Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

REVIEW

THERMOGRAVIMETRY IN SELF-GENERATED ATMOSPHERES
A DECADE OF PRACTICE AND NEW RESULTS*

ARTHUR E. NEWKIRK
General Electric Research and Development Center, Schenectady, New York 12301 (U. S. A.)

(Received April [illegible], 1970)

CONTENTS

ABSTRACT

Thermogravimetry in self-generated atmospheres consists of decomposing a solid sample in a crucible that has a small vapor volume with a small opening to the atmosphere. As a consequence, except for the air initially present, decomposition occurs in an atmosphere of the gaseous decomposition products, hence, a self-generated atmosphere. The technique, as described by Garn and Kessler and by Forkel in 1960, appears to have been used only occasionally, perhaps because special crucibles are necessary. This paper reviews the literature, outlines the advantages and limitations of the method, describes several new crucibles which are light and easy to make, and compares results obtained with them in the study of lead(II) oxide, lead(II) carbonate, and manganese(II) acetate tetrahydrate.

A. THE FIRST CRUCIBLES FOR SELF-GENERATED ATMOSPHERE STUDIES AND THEIR PRECURSORS

The important effect of the atmosphere on thermogravimetric results has long been recognized[1], but it was not until 1960 that Garn and Kessler[2] in this country

---

*Presented at the Recent Advances in Thermal Analysis Symposium, American Chemical Society Meeting, February 22–27, 1970, Houston, Texas, U. S. A.

and Forkel[3] in Germany described crucibles that permitted an appropriate atmosphere to be applied to any reaction. Their crucibles were different in principle, see Fig. 1. Garn and Kessler used a piston and cylinder in which the clearance between the two provided a long diffusion path and effectively prevented contamination from the atmosphere. The Forkel crucible had a lid containing a ball valve to insure separation of the sample atmosphere and the atmosphere in the furnace. In both designs the gas generated by a small amount of decomposition displaced the air originally present in the crucible and a major fraction of the decomposition subsequently occurred at a pressure of one atmosphere of the gas evolved. The effect of using these crucibles to decompose lead carbonate is shown in Fig. 2. Forkel used a differential thermobalance. The curve of Garn and Kessler has been redrawn in derivative form for ease of comparison. The thermograms, when compared to that obtained from

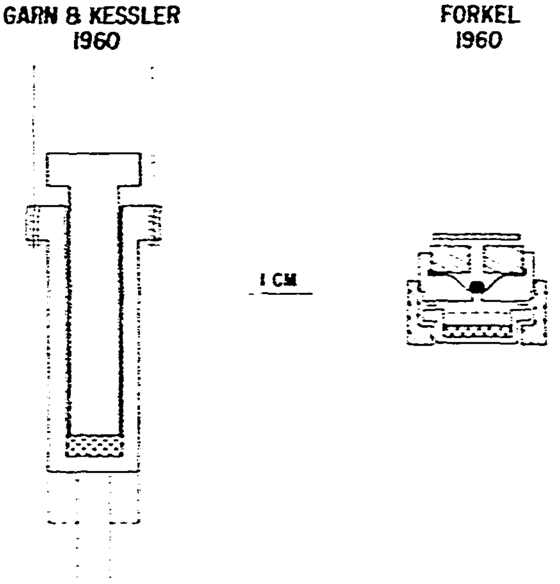

Fig. 1. First crucibles for thermogravimetry in self-generated atmospheres.

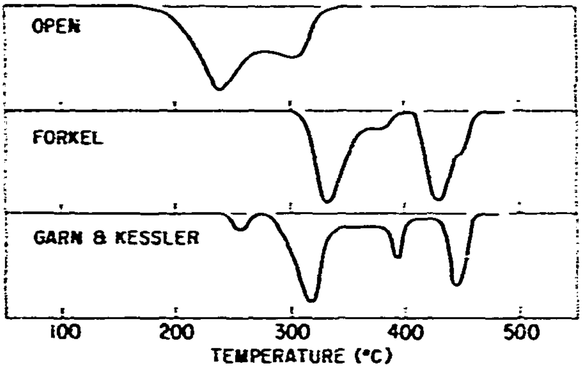

Fig. 2. Thermograms for lead carbonate (redrawn for comparison).

lead carbonate decomposed in an open crucible, show a shift to higher temperatures for the reaction stages, and a clearer indication of the intermediate compounds formed in the decomposition. The results in the two crucibles were not quite the same as will be discussed later.

The development of crucibles for self-generated atmosphere experiments was foreshadowed by earlier thermal analysis studies, and four of these are of particular interest. In 1937–1938 Vallet and Bassière[4,5] reported a thermogravimetric study of the dehydration of zinc sulphate heptahydrate, $ZnSO_4 \cdot 7H_2O$, in controlled atmospheres and in shallow dishes and deep crucibles, see Fig. 3. They recognized the influence of the deep crucible in providing a partial self-generated atmosphere above the sample and observed a disadvantage when they found that fusion of the sample occurred and produced a pseudo-plateau between the monohydrate and the anhydrous salt. An interesting result was obtained with large single crystals. When these were roughly equi-dimensional and did not shatter on heating they yielded a short plateau at the composition zinc sulphate tetrahydrate, but when they were long and thin or shattered, a plateau was not obtained at the tetrahydrate level. This might be considered a special case of a self-generated atmosphere in which the crystal acted as its own crucible.

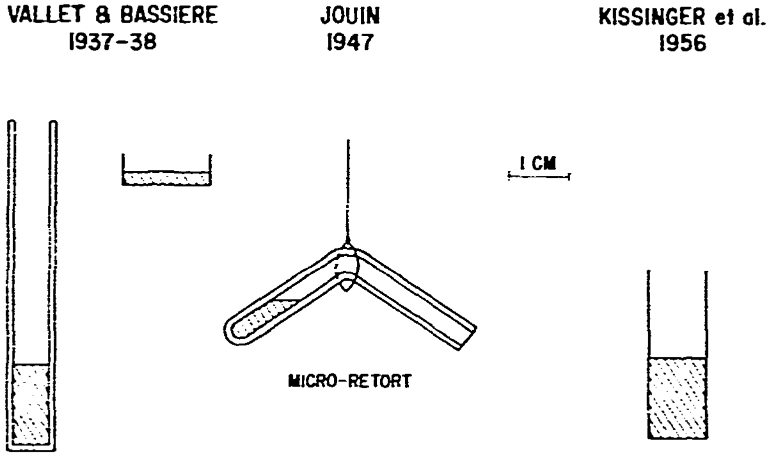

Fig. 3. Precursors to crucibles for self-generated atmosphere experiments.

The quartz micro-retort of Jouin[6] (Fig. 3) came much closer to providing a good self-generated atmosphere than did the deep crucible. In a study of lignite, the gases evolved on heating a 200-mg sample in the closed end formed a protective layer up to the peak of the retort and prevented combustion. Thermograms were obtained up to 1000 °C and were reproducible. The volatile content of the residue, 18% at 525 °C, was the same as that of a semi-coke prepared on a much larger scale in an industrial furnace at the same temperature. Jouin also determined the temperature of spontaneous combustion of carbonaceous materials by observing the temperature at which a thermogram of a sample heated in air in an ordinary crucible first deviated from the thermogram of a sample heated in the micro-retort. Typical values were: lignite, 300 °C; wood charcoal, 400°; and anthracite, 550 °C. Jouin's micro-retort seems not to have been used by later investigators, despite its simplicity and apparent utility.

During the decade following Jouin there was increasing concern among experimenters about the large differences between results obtained by thermogravimetric analysis and those obtained by differential thermal analysis. The importance of the self-generated atmosphere was recognized particularly by Kissinger[7] who realized that conditions common for differential thermal analysis, tall narrow tubes closed at one end and largely blocked at the other by the thermocouple, resulted in solid–gas decompositions occurring essentially at a pressure of one atmosphere of the gas evolved. He studied the decomposition of iron(II) carbonate and manganese(II) carbonate by DTA and TGA in deep crucibles of the same size for both measurements (Fig. 3) and obtained concordant results. Fruchart and Michel[8] also recognized the importance of the self-generated atmosphere and were able to obtain good concordance between DTA and TGA for magnesium sulphate heptahydrate by performing the TGA in a cup described only as having a large base, but a small opening.

These are only a few examples that illustrate the increasing recognition of the effect of the self-generated atmosphere in thermogravimetry, but it was not until the work of Garn and Kessler and of Forkel in 1960 that the concept was carried to the practical end of providing a crucible that would insure sample decomposition in a self-generated atmosphere. The use of a self-generated atmosphere with other thermal methods appears to be very recent. For evolved gas analysis see Forrester[9], and for differential thermal analysis see Barrall, II and Rogers[10].

B. CHARACTERISTICS OF CONSECUTIVE REACTIONS

Since the usual purpose of using a crucible that emphasizes the effects of a self-generated atmosphere is to obtain a better separation of consecutive reactions and a more exact identification of the intermediate phases, it is desirable to examine the characteristics of consecutive reactions so as to determine the nature of the factors influencing the separation. Consecutive reactions may be represented by the general equations:

$$\mathrm{A(s)} \rightleftharpoons \mathrm{B(s)} + \mathrm{gas}$$
$$\mathrm{B(s)} \rightleftharpoons \mathrm{C(s)} + \mathrm{gas, etc.}$$

In these reactions, the best separation is one in which the final temperature of the first reaction, $(T_f)_A$, is lower than the initial temperature of the second reaction, $(T_i)_B$, giving rise to a plateau between them. It will also be useful to have a small reaction interval$(T_f - T_i)$, for each stage. Consecutive reactions may yield the same or a different gaseous product at each stage, may yield several gaseous products from sequential or parallel reactions at each stage, and may be reversible or irreversible. The thermogravimetry of consecutive reactions has been discussed by Simons and

Newkirk[11] and by Pannetier *et al.*[12,13]. The effect of the gaseous atmosphere has been discussed by Garn[14]. The important factors and the resultant desirable experimental conditions are summarized in Table I as they apply to reversible reactions.

TABLE I

THE INFLUENCE OF THERMODYNAMIC, PHYSICAL, AND KINETIC FACTORS ON CONSECUTIVE REACTIONS[12]

Thermodynamic	
(1) T_i and $T_f - T_i$ depend on the gas pressure, P_G	(1) Control P_G at some known and constant value
(2) T_i increases as P_G increases	(2) Select appropriate P_G for particular separation
(3) $T_f - T_i$ decreases as P_G increases	(3) Work at large values of P_G
Physical	
(*a*) *External diffusion*	
Gas diffusing against external pressure causes local increase in P_G and decrease in rate of weight loss	(1) Use self-generated atmosphere crucible, or (2) Use controlled P_G
(*b*) *Internal diffusion*	
Gas cannot escape easily from large, thick samples, separations poor	Use small, thin layer samples
Kinetic	
(1) Induction period and nucleation	Tend to raise T_i for all stages
(2) Propagation, follows approximately a relation such as:	
$\frac{da}{dT} = \frac{k}{b} \times \frac{A_o}{M_o} \times a^n e^{-E/RT}$	Large da/dT desired for small $T_f - T_i$
a = residue	
T = absolute temperature	
k, n, e, R = constants	
b = rate of heating	Should be small
A_o = initial surface	Should be large, therefore fine particle size
M_o = sample weight	Should be small
e (exp. $-E/RT$)	Increases with increase in T, larger P_G causes higher T

Crucibles which lead to decomposition in self-generated atmospheres have their primary influence in increasing the pressure of gas evolution to one atmosphere, which gives rise to favorable thermodynamic, physical, and kinetic effects. The control is not exact, and Pannetier *et al.*, being concerned with the precise thermogravimetry of solid–gas systems, consider the use of self-generated atmospheres to be a makeshift or last resort[12]. In many instances, however, precise atmosphere control is not available, or is difficult or impossible because the reaction products are complex or unknown. The self-generated atmosphere method has a sound theoretical basis and, in such instances, would seem to be a good choice for the initial thermogravimetric study of a complex solid–gas system.

Consideration of reaction characteristics also leads to the conclusion that a crucible for utilizing the effect of the self-generated atmosphere should have as small a vapor volume as possible (see also section C). A large vapor volume will allow gas pressure gradients in the sample, may result in different reactions, and, it is claimed[2], may cause non-stoichiometric weight losses. A large vapor volume will also make it more difficult to locate T_i and hence to compare results by different workers. As has been pointed out[12] it is wasteful to debate the value of T_i or the existence of a compound in a particular temperature range if the gas pressure is variable and unknown. The use of a self-generated atmosphere crucible of standard design by different workers would help make their results more directly comparable.

In a self-generated atmosphere crucible the atmosphere produced by the first reaction may have a beneficial or detrimental effect on the following reaction. For example, in consecutive hydrate decompositions the presence of water vapor facilitates the recrystallization of the new phase[15], and the decomposition of anhydrous calcium oxalate is accelerated if water is present from the decomposition of the hydrate[11].

C. SGA CRUCIBLES AND THEIR PERFORMANCE

It seems not to have been recognized heretofore that the vapor space in SGA crucibles and the buoyant effect of the evolved gases can have an important influence on the interpretation of results. In this section there will be a general development of the effect of vapor space and the effect of changing buoyancy, and then previously described SGA crucibles and examples of their performance will be discussed.

(i) Vapor space and extent of decomposition

The size of gas spaces in powders and in crucibles and the extent of decomposition necessary to fill them can be easily calculated for a typical decomposition. If 100 mg of calcium carbonate with an average particle diameter of 1 μm and a bulk density of 6 10 of the true density is placed in the bottom of a 4.0 porcelain crucible with a volume of 4 ml, it will require decomposition of 0.03% of the calcium carbonate to form enough carbon dioxide to fill the voids in the sample at 600 °C, 0.024 ml, and decomposition of 5.6% of the calcium carbonate to fill the crucible, assuming that the carbon dioxide exactly displaces the air and there is no loss by diffusion. Both percentages will decrease in magnitude with increase in temperature. The decomposition necessary to displace the air in the powder is negligible, but that required to fill the crucible is substantial. For this reason, crucibles for work in self-generated atmospheres should have the smallest possible vapor volume. If the vapor volume is small the thermogram will show a sharp transition from constant weight to rapid decomposition. If the vapor volume is large, there will be a temperature range over which there is a slow but increasing weight loss followed by a sharp transition. These effects will be noted in later examples. A small vapor volume is also desirable to reduce the weight changes due to the buoyant effect of different gases.

(*ii*) *Corrections of observed weight changes for varying buoyancy caused by changes in the gas composition and density in the crucible*

(*a*) *SGA crucibles with fixed vapor volumes.* — The vapor space in an SGA crucible with a fixed vapor volume, or in an ordinary covered crucible, is usually full of air at the beginning of an experiment. As decomposition of the sample occurs, the air is gradually displaced by the gaseous decomposition product or products until the pressure of the gas equals the ambient pressure in the thermobalance, usually one atmosphere. Increasing the temperature further results in escape of the excess gas. The gas composition in the vapor space remains constant, but the gas density decreases due to the increasing temperature. When a second decomposition occurs, the same process is repeated with the second gaseous product displacing the first. If the reaction is reversible, the partial pressure of the product gas at a given temperature will be approximately equal to the dissociation pressure of the compound up to the temperature at which it exceeds the ambient pressure in the thermobalance. If two sequential decompositions produce the same gaseous product, the first decomposition will at first take place at less than one atmosphere pressure of the gaseous product, but the entire decomposition of the intermediate solid will occur at one atmosphere pressure of the gaseous product.

At any temperature the weight of the gas, W_g, in the crucible will be, in mg

$$W_g = \frac{V \times 273.16 \times M \times 1000}{T \times 22.414} = 12.187 \times \frac{VM}{T}$$

where V is the volume of the vapor space in ml
T is the absolute temperature
M is the molecular weight of the gas

The change in weight, ΔW_g, due to change in gas composition and density will equal the weight of air minus the weight of the gas

$$\Delta W_g = (12.187V/T)(M_{\text{air}} - M_{\text{gas}})$$

The corrected weight change of the sample, ΔW_s will equal the observed final weight, W_2, minus the observed initial weight, W_1, plus the change in gas weight

$$\Delta W_s = W_2 - W_1 + \Delta W_g$$

where the changes in sample weight and gas weight may be positive or negative, that is, may represent a gain or loss of weight.

Thus, when a crucible initially full of air becomes full of a lighter gas, such as water vapor, ΔW_g will have a positive sign and the correct sample weight will be larger than that observed. A heavy gas will have the reverse effect.

(*b*) *Piston type SGA crucibles.* — In a piston type SGA crucible with a well fitting piston, the vapor volume will increase on heating up to the volume of the cylinder, or to some limiting volume less than this if the piston is fitted with a by-pass groove. From this point the piston type crucible behaves as a fixed volume crucible and corrections can be made for the weight of the gas. If the fit of the piston is such that its position is sensitive to the rate of evolution of the gas for any major part of the decomposition, then the magnitude of the correction becomes uncertain since it is generally not possible to measure the piston position during a run. If the piston fits loosely, the vapor volume will be small and constant and a separate buoyancy correction may not be necessary.

(*iii*) *Crucible designs and results*

Crucibles for thermogravimetry in self-generated atmospheres have been primarily of the two types already mentioned, piston and ball-valve. As shown in Fig. 4, there has been some evolution of the designs. Compounds of a number of differen types have been studied, but the total list is quite short as shown by Table II.

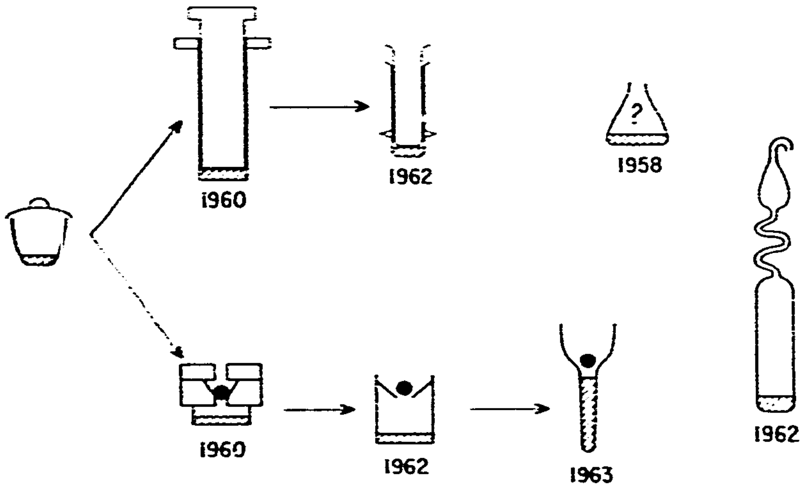

Fig. 4. Evolution of crucibles for experiments in self-generated atmospheres.

The simple covered crucible was found by Butcher *et al.*[16] and by Currell and Khodabocus[17] to give improved resolution in a study of boron–nitrogen compounds. Thus, the thermogram for *n*-propylammonium tetraphenyl borate showed only one intermediate in an open crucible, but with a lid, two intermediates were resolved according to the equation:

$$\begin{array}{ll} RNH_3BPh_4 \xrightarrow{(110-120°C)} & RNH_2BPh_3 + PhH\uparrow \\ & \quad \downarrow (140-150°C) \\ & RNHBPh_2 + PhH\uparrow \\ & \quad \downarrow \\ & \text{vaporized} \end{array}$$

Two designs do not fit the general pattern. Fruchart and Michel[8] used a cup with a large base but a small opening (not otherwise described) to slow down the elimination of water vapor and to obtain thermogravimetric results on magnesium sulfate heptahydrate that were in good concordance with DTA results. The capillary crucible used by Amiel and Paulmier[18] and later by Lagier *et al.*[19] was designed to prevent mechanical loss of product caused by the rapid decomposition of cobalt(II) oxalate in vacuum.

TABLE II

SUBSTANCES THAT HAVE BEEN STUDIED IN SELF-GENERATED ATMOSPHERES

Reference	*Crucible*[a]	*Compound*
2	P	Ammonium carbonate monohydrate
6	MR	Anthracite
22	P	Brucite [$Mg(OH)_2$]
16	C	*n*-Butylammonium tetrachloroborate
16	C	*t*-Butylammonium tetrachloroborate
17	C	i-Butylammonium tetraphenylborate
17	C	*s*-Butylammonium tetraphenylborate
2	P	Cadmium carbonate
24	BV	Cadmium(II) sulphate (8/3) hydrate
22	P	Calcite ($CaCO_3$)
3, 23	BV	Cerussite ($PbCO_3$)
6	MR	Charcoal (wood)
22	P	Chrysotile
6	MR	Coal
27	BV	Cobalt(II) acetate tetrahydrate
18, 19	CC	Cobalt(II) oxalate dihydrate
2, 20	P	Cobalt oxalate hydrate
26	BV	$CuSO_4 \cdot 3Cu(OH)_2 \cdot xH_2O$
26	BV	$CuSO_4 \cdot 2Cu(OH)_2$
20, 25	P, BV	Copper sulphate pentahydrate
16	C	Ethylammonium tetrachloroborate
23	BV	Gypsum ($CaSO_4 \cdot 2H_2O$)
7	DC	Iron(II) carbonate
2, 20	P	Lead(II) carbonate
This	C (powder), P, CC	Lead(II) carbonate
This	CC, C	Lead(II) oxide
6	MR	Lignite
22	P	Magnesite ($MgCO_3$)
8	CC	Magnesium sulphate heptahydrate
This	CC, C, P	Manganese(II) acetate tetrahydrate
7,2	DC, P	Manganese(II) carbonate
16	C	*n*-Octylammonium tetrachloroborate
16	C	*n*-Propylammonium tetrachloroborate
17	C	*n*-Propylammonium tetraphenylborate
7	DC	Rhodochrosite ($MnCO_3$)
7	DC	Siderite ($FeCO_3$)
2	P	Silver carbonate
2	P	Sodium oxalate
22	P	Talc
21	P	Thorium(IV) nitrate pentahydrate
21	P	Thorium(IV) oxalate hexahydrate
20	P	Uranyl sulphate hydrate
4, 25	DC, BV	Zinc sulphate heptahydrate

---

[a] Key to crucibles: BV, ball valve; C, covered; CC, capillary crucible; DC, deep crucible; MR, microretort; P, piston.

Garn and Kessler[2-20] used the decomposition of carbonates, hydrates, and oxalates to demonstrate the value of the piston crucible, but they recognized that the original model made of alumina was too heavy, 44 g, for many thermobalances. A lighter crucible was made of Pyrex by Claudel[21] in which the piston moved with mild friction and projections on the crucible supported it on the ring of a Chevenard thermobalance. In a study of the decomposition of thorium oxalate hexahydrate and thorium nitrate pentahydrate Claudel observed poorer separation of hydrate plateaus with a piston crucible than with an ordinary crucible. Also with the latter compound there was the adverse effect that the increased temperature of hydrate decomposition caused it to overlap the nitrate decomposition. He also reports a final stage of weight loss as due to gas desorption, and that at high temperatures the product expanded out of the crucible. All in all, Claudel seems to have had an unhappy experience with the piston crucible. Monkman[22], on the other hand, used a piston crucible of Inconel 600 in a successful study of asbestos and related minerals. He found that the combination of the piston crucible and a heating rate of 42 °C/h, which minimized temperature differences within the specimen, reduced the effect of particle size variation and standardized the effect of crucible geometry to yield more reproducible results.

Forkel used the ball-valve crucible he invented to study gypsum and the lead carbonate mineral, cerussite[23]. His results with the latter were almost identical with those obtained by heating the mineral in an open dish in an atmosphere of carbon dioxide. The differential thermogram of gypsum in air in an ordinary crucible shows only a broad, nearly flat topped peak, whereas in the ball-valve crucible T_i is increased from about 90 to 130 °C and the weight loss shows as two clearly separated peaks of which the first is the larger.

Pannetier *et al.*[24] built a Forkel type crucible using a platinum bucket with an indented top having a hole closed by a quartz ball. This was used to study the dehydration and decomposition of cadmium sulfate 8/3 hydrate. A sharper inflection was

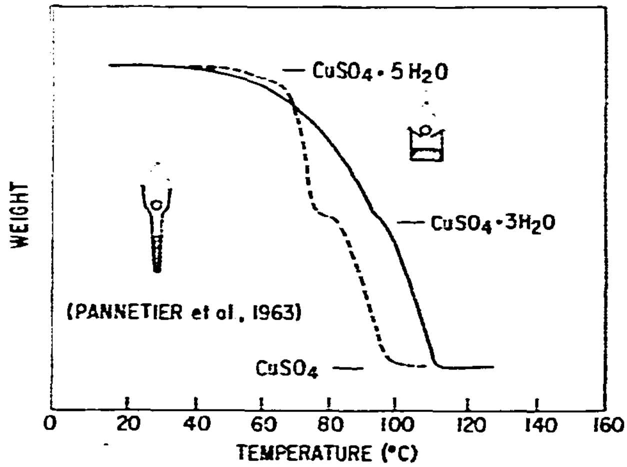

Fig. 5. Thermograms for copper sulfate pentahydrate. Heating rate 130 °C/h: (———) Forkel type crucible, (------) Filiform crucible with valve.

obtained with the ball-valve crucible than with an open crucible, even when a slower heating rate was used with the open crucible. The ball-valve crucible was later modified to improve the heat transfer and tested on copper sulfate pentahydrate with the results[25] shown in Fig. 5. This filiform crucible also has the advantage (not mentioned by its inventors) of having a smaller vapor volume which may be the cause of the sharper initiation of reaction. Pannetier and co-workers used these crucibles in a detailed study of the dehydration of zinc sulfate heptahydrate and found them of advantage in revealing the hexahydrate.

Later they reported results on $CuSO_4 \cdot 3Cu(OH)_2 \cdot xH_2O$ and $CuSO_4 \cdot 2Cu(OH)_2$. Sample weights of 50 mg or less in the ball-valve crucibles and a heating rate of 130°C/h were found necessary to obtain good resolution of the intermediate stages[26]. The ball-valve crucible (not further described) was also used by Doremieux[27] to study the dehydration and decomposition of cobalt(II) acetate tetrahydrate. Plateaus were much clearer than in open crucibles and two new intermediates were identified, the dihydrate and $Co_3(OAc)_5OH$.

This review shows that crucibles for self-generated atmospheres have not always been helpful in resolving reaction stages. Most investigators have been concerned with specific results rather than the method and, except for Garn and Kessler, and Forkel, the crucibles have not been adequately described nor have principles of their application been discussed. It seems evident that to take full advantage of this technique new crucibles are needed that are light, easy to make, and have a small vapor volume. The performance of these crucibles needs to be compared directly with the performance of existing designs.

D. NEW RESULTS

(*i*) *Experimental, materials, and apparatus*

Lead(II) oxide, yellow reagent powder (Matheson, Coleman, and Bell). Lead(II) carbonate, to ACS specifications (City Chemical Co.). Manganese(II) acetate tetrahydrate, certified reagent grade (Fisher Scientific Co.), ground slightly to obtain a powder from the initially large flakes. It had a strong odor of acetic acid.

Thermogravimetric experiments were carried out in a Chevenard thermobalance model TH 59 IIC modified slightly for use in air or controlled atmospheres. The protective cover of the balance was flushed with air at 2 liter/min. This was found necessary, particularly when carbon dioxide was used, in order to prevent it from progressively mixing with air in the balance case and causing an apparent weight gain increasing with time. The temperature was measured by a thermocouple in a well just above the sample. Reported weight changes have been corrected appropriately for apparent weight gain. Powder X-ray diffraction patterns were obtained photographically in a 5-cm diameter camera using FeK_α radiation. The interplanar spacings were read from the film with a spacing template and compared in position and intensity with standard patterns.

The sample holders used were as follows:

(1) crucible, Coors 4 0 porcelain, high form, open or with cover;

(2) shallow dish, quartz, 20 mm OD, 15 mm ID, 6 mm high, 4 mm deep;

(3) piston crucible (Fig. 6, right side). Pyrex. Made from 10 cc hypodermic syringe. Cylinder, 18 mm OD, 14.4 mm ID, 45 mm high. Piston, 14.4 mm OD, 45 mm high. Total weight 17 g. The piston had a groove in the side that allowed more rapid escape of the vapor when the internal volume exceeded 5 ml;

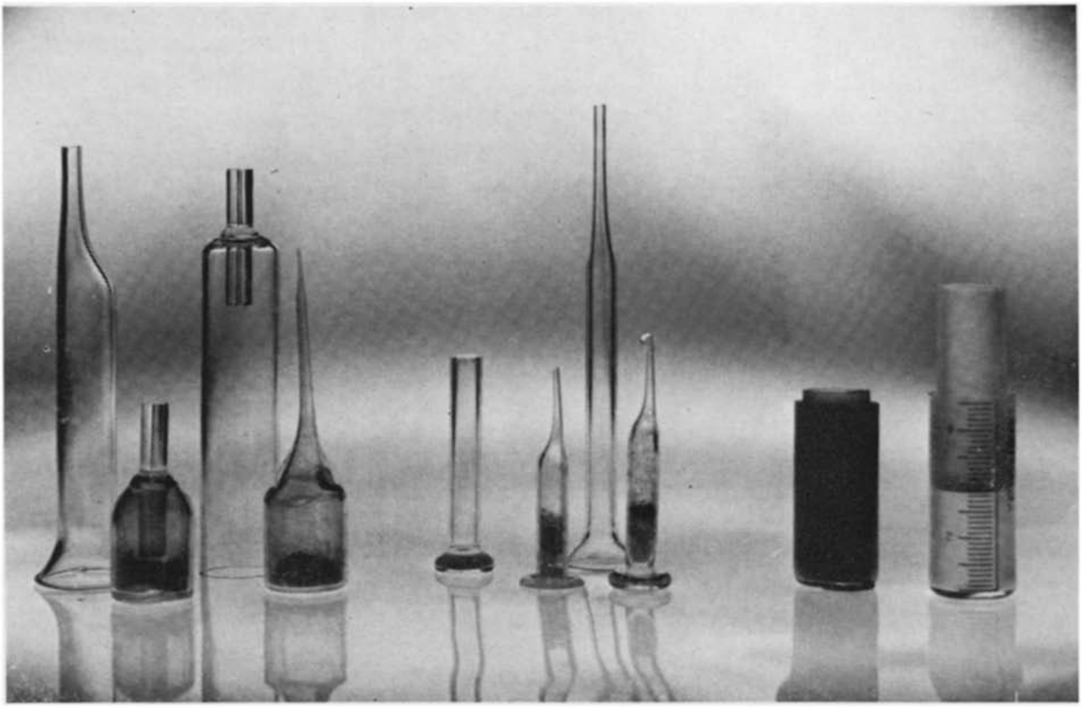

Fig. 6. Crucibles, see text (section D, *i*).

(4) capillary crucible (Fig. 6, center). Pyrex. Base 13 mm dia., 2 mm thick; body, 7 mm OD, 4.5 mm ID, 50 mm high. After loading and drawing capillary; height, 55 mm; length inside to shoulder, 25 mm; diameter of capillary, 1 mm.

The capillary crucible is loaded (before drawing the capillary) with the aid of a special powder funnel which fits inside the crucible to the bottom. This permits placing the sample without getting any particles on the inside wall of the crucible above the sample level. The empty crucible is weig[illegible] loaded, and reweighed to obtain the sample weight. The crucible is then wrap[illegible] with asbestos paper up to a short distance above the level of the sample. The c[illegible] is held by this part, a glass rod fused to one edge of the top and the capillary d[illegible] about a centimeter above the sample. After cooling, the asbestos paper is removed, the crucible wiped clean and the capillary broken at a suitable point. The sample and crucible are then ready for use.

Several other types of capillary crucibles are shown in Fig. 6. A capillary of known diameter and length can be fused into a larger tube as shown at the left, and the sample loaded and sealed as described above. More simply for large samples, a large flat bottom tube with an initial partial constriction can be used in the same way, the completed form is shown.

(*ii*) *Results and discussion — compounds*

(*a*) *Lead(II) oxide.* — The utility of a self-generated atmosphere in reagent testing is illustrated by Fig. 7. Pure lead(II) oxide should be stable in air to nearly 400°C above which it should gain weight due to oxidation[28]. Curve A is a thermogram for the reagent sample in an open crucible in air. There is no plateau between the maximum weight loss, 0.7%, and the subsequent weight gain, which indicates that they are caused by overlapping reactions.

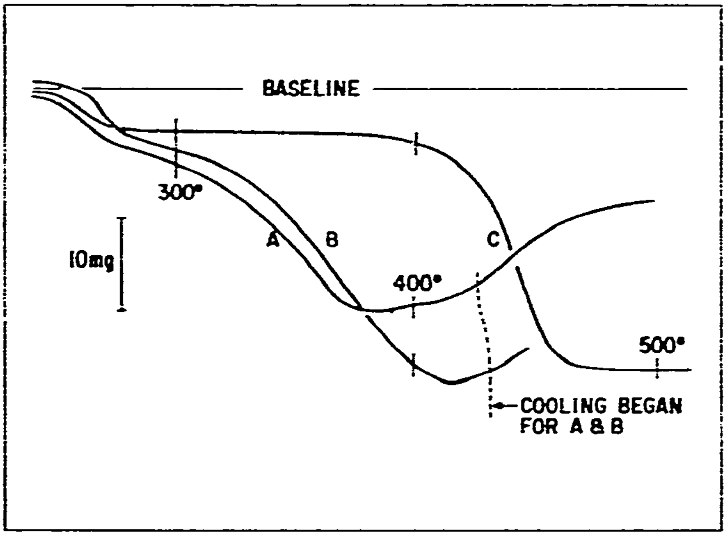

Fig. 7. Thermograms for reagent lead(II) oxide in air at a heating rate of 150°C/h as recorded; A, 4.0005 g in open 4/0 crucible; B, 4.0010 g in a covered 4/0 crucible; C, 3.9919 g in a capillary crucible.

A better estimate can be obtained from curve B, which was made in a covered crucible. The thermogram is shifted to the right and the total weight loss is much greater. There is, however, still some question about the amount of impurity because there is no plateau between the weight loss and the onset of oxidation.

A much clearer idea of the behavior of the impurity can be obtained by using a capillary crucible as shown in curve C. There is an initial loss beginning about 50°C and tending towards a plateau at 225°C. This could be due to adsorbed and hydrate water. It is followed by an additional loss in two clearly defined stages that can be measured exactly.

(*b*) *Lead(II) carbonate.* — The use of thermogravimetry in self-generated atmospheres in the present instance was stimulated by the need to examine a sample of lead(II) carbonate and by the obvious discrepancies between the thermograms of

Forkel and of Garn and Kessler, see Fig. 2. Examination of the literature showed many other discrepancies, and the first three samples of analytical reagent grade lead(II) carbonate that were tried were found to be impure. Despite a considerable amount of additional work, a consistent explanation for the entire course of the decomposition has not yet been achieved. Rather than review all the complexities, only a few selected results illustrating the influence of self-generated atmospheres will be presented here. Brief reviews and recent work may be found in papers by Pannetier and coworkers[29,30], and by Burriel-Marti and Clavel[31].

One way of retaining the atmosphere over the sample in an ordinary crucible is to cover it with a layer of an inert powder. The results of such experiments with lead(II) carbonate are much less striking than expected.

Thermogram A in Fig. 8 is that for lead carbonate heated in air. If a thin layer of alundum, 0.4575 g, is placed over the lead carbonate, the thermogram is shifted slightly to the right of A. Only if a very large amount of alundum is used (5 g) an appreciable shift is obtained (curve B). As might be expected very large corrections are required for both apparent weight gain and for water adsorbed on the alundum.

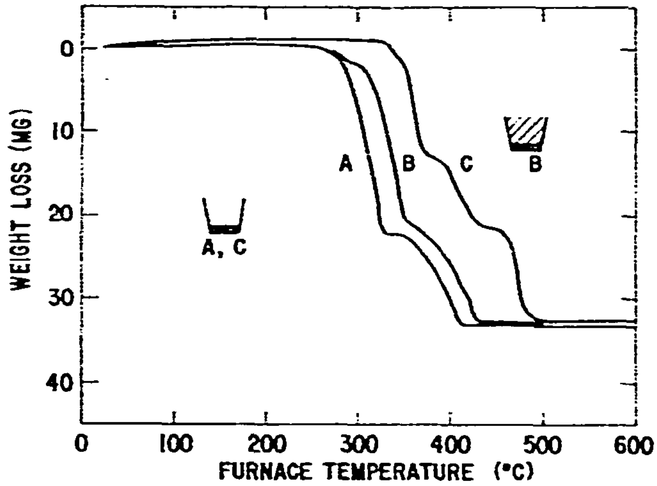

Fig. 8. Thermograms for lead(II) carbonate at a heating rate of 300°C/h; A, 200.4 mg in open 4/0 crucible in air; B, 200.6 mg covered with 5.0008 g Norton No. 240 alumina in an open 4/0 crucible in air; C, 200.3 mg in open 4/0 crucible in flowing CO_2.

For comparison, curve C shows a thermogram obtained in an atmosphere of carbon dioxide. The only advantage of the powder layer curve B is to bring out an indication of a small reaction stage near the beginning. It does not help bring out the stage near 12-mg weight loss, and it gives a poorer indication of the stage near 22-mg weight loss. This method might give better results with finer, less absorptive powders, but it has not been investigated further.

A similar trick would be to cover the sample with a thin disk of alumina whose diameter was about the same as that of the inside of the crucible at the level of the top of the sample. When this was done the thermogram obtained was very similar to Fig. 8B.

When lead(II) carbonate is heated in piston or capillary crucibles the results, at a heating rate of 300 °C/h, are so similar to those of Fig. 8, curve C that they cannot conveniently be shown on the figure at this scale. For these experiments the small capillary crucible is advantageous because it requires a much smaller correction for apparent weight gain and gas buoyancy than the piston crucible.

(c) *Manganese(II) acetate tetrahydrate.* — (*1*) *Literature.* The literature on the thermal analysis of this salt contains a number of conflicting results, but may be summarized in the following two equations for decomposition in nitrogen[32–36].

$$Mn(CH_3CO_2)_2 \cdot 4H_2O(s) \rightarrow Mn(CH_3CO_2)_2(s) + 4H_2O(g) \qquad (1)$$

$$Mn(CH_3CO_2)_2(s) \rightarrow MnO(s) + (CH_3)_2CO(g) + CO_2(g) \qquad (2)$$

Reaction (1) is actually more complicated, as revealed particularly by differential thermal analysis, and may involve decomposition in stages, incongruent melting, and evaporation of liquid water. Reaction (2) involves the simultaneous loss of acetone and carbon dioxide in contrast to calcium acetate in which the acetone is lost in a separate step with the formation of calcium carbonate, which on further heating loses carbon dioxide. The initiation of reaction (2) in air has been reported as overlapping reaction (1)[33], and as beginning at 225[32], 220[34], and 200°C[35,36]. In nitrogen the initial temperatures are 290[32] and 255°C[34]. The agreement between different workers is about as good as can be expected.

Neither of the two published thermogravimetric curves[33,35] show inflections in the first stage weight loss. The differential thermal analysis curve of Manabe and Kubo[35] shows four endothermic peaks with initial deviation from the baseline at 40 and peak temperatures of 60, 80, 120 (large) and 200 °C (very small).

The second stage weight loss has also been reported as without inflections, but the anhydrous acetate gave a complex DTA curve as reported by Arnoul[34]. He observed endothermic peaks in nitrogen at 190 (small), 270 (small), and 300 °C (large), the latter two overlapping.

In the description of experiments that follows, it will be assumed that the two stage mechanism given above is correct. The emphasis of the description will be on the differences of the thermograms obtained in different crucibles and on the weighing errors due to buoyancy effects.

(*2*) *Decomposition in nitrogen.* The thermogram for manganese(II) acetate tetrahydrate in flowing nitrogen is shown in Fig. 9A. The sample loses weight immediately at room temperature. The vapor lost may be partly water, but it is certainly partly acetic acid since the sample has a very strong odor of this substance. The two major stages of weight loss on heating correspond approximately to the loss of hydrate water and the decomposition of the anhydrous salt to manganese(II) oxide. The plateau from 130 to 260 °C indicates constant weight within the random error of the instrument. Both stages of weight loss show inflections. Because of the rapid initial weight loss, stoichiometric calculations were made from a baseline representing the weight of the empty crucible rather than in the usual way from the initial weight of the sample. The results are shown in Table III and compared to the calculated values

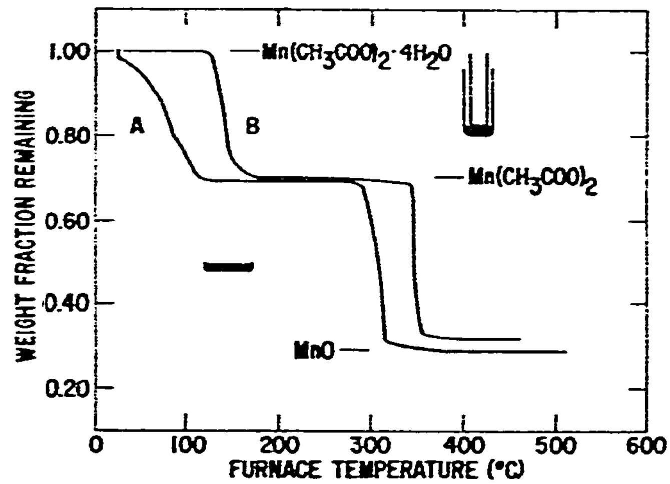

Fig. 9. Thermograms of manganese(II) acetate tetrahydrate, heating rate 150°C/h; A, Sample weight 153.8 mg in a shallow dish in flowing nitrogen, 250 ml/min; B, Sample weight 102.6 mg in piston crucible in air.

and to the results reported by Dollimore and Tonge[32]. Their sample was probably partially dehydrated whereas the present sample contains acetic acid and perhaps a slight excess of water.

TABLE III

THERMOGRAVIMETRY OF MANGANESE(II) ACETATE TETRAHYDRATE IN NITROGEN

	Observed	*Calculated*	*Dollimore and Tonge*
T_i, first stage (°C)[a]	25		55
T_f, first stage (°C)[b]	130		140
Loss to $Mn(OAc)_2$ (%)	30.6	29.40	28.3
T_i, decomposition (°C)	260		290
T_f, decomposition (°C)	350		370
Loss to MnO (%)	71.8	71.06	70.1

[a] T_i = temperature at which the loss is initially detected. [b] T_f = temperature at which the loss is final.

There is no indication from the thermogram that hydrolysis occurred during drying. The plateau ascribed to anhydrous manganese(II) acetate has a constant weight over a long temperature interval and is at a level close to the calculated weight fraction remaining expected. The inflection in the first stage loss was at 85°C and a weight fraction of 0.794.

Although attempts to prepare the anhydrous acetate by air drying always gave a colored product containing trivalent manganese, it was concluded from the thermogravimetric results that anhydrous manganese(II) acetate could be made by heating the hydrate at a relatively low temperature in flowing dry nitrogen. A sample was prepared in this way at 50°C by Mr. Arthur Lavallee.

Anal.	MnO(TG)	Mn^{2+}	Mn^{3+}	C	H
Calc.	41.00	31.75	0	27.77	3.50
Found	41.0	31.4	0.12	28.65	3.46

Thermogram for 139.4 mg at 300 °C/h, $T_i = 265, T_f = 390$ °C. Arnoul[34] for 30 mg at 250°/h, $T_i = 255$, $T_f = 330$ °C.

(3) *Decomposition in a piston crucible.* The thermogram for manganese(II) acetate tetrahydrate heated in a piston crucible in air is shown in Fig. 9B. For this run, the bottom of the piston was positioned about 2 mm above the sample because in a prior experiment with the piston on the sample melting caused the piston to stick then subsequently to be expelled from the cylinder illustrating dramatically a disadvantage of the piston crucible.

The effect of the self-generated atmosphere in increasing the initial weight loss temperature, T_i, is clearly shown by comparison with Fig. 9A, as is the decrease in reaction interval. The increase in T_i has the beneficial effect of eliminating the initial weight loss at room temperature with its resulting uncertainty about the starting point for the thermogram. This indicates that the piston crucible may be useful for the study of relatively volatile compounds. Forrester[9] has used a piston crucible in this way for an evolved gas analysis study of ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$.

The inflection during loss of water is located at 135 °C and a weight fraction of 0.908, but is much less prominent. Since the rate of weight loss increases after the inflection it may occur at the point the piston is extended enough to expose the groove and allow more rapid escape of gas. The second stage weight loss occurs in two approximately equal parts, a very rapid and uniform initial loss followed by a less rapid but still fairly uniform second loss. The inflection is too vague to be connected clearly with separate losses of acetone and carbon dioxide.

Fig. 9B shows a sloping plateau for the anhydrous acetate and a final plateau at a level above that expected for manganese(II) oxide and therefore indicating oxidation of the manganese. However, as has already been described, both of these levels need to be corrected further for the buoyant effect of the increased gas volume, as the piston moves.

The corrected results are given in Table IV. Comparison with Table III shows that both stages have lower losses than expected, but are in better agreement with the calculated values than the sample run in nitrogen. A corrected thermogram would show a sloping plateau for the anhydrous acetate slightly higher than in Fig. 9B, and

TABLE IV

THERMOGRAVIMETRY OF MANGANESE(II) ACETATE TETRAHYDRATE IN A PISTON CRUCIBLE

	Observed			*Calculated*
	Initial		*Corrected*	
T_i, first stage (°C)		112		
T_f, first stage (°C)		205		
Loss to $Mn(OAc)_2$ (%, 205 °C)	30.3		29.0	29.40
T_i, decomposition (°C)		340		
T_f, decomposition (°C)		367		
Loss to MnO (%, 450 °C)	68.8		70.6	71.06

a final plateau somewhat lower. The sloping intermediate plateau may be due to a slight amount of hydrolysis.

The results in the piston crucible could be quite misleading unless corrected. Thus, the final weight loss, 68.8%, shown in Fig. 9B is closer to that calculated for Mn_3O_4, 68.88%, or even to Mn_2O_3, calc. 67.8%, than to MnO. That the experimental product from the piston crucible was, in fact, manganese(II) oxide was confirmed by X-ray diffraction which showed principally lines due to this substance and a few weak lines which matched the data for Mn_3O_4*.

An advantage of a close fitting piston crucible is that a run can be stopped at any point, the crucible cooled and removed, and the gas analyzed. This was done with a related acetate and the first stage products identified by mass spectrometric analysis as water and acetic acid. The crucible was then replaced, the heating continued, and the second stage products were identified in a similar way as acetone and carbon dioxide.

(*4*) *Decomposition in air in open and covered crucibles.* The results are shown in Fig. 10 and Table V. In the covered crucible the temperature at which a given weight loss occurred is greater than in the uncovered crucible for both stages and both show other differences in behavior. The water loss appears to occur in two stages and the inflection between them is at 90°C and 0.917 weight fraction in the open crucible and at 112°C and 0.880 weight fraction in the covered crucible. The loss of acetone and carbon dioxide is accompanied by oxidation of the manganese in the open crucible, but oxidation appears to occur to a much smaller extent in the covered crucible.

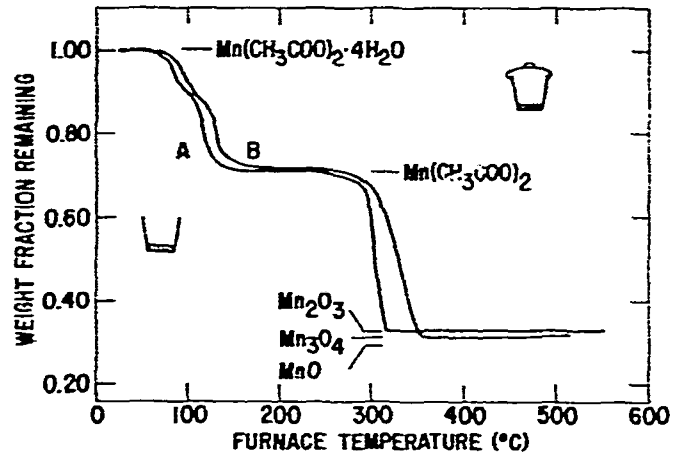

Fig. 10. Thermograms of manganese(II) acetate tetrahydrate in air, heating rate 150°C/h; A, Sample weight 154.3 mg in an open 4/0 crucible; B, Sample weight 153.6 mg in a covered 4/0 crucible.

The position of the levels observed in the covered crucible is, however, somewhat misleading because of the different buoyant effect of the evolved gases. Thus in the

---

*I am indebted to Mrs. A. M. Davis for this identification.

closed crucible the curve for anhydrous manganese(II) acetate appears to be a sloping plateau above the plateau observed in the open crucible. If we assume that the evolved gas is relatively quickly and completely replaced by air in the open crucible, but that the evolved gas replaces air completely in the covered crucible we may calculate the maximum magnitude of the effect as previously described. For curve B in Fig. 10 at 180°C the 4/0 crucible would be full of water vapor and the measured weight would be lighter by 1.20 mg than it appears to be. The loss would therefore decrease from 28.5 to 27.7%, in poorer agreement with the value of 28.9% observed in the open crucible. The difference would be less at a higher temperature and the plateau therefore has a greater slope than shown in the figure. An additional uncertainty is that the presence of any acetic acid in the vapor space would require a correction in the opposite direction. These considerations indicate how difficult it is to correct the observed values to obtain reliable weights.

TABLE V

THERMOGRAVIMETRY OF MANGANESE(II) ACETATE TETRAHYDRATE IN AIR (%)

	Calculated	*Dollimore and Tonge*	*Observed*	
			Open crucible	*Covered crucible*
Loss to $Mn(OAc)_2$	29.40	29.30	28.9	28.5
Loss to Mn_2O_3	67.80	68.50	67.6	68.8
Loss to MnO	71.06			

At 365°C the vapor in the crucible is a mixture of acetone and carbon dioxide, which is considerably heavier than air. The calculated effect is 1.70 mg and the weight loss in the covered crucible becomes 69.9%, much greater than that in the open crucible, 67.6%. This indicates that less oxidation has occurred in the closed crucible than shown by the uncorrected thermogram.

Thus a consideration of the buoyancy effects of the evolved gases would lead us to suspect that the sloping plateau for "anhydrous manganese(II) acetate" in the closed crucible may indicate some hydrolysis and, similarly, the weight gain above 360°C is probably due both to the effect of acetone and carbon dioxide vapors being replaced by air and to oxidation. The covered crucible is not a good container for most kinds of self-generated atmosphere experiments.

(5) *Decomposition in a capillary crucible.* A thermogram obtained by heating manganese(II) acetate tetrahydrate in a capillary crucible is shown in Fig. 11A. The vapor volume is only about 0.25 ml so that the maximum buoyancy correction is less than 0.1 mg and can be neglected. A comparison with Fig. 9 shows that the thermogram is very similar to that obtained in the piston crucible, but that the observed weight losses to anhydrous manganese(II) acetate (28.1% at 215°C) and to the plateau at about 400°C (68.9% at 418°C) are respectively smaller and larger in the capillary crucible than in the piston crucible as would be expected from the smaller buoyancy

correction. Comparison with Fig. 10 shows that the capillary crucible is much better than the covered porcelain crucible in providing a self-generated atmosphere. A further advantage of the capillary crucible is that the sample can be easily recovered and protected at any point merely by lifting the furnace and melting the tip of capillary to close it. The capillary crucible is not as effective as the piston crucible in keeping out air as indicated by the weight gain above 420 °C. Air could be more effectively excluded by drawing a finer capillary.

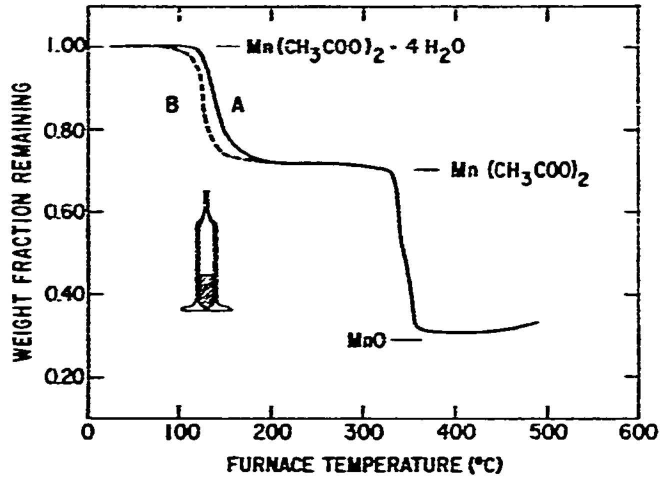

Fig. 11. Thermograms of manganese(II) acetate in a capillary crucible; A, Sample weight 155.4 mg, heating rate 150 °C/h; B, Sample weight 149.2 mg, heating rate 25 °C/h.

An experiment was also carried out in a capillary crucible at a slow rate of heating with the results shown in Fig. 11B. The curve is to the left of curve A, as would be expected. Although the figure shows only slightly more detail, in the original thermogram there is clearly a slow initial loss, a period of rapid loss from 120 to 127 °C, and a slow final loss to the plateau. There is no plateau or inflection that can be ascribed to an intermediate hydrate.

(*iii*) *Discussion — crucibles*

Decompositions in self-generated atmospheres are often characterized by thermograms that show a gradually increasing weight loss preceding a sudden rapid weight loss. This is particularly noticeable at the start of the second stage loss in Figs. 9B and 11A. It probably represents the effect of the gradual replacement of the gas in the vapor space by the self-generated atmosphere. That is, for a short period the decomposition is occurring at a gradually increasing partial pressure of the gas evolved. While this causes some uncertainty in the exact location of T_i, the major portion of the reaction usually occurs after the sharp change in slope that separates this early loss from the decomposition at one atmosphere partial pressure of the evolved gas. A small vapor volume in the crucible reduces the temperature range over which this preliminary decomposition occurs and makes it reasonable to designate as T_i the point of the sharp initial change in slope.

The experiments lead to some general comments about crucibles.

(*a*) *For piston crucibles*

1. If the piston fits tightly it will be pushed out the top because it will not allow the gas generated to leak out rapidly enough.

2. If the piston fits tightly, but is provided with a vent near the top, it will tend to operate at a fixed expanded volume and require a large and variable buoyancy correction.

3. A tight fitting piston with a vent has the advantage that it may be removed from the thermobalance at any stage for separate analysis of the gaseous products

4. If the piston fits loosely it will work for the samples that do not melt, but when a sample melts capillary action may cause the liquid to fill the space between the piston and the crucible. When the sample subsequently solidifies it may expand out of the crucible or it may seal the piston, which will subsequently be blown out the top.

5. These considerations lead to the suggestion, not yet tried experimentally, that piston crucibles for general work should be constructed with a relatively loose fit and a stop on the piston that fixes the size of the vapor space at somewhat greater volume than that of the sample.

(*b*) *For capillary crucibles*

1. They are lighter and easier to make than the previously described piston and ball-valve crucibles.

2. They permit easy isolation and protection of intermediates and final products.

3. They have a small vapor space so that corrections for changing gas density in the vapor space are negligible.

E. LIMITATIONS, ADVANTAGES, RECOMMENDED USES

(*i*) *Limitations of thermogravimetry in self-generated atmospheres*

1. Buoyancy corrections vary depending on the molecular weight of the gas filling the crucible.

2. Large, heavy crucibles will cause a greater uncertainty in sample temperature[21].

3. In dehydration of hydrates, the chances of melting and the appearance of pseudo-plateaus may be enhanced[4].

4. Poorer resolution may result if the first reaction is delayed to a temperature at which a subsequent reaction begins[21].

5. Secondary reactions with the evolved gas may make interpretation difficult[18,19].

(*ii*) *Advantages of thermogravimetry in self-generated atmospheres*

(*a*) Thermogravimetry in self-generated atmospheres is primarily of value in the study of consecutive reactions. It will generally have the following advantages compared to thermogravimetry in open crucibles.

1. The reaction interval will be narrower, overlapping reactions will be more clearly resolved, and intermediates more accurately identified[2,14,22,24,27].

2. New phases will be revealed[4].

3. Reactions will proceed, for the most part, at a fixed pressure of the gaseous products equal to atmospheric pressure. The course of reactions, except at the start, will not be affected by varying partial pressure[3,21].

4. The observed initial decomposition temperature will be more closely related to an equilibrium decomposition temperature[2].

5. The results will be more directly comparable with results from separate differential thermal analysis experiments[8,37].

6. Experiments can be performed on materials subject to oxidation at elevated temperatures with little interference from oxidation.

7. Very fast reactions can be studied without loss of solid product[19].

8. Better results will be obtained on materials with an appreciable vapor pressure at room temperature. The sample can be weighed more accurately and will yield a horizontal baseline on the thermogram.

9. The effects of particle size differences will be reduced and the effects of crucible geometry standardized. This is particularly important with inhomogeneous materials such as rocks and minerals[22].

10. The recrystallizations of new phases from hydrates or hydroxides will be facilitated[15,38].

11. It has been claimed that irreversible decompositions will show better resolution and a smaller reaction interval in some instances, though it is not known why[2].

(*b*) Thermogravimetry in self-generated atmospheres also has some advantages over controlled atmosphere thermogravimetry.

1. The balance need not be protected from condensible or corrosive gases[3].

2. No additional apparatus is needed except the sample holder[2].

3. The advantages of controlled atmosphere thermogravimetry are available even when different stages require different atmospheres.

4. The advantages of controlled atmosphere thermogravimetry are available even when the gaseous product is a mixture or is unknown[21].

(*iii*) *Recommended uses*

Thermogravimetry in self-generated atmospheres may be useful for studies of:

1. Consecutive reactions, and particularly for hydroxides, hydrates, ammoniates, carbonates, acetates, oxalates, and sulfates.
2. Inhomogeneous materials.
3. Compounds that decrepitate or explode.
4. Air sensitive materials.
5. Volatile materials.
6. Materials that decompose to yield several gaseous products.
7. Destructive distillation.

REFERENCES

1 H. Saito, *Rept. Tohoku Imp. Univ., Ser. I*, 16 (1927) 37.

2 P. D. Garn and J. E. Kessler, *Anal. Chem.*, 32 (1960) 1563.

3 W. Forkel, *Naturwissenschaften*, 47 (1960) 10.

4 P. Vallet and M. Bassière, *Bull. Soc. Chim. Fr.*, [5] 5 (1938) 546.

5 P. Vallet, *Compt. Rend.*, 204 (1937) 496.

6 Y. Jouin, *Chim. Ind., Paris*, 58 (1947) 24.

7 H. E. Kissinger, H. F. McMurdie, and B. B. Simpson, *J. Amer. Ceram. Soc.*, 39 (1956) 168.

8 R. Fruchart and A. Michel, *Compt. Rend.*, 246 (1958) 1222.

9 J. A. Forrester, *Chem. Ind.* (London), (1969) 1244.

10 E. M. Barrall, II and L. B. Rogers, *J. Inorg. Nucl. Chem.*, 28 (1966) 41.

11 E. L. Simons and A. E. Newkirk, *Talanta*, 11 (1964) 549.

12 G. Pannetier, J. Guenot, and J.-M. Manoli, *Bull. Soc. Chim. Fr.*, (1964) 2828.

13 G. Pannetier, J. Guenot, and J.-M. Manoli, *Bull. Soc. Chim. Fr.*, (1964) 2832.

14 P. D. Garn, *Thermoanalytical Methods of Investigation*, Academic Press, New York, N.Y., 1965, Ch. VII.

15 R. M. Dell and V. J. Wheeler, in G. M. Schwab (Ed.), *Reactivity of Solids* (*5th Int. Symp., Munich, August 1964*), Elsevier, Amsterdam, 1965, p. 395.

16 I. M. Butcher, B. R. Currell, W. Gerrard, and G. K. Sharma, *J. Inorg. Nucl. Chem.*, 27 (1965) 817.

17 B. R. Currell and M. Khodabocus, in J. P. Redfern (Ed.), *Thermal Analysis 1965*, MacMillan, London, 1965, p. 140.

18 J. Amiel and C. Paulmier, *Compt. Rend.*, 225 (1962) 2443.

19 J.-P. Lagier, R. Ouahes, and C. Paulmier, *Bull. Soc. Chim. Fr.*, 5 (1964) 1082.

20 P. D. Garn, *Anal. Chem.*, 33 (1961) 1247.

21 B. Claudel, Thesis, Université de Lyon, 1962.

22 L. J. Monkman, *Abstr. Conf. on the Physics and Chemistry of Asbestos Minerals, Oxford, 19-21 July, 1967*, Abstr. 3-9.

23 W. Forkel, *Z. Instrumentenk.*, 69 (1961) 215.

24 G. Pannetier, J. M. Bregeault, and J. Guenot, *Bull. Soc. Chim. Fr.*, (1962) 2158.

25 G. Pannetier, A. Michel, J.-M. Bregeault, and G. Djega-Mariadassou, *Bull. Soc. Chim. Fr.*, (1963) 1204.

26 G. Pannetier, J.-M. Bregeault, G. Djega-Mariadassou, and M. Grandon, *Bull. Soc. Chim. Fr.*, (1963) 2616.

27 J. L. Doremieux, *Compt. Rend.*, 259 (1964) 579.

28 A. E. Newkirk and V. B. Hughes, *Inorg. Syn.* (1969), submitted for publication.

29 G. Pannetier, S. Fenistein, and G. Djega-Mariadassou, *Bull. Soc. Chim. Fr.*, (1964) 701.

30 G. Pannetier, S. Fenistein, and L. Davignon, *Bull. Soc. Chim. Fr.*, (1965) 109.

31 F. Burriel-Marti and M. E. Garcia Clavel, *An. Real. Soc. Espan. Fis. Quim., Ser. B.*, 63 [3] (1967) 317.

32 D. Dollimore and K. H. Tonge, in G. M. Schwab (Ed.), *Reactivity of Solids* (*Proc. 5th Int. Symp., Munich, August 1964*), Elsevier, Amsterdam, 1965, p. 497.

33 F. Burriel-Marti, S. Jimenez-Gomez, and C. Alvarez-Herreso, *An. Edafol. Fisiol. Vegetal* (Madrid), 14 (1955) 213.

34 A. M. Arnoul, *Compt. Rend.*, 262 (1966) 1372.

35 K. Manabe *et al.*, *Abstr. Calorimetry Conf. Chem. Soc. Jap., Osaka, November 1967*, A-203.

36 K. Manabe and T. Kubo, *Kogyo Kagaku Zasshi*, 71 (1968) 109; *Therm. Anal. Rev.*, 5 [5] (1969) 1561.

37 K. J. Notz and H. H. Jaffe, *J. Amer. Ceram. Soc.*, 43 (1960) 53.

38 R. Sh. Mikhail, *J. Phys. Chem.*, 67 (1963) 2050.