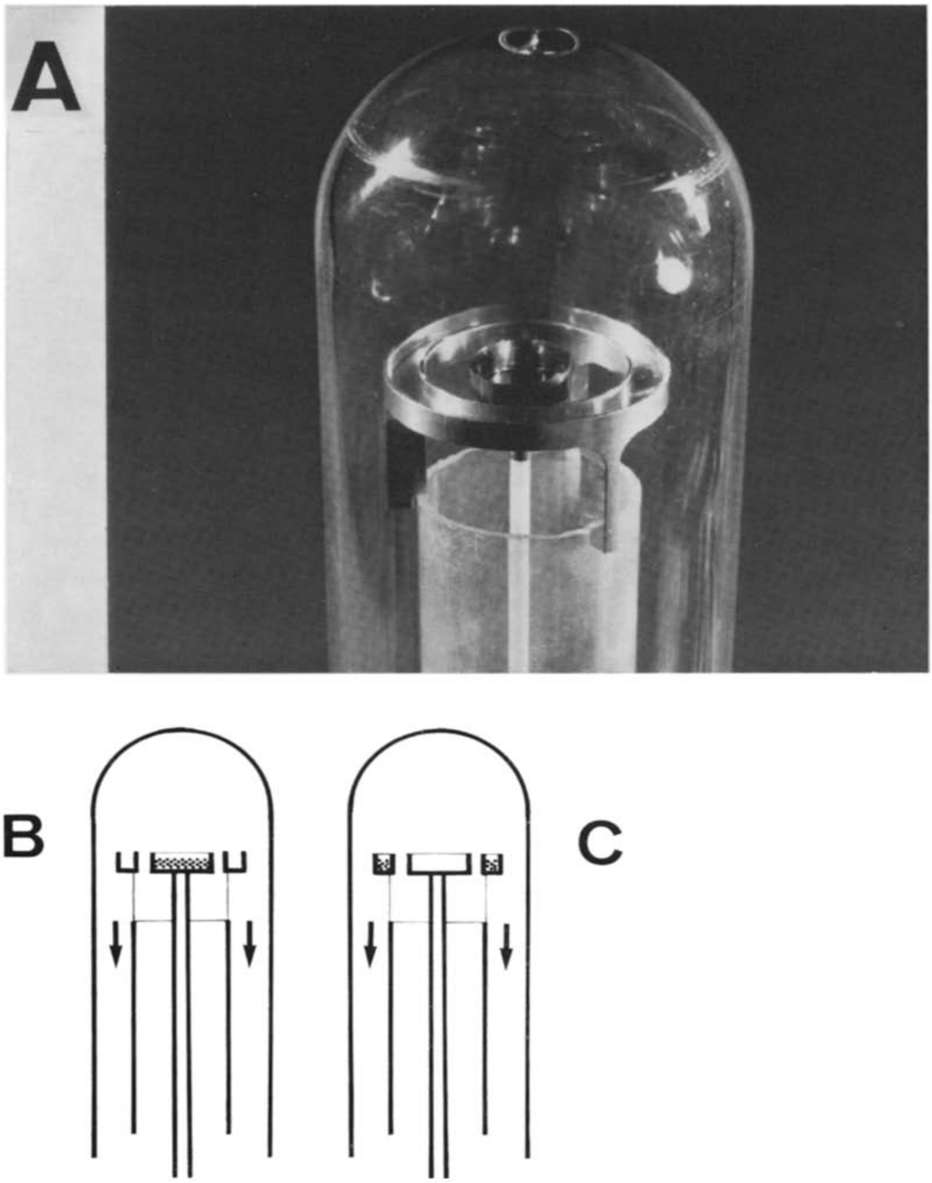

Fig. 3. A, Furnace tube with plate-type crucible and ring. B, Plate-type crucible with substance arranged on the balance. C, Ring with substance beside the empty plate-type crucible.

Figure 3A shows the furnace tube with a plate-type crucible and ring and Figs. 3B and 3C show, as described above, the two kinds of experimental procedures with the different arrangements of the probe. Figure 2A shows the result of the two measurements as well as the curve (broken line) obtained by subtraction of the two recorded curves, which serves as the basis for kinetic measurements[6]. The simultaneously recorded pressure change (Fig. 2B) was the same for both decompositions.

The same effect has been observed by Houde[7] when he vaporized silver on a balance pan; because evaporation took place from below against a suspended balance pan, a weight decrease was simulated. Friedman[8] also has seen this effect in the decomposition of polymers.

MEASURING EQUIPMENT

In order to investigate the observed effect of weight gain at the beginning of decomposition under variable conditions, the process of decomposition may be

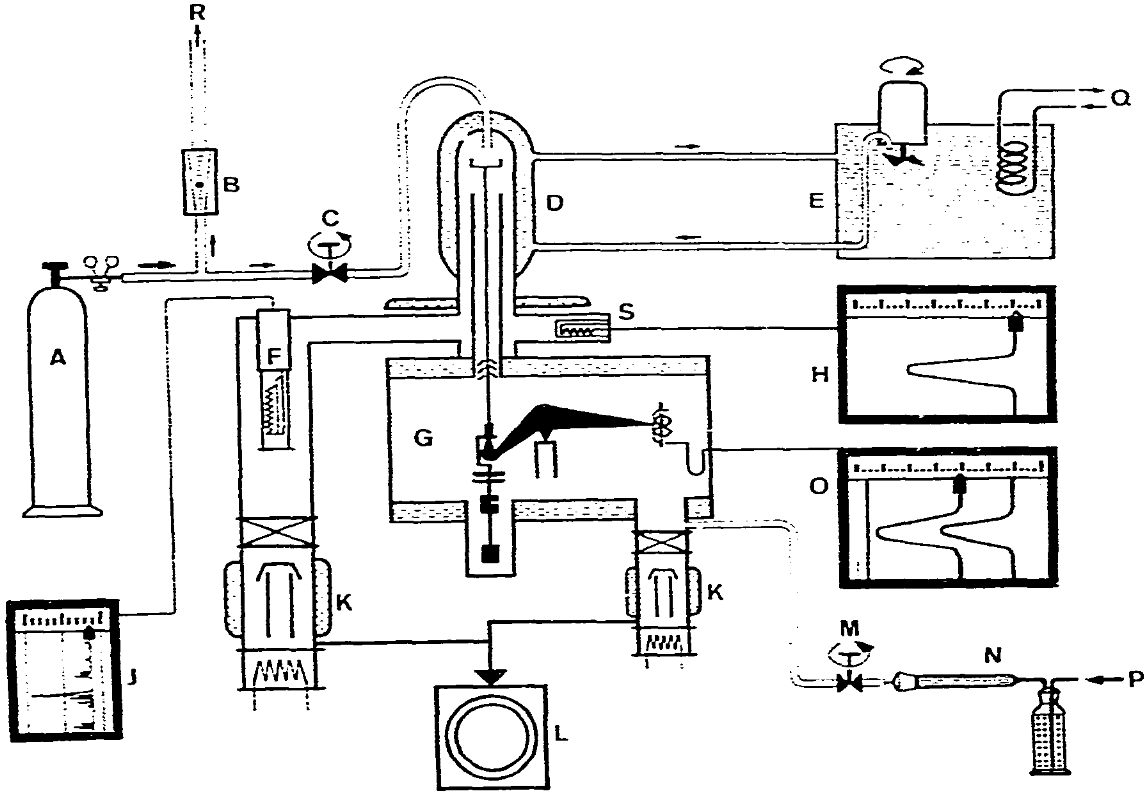

Fig. 4. Experimental equipment. A, gas cylinder; B, flow meter; C, needle valve with servomotor; D, thermostatically controlled reaction chamber; E, thermostat; F, analyzer of mass spectrometer; G, thermostatically controlled balance compartment and balance; H, recorder for pressure registration (high vacuum); I, recorder (mass spectrometer); K, diffusion pumps; L, rotary pump; M, needle valve; N, gas purification; O, 12-channel multipoint recorder (recording of the weight temperature preliminary vacuum); P, intake stack for air; Q, thermostat cooling; R, gas outlet; S, high vacuum measuring cell.

simulated on a vacuum thermobalance[9,10]. This is done by introducing gases in measured quantities through a separate inlet into the reaction chamber above the balance pan. The balance housing has been evacuated before each analysis by the vacuum system to approximately 5×10^{-6} mm Hg.

The reaction chamber (Fig. 4D), as well as the balance (G), is kept at 25 °C by a thermostat during the measurements. For the measurements up to 1000 °C a quartz tube furnace is used instead of the temperature regulated furnace tube. The gases which are used for the investigation, are directed through metal supply pipes to the needle valve (C) with servomotor and to the oulet (R). The gas flow is continuously measured by an ionization gauge and recorded on the recorder (H). The measuring point (S) is arranged next to the reaction chamber. The sample weight, the preliminary vacuum and the temperature are registered on the recorder (O). The temperature measuring point is in direct contact with the plate-type crucible in the reaction

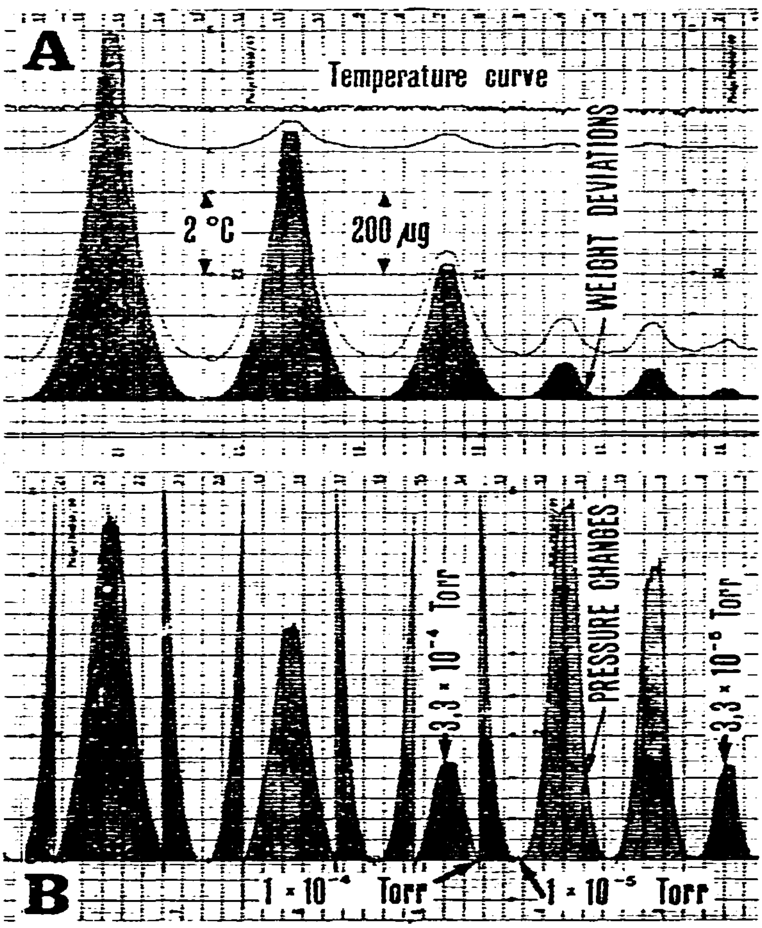

Fig. 5. Diagram A shows different weight changes which are due to the introduction of different quantities of argon into the reaction chamber above the pan of the balance evacuated to 1×10^{-5} mm Hg. The corresponding pressure changes which have been recorded simultaneously with the weight changes can be seen in the diagram B.

chamber (D). Above one of the diffusion pumps (K) an analyzer (F) of a mass spectrometer* is fitted into the vacuum system of the thermobalance. Combined with the recorder (J) mass spectra or individual masses can be continuously recorded. With the needle valve (M) different pressures can be regulated by sucking in air or other gases through the gas purification (N) and the gas inlet (P). Before each measurement the starting pressure of 1×10^{-5} mm Hg was adjusted by this valve.

The weight changes were recorded in a balance sensitivity range corresponding to 1000 micrograms per full chart width. Figure 5A shows an original diagram with an indication of the sensitivity per scale division.

DISCUSSION OF THE MEASURED RESULTS

The observed effect on the "apparent" increase of the mass of a balance pan (plate-type crucible) when impulse-wise charged with introduced gas has been investigated under different conditions. For all measurements at room temperature a temperature regulated furnace tube made of pyrex glass was used (Fig. 6). The most important dimensions of the furnace tube are: diameter of the supply pipe: 3 mm; diameter of the reaction chamber: 45 mm; distance between supply pipe and balance pan: ~ 85 mm.

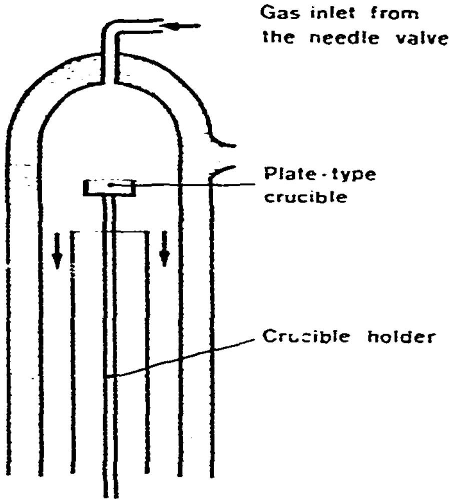

Fig. 6. Thermostatically controlled furnace tube with gas inlet pointing at the empty balance pan; ↓, suction direction of the vacuum system.

Purified argon was used as the experimental gas. The gas was introduced through a servomotor controlled needle valve (Fig. 4C). The pressure difference was regulated by opening the needle valve. The opening and the closing of the valve took

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*Balzers AG, Balzers, Principality of Liechtenstein, Quadrupole high frequency mass spectrometer, QMG 101, Bulletin, p. 51-30e.

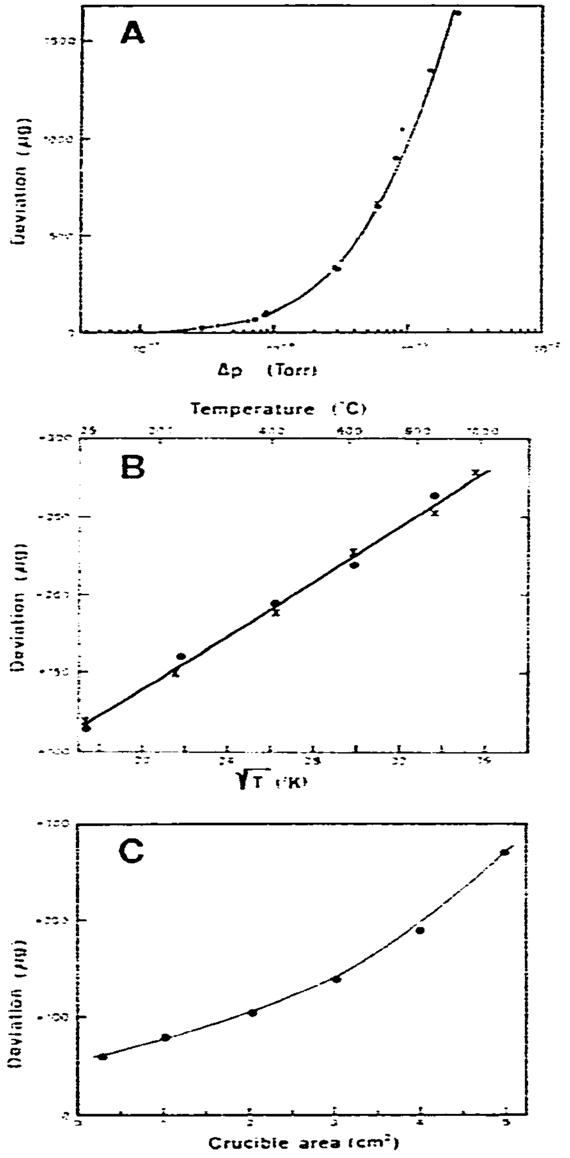

Fig. 7. Maximum values of an "apparent" increase of the mass of a balance pan (plate-type crucible) when impulse-wise charged with introduced argon. Diameter of the supply pipe: 3 mm; diameter of the reaction chamber: 45 mm; distance between supply pipe and balance pan (plate-type crucible): 85 mm; starting pressure in reaction chamber: 1×10^{-5} mm Hg. A, Constant temperature, 25.5 °C. Impact surface of balance pan (plate-type crucible), 1.16 cm^2. Change of the pressure difference ΔP from 1.25×10^{-5} to 9.2×10^{-4} mm Hg (ΔP by different valve openings). B, Temperature isotherm in steps between 25 and 985 °C. Impact surface of balance pan (plate-type crucible), 1.16 cm^3. Constant pressure change ΔP 8.2×10^{-5} mm Hg (ΔP by equal valve openings). Temperature is measured by thermocouples of platinum/platinum-rhodium (10%) directly on the plate-type crucible. C, Constant temperature, 25.5 °C. Impact surface of balance pan (plate-type crucible) from 0.3 to 5 cm^2. Constant pressure change $\Delta P = 8.2\times10^{-5}$ mm Hg (ΔP by equal valve openings).

place at the same speed. A series of original measurement results is shown in Fig. 5; the upper diagram shows the curve of the weight changes at a constant temperature (25.5 °C). In the lower diagram the corresponding pressure changes are recorded.

Figure 7A shows the deflection in micrograms at different pressure changes (pressure difference $\Delta P = 1.25 \times 10^{-5}$ to 9.2×10^{-4} mm Hg). The starting pressure for all measurements was 1×10^{-5} mm Hg. The temperature was kept constant at 25.5 ± 0.1 °C.

Figure 7B shows the deviation in μg at a constant pressure change ($\Delta P = 8.2 \times 10^{-5}$ mm Hg) and at temperatures between 25 °C and 985 °C. A quartz-tube furnace (Figs. 4B and 4C) with reflector system[9] was used—the introduced gas being heated up to the furnace temperature before entering the reaction chamber.

The pressure changes were carried out under isothermal conditions. The deviation M in μg is nearly proportional to the root of the absolute temperature. With the aid of a regression analysis the following relation may be obtained

$$M(\mu g) = a\sqrt{T} + b \cdot T. \qquad (1)$$

These measurements have also been carried out on carbon dioxyde, nitrogen and oxygen. The same kind of temperature dependence was obtained, but with slightly different constants. The constants of the different waves are summarized in Table 1.

TABLE 1

EXPERIMENTAL CONSTANTS OF EQUATION (1) FOR DIFFERENT GASES AS OBTAINED BY A REGRESSION ANALYSIS

Gas	*a*	*b*
Ar	5.92	0.0543
N_2	6.32	0.0370
O_2	6.78	0.0304
CO_2	5.29	

The correction values b are very small. This would allow the measurement of a high gas temperature in relation to the "apparent" mass increase[13,14]. According to the Maxwell theory, this "apparent" mass increase should be approximately proportional to the average velocity of the molecules.

Figure 7C shows the dependence of the deviation on the crucible surface areas, which varied from 0.3 to 5 cm^2. The measurements have been carried out at a constant temperature (25.5 °C) and at a constant pressure change ($p = 8.2 \times 10^{-5}$ mm Hg). The introduction of the gas was always continuously analysed by means of a mass spectrometer, as a further check on purity and pressure*.

Further research on the deviation M as a function of the temperature up to 2000 °C for various gases is presently being carried out.

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*See footnote on p. 263.

THERMAL DECOMPOSITION AND SIMULTANEOUS MASS SPECTROMETRIC ANALYSIS OF THE DECOMPOSITION PRODUCTS

The Balzers Quadrupole high frequency mass spectrometer Q101* which was used, consists of two units—the analyzer and the electronic control unit. In our case, the mass analyzer was installed directly into the vacuum system of the thermoanalyzer[9,10].

Simultaneous mass spectrometric investigations, besides TG and DTA analysis[11] in high vacuum (already mentioned), require a certain sample size not to be exceeded. The amount of gas released during decomposition has also to be compatible with the pumping speed of the vacuum system. Furthermore the maximum pressure for the mass spectrometer shall not be exceeded.

A sample mass of 8 mg and a heating rate of 2 °C/min were used for the measurements (Fig. 8). As sample carrier a DTA measuring head was used. The water vapor pressure was checked with the mass spectrometer before each test. Heating was started only when the sample partial pressure was reached each time. This improved the reproducibility considerably.

Figure 8 shows the relation between TGA, DTA and mass spectrometric results for the decomposition of zinc oxalate dihydrate. In addition to the DTA–TG traces, the total or composite pressure curve measured by an ionization gauge on the reaction chamber was continuously recorded during the entire test on a 12-channel recorder.

The different partial pressure curves were determined in the following two ways: (1) from approximately 230 continuously recorded single spectra and (2) from the pressure curves of the single masses of H_2O, $CO(N_2)$ and CO_2. This means that the tests were repeated per single mass and each time recorded simultaneously with the other parameters such as partial pressure, TG and DTA. The resulting partial pressure curves obtained in these two different ways can be considered as equivalent except for minor deviations. The partial pressure of carbon monoxide at room temperature after allowing for the nitrogen base (or background) is somewhat lower than the partial pressure of carbon dioxide ($\sim 10^{-7}$ mm Hg) at 25 °C.

During the release of water, similar peaks occurred on the total pressure curve as well as on the partial pressure curve for water vapor: these correspond to the pressure change in the reaction chamber of the thermoanalyzer. At the same time, a small pressure change on the partial pressure curve of CO_2 was noticed, which could have been caused by CO_2 dissolved in physically absorbed water. This could not be considered as an early breakdown of the oxalate. As already indicated above, the partial pressure of carbon monoxide, after allowing for the nitrogen base, was less than the pressure of carbon dioxide in these measurements at room temperature (Fig. 8).

The less sensitive partial pressure curve seems to indicate that the beginning of

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*See footnote on p. 263.

the CO release takes place at a considerably lower temperature than the CO_2 release which begins at approximately 150°C. In principle, the CO release is temperature-wise similar to the CO_2 release. When the TG and pressure curves are compared, it shows that increasing CO_2 release is about at the same height as the end of the water release. A small amount of water can be detected during the CO–CO_2 release. The

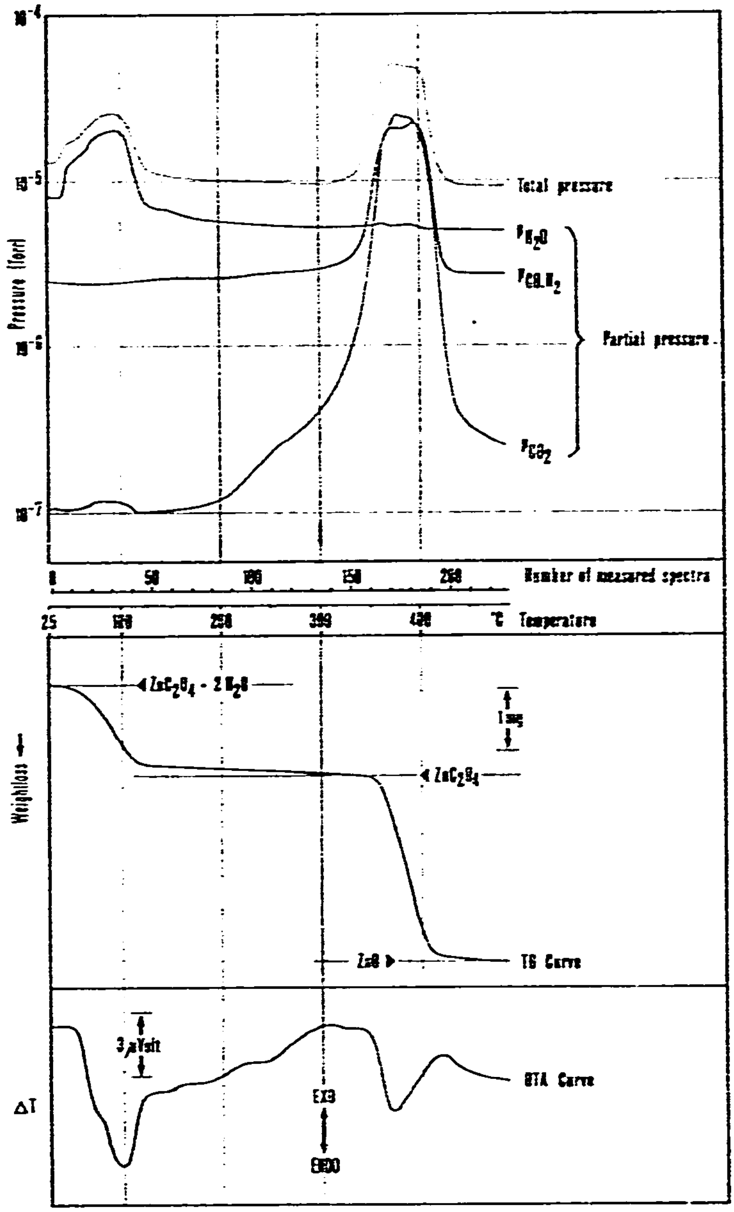

Fig. 8. Decomposition of $ZnC_2O_4 \cdot 2H_2O$ in high vacuum combined with a mass spectrometric analysis of effluent gas. Total pressure curves as well as pressure curves for the separate masses of water (18), $CO(N_2)$ (28) and CO_2 (44) are shown next to the simultaneously recorded TG and DTA traces as function of temperature.

DTA curve shows a clearly defined peak for the main water release, which is followed by a wavy line indicating a reverse reaction on the dehydrated oxalate with the water. The CO–CO_2 release shows up as an additional DTA peak. The DTA trace approaches the base line again only after complete release of the carbon dioxide.

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