THERMOANALYTICAL INVESTIGATIONS
IN DIFFERENT CONTROLLED ATMOSPHERES*

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The influences of inactive, flowing atmospheres (noble gases, nitrogen, carbon dioxide, synthetic air) and vacuum (10^{-2} and 10^{-5} torr) on the thermal decompositions of inorganic and organic substances are discussed on the basis of literature and experimental data.

The fact that it is necessary to use a controlled gas atmosphere from the preparation of samples up to the study of the mechanisms of solid-state reactions is proved by several examples. Results are presented relating to the decompositions of silver(I) oxalate, potassium acetate, and a natural mixture of clays and alkaline earth metal carbonates, to the behaviour of β-manganese(IV) oxide and to the low-temperature dehydroxylation of kaolin, as studied especially by TG, DTG, DTA and MS methods.

It is well known that thermoanalysis is far more favourable in a dynamic atmosphere than in a static one. From the point of view of the solid substances the dynamic atmosphere can be either active, that is to say it enters into reaction with the solid material or with any of the reaction products, or inactive (inert), when it can take part in the removal of the decomposition products. The majority of papers on thermoanalysis discuss or refer to the chemical effects of the atmosphere.

Furthermore, the physical effects of a so-called inactive atmosphere may influence the morphology of the solid products formed during decomposition, the particle size of the samples, the surface area and lattice dislocations, to mention only the most important. The natures of such effects have not yet been clarified.

We shall discuss first of all the primarily non-chemical effects observed in the course of our investigations in dynamic, particularly inert gases, and in vacuum.

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Experimental

The thermoanalytical investigations were carried out with a Mettler Vacuum Thermoanalyzer. This thermobalance operates on electromagnetic compensation principles and has a thermostatically-controlled compartment. The whole unit is capable of operation at pressures down to 10^{-5} torr with the aid of two oil diffusion pumps.

The thermobalance is connected to a Balzers Quadrupole mass-spectrometer. Gaseous decomposition products come immediately into the mass-analyzer. The vacuum system is a dynamic one and belongs to both the balance and the mass-analyzer.

In every case gases of high purity were used, after further rigorous purification and drying. The compositions of the gases were checked by mass-spectrometric analysis before their application.

The particle size of the samples was less than 0.045 mm.

Results and discussion

First of all the effects of different gases on the decomposition of silver(I) oxalate will be discussed [1]. It has been established that the decomposition starts with an induction period, its length depending on the "rinsing effect" of the gas applied.
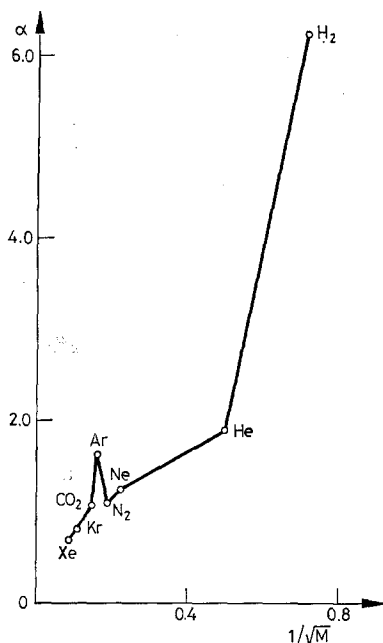
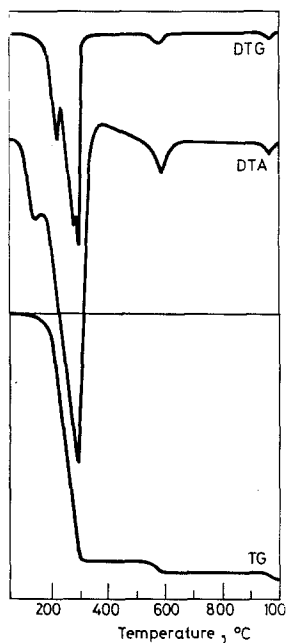Fig. 1. Rates of decomposition of silver(I) oxalate in various gases

Fig. 2. Decomposition of p.a. $Mn(NO_3)_2.xH_2O$ in a derivatograph (by K. Vargha). Sample weight: 650 mg; heating rate: 4°/min; N_2 30 1/h. Processes taking place in the steps: $Mn(NO_3)_2.xH_2O \rightarrow MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4$
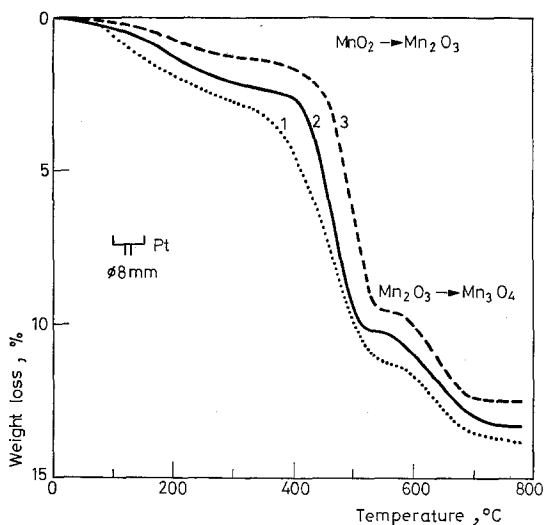

Fig. 3. TG curves of β-MnO_2 at 10^{-5} torr. Sample weight: ~20 mg; heating rate: 4°/min. β-MnO_2 samples were prepared in a derivatograph: 1. isothermal heating to 140°; 2. heated up to 330° in N_2; 3. heated up to 445° in air

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In Fig. 1 it is clearly seen that α, the rate of decomposition, is proportional to $1/\sqrt{M}$. A small deviation was found only for argon.

These investigations proved that the various inactive gases promote the escape of carbon dioxide from the solid material. Thus, the different rates of decomposition process can be explained by the rinsing effect.
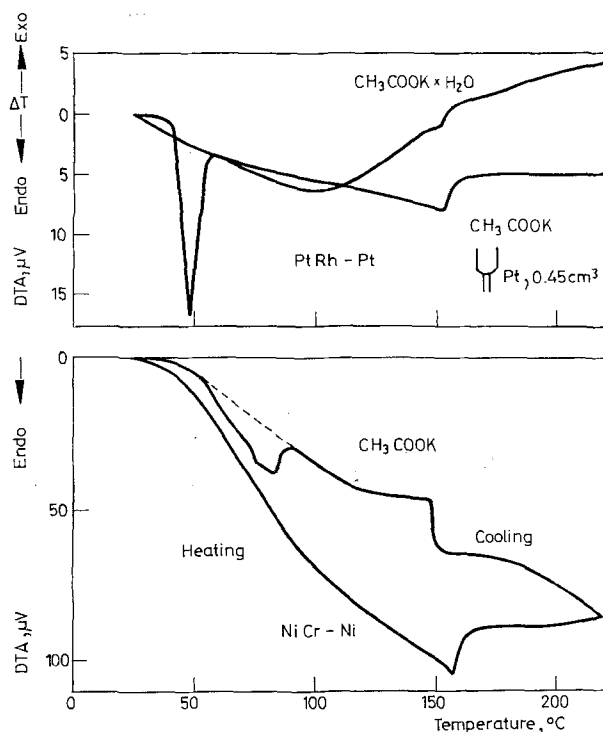

Fig. 4. DTA curves of potassium acetate samples. Sample weight: ~ 20 mg; heating rate: $4°/min$; flow-rate: 78 cm³/min

Figure 2 shows the thermal decomposition of manganese(II) nitrate. It is well known that the β-manganese(IV) oxide obtained is a very important material as a semiconductor. The trace contaminants in such material cause serious problems.

The decompositions were carried out in a derivatograph. The question was whther the samples obtained, identified by X-ray diffraction, contain trace contaminants or not.

Figure 3 shows TG curves of samples of β-manganese(IV) oxide in vacuum. The substances were prepared very carefully in a derivatograph, sample 1 by isothermal heating at 140°, sample 2 by heating in flowing nitrogen at 330°, and sample 3 in flowing air at an even higher temperature.

The X-ray diffraction patterns show the same crystal structure in the three cases. In contrast, the TG curves indicate differences between the samples, in particular the first parts of these curves proving that substances with different behaviours were obtained. We assume that this is due to the different preparative methods.

The TG measurements were supplemented with mass-spectrometric analysis. These spectra proved that all three samples still contain some nitrate contamination. TG data showed its amount to be the greatest in sample 1, about 3%. In sample 3 only traces of nitrate were found, but the mass-spectra indicated carbon dioxide evolution too. It is worth mentioning again that this sample was made in flowing air at the highest temperatures.
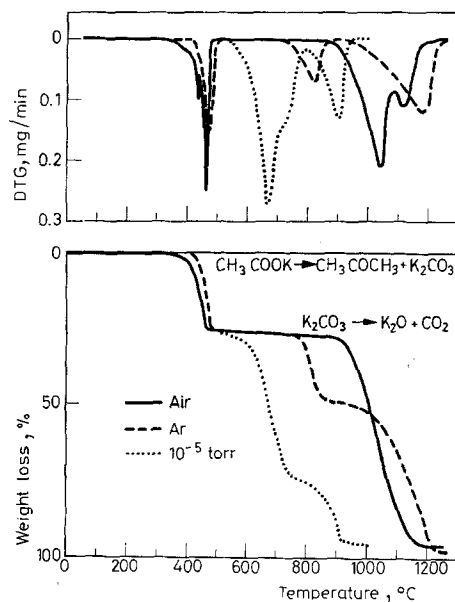

Fig. 5. Decomposition of potassium acetate in different atmospheres and at 10^{-5} torr. Sample weight: ~ 10 mg; crucible: 0.1 cm^3, Pt; heating rate: 4°/min; flow-rate: 78 cm^3/min

It can be concluded that the atmosphere has a significant effect in the preparative method.

Figure 4 shows DTA curves of potassium acetate. It is known that the "anhydrous" material still contains some water [2]. The upper part of this figure is a DTA trace of hygroscopic potassium acetate. The first endothermic peak indicates the melting of the wet material. In the second case the substance was placed in the thermobalance and subjected to 10^{-2} torr. After a rather long evacuation no weight loss was observed in the TG curve. The DTA curve has only an endothermic course and the melting process naturally did not occur.

The endothermic peak at $155-158°$ is a reversible one. It is known from literature data that at the temperature of the second peak the molar volume of potassium acetate changes. Our investigations in this field are continuing, to elucidate the reason for this endothermic change.

TG and DTG data on the decomposition of potassium acetate in various dynamic gas atmospheres and at 10^{-5} torr indicate (Fig. 5) that there are differences between the TG curves in argon and in synthetic air. The first parts of the curves relate to the decomposition of acetate, and the second parts to the carbonate which was the solid reaction product.

The investigations proved that the carbonate formed decomposes in two steps (see the TG curves) in argon and in vacuum. The DTG curve showed the same in the case of air. It may be assumed that the potassium carbonate obtained has an inhomogeneous composition. The catalytic effect of the platinum crucible may also influence some processes.

In the following we report some results on a pure natural kaolin [3]. The main structural changes of kaolinite on heating are well known:

$$Al_2O_3.2SiO_2.nH_2O \xrightarrow{\sim 500°} Al_2O_3.2SiO_2$$
kaolinite　　　　　　　metakaolinite ("defect structure")

$$2(Al_2O_3.2SiO_2) \xrightarrow{\sim 950°} 2Al_2O_3.3SiO_2 + SiO_2$$
Al$-$Si "defect spinel"

$$2Al_2O_3.3SiO_2 \xrightarrow{\sim 1100°} 2(Al_2O_3.SiO_2) + SiO_2$$
1 : 1 mullite
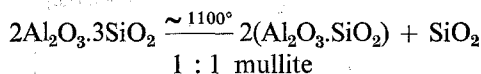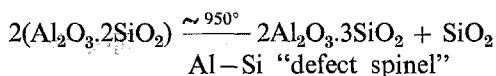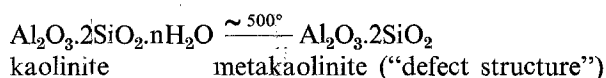
The weight losses of the kaolin samples in various atmospheres, but otherwise under the same experimental conditions are listed in Table 1. It can be seen that the greatest weight loss occurs at 10^{-5} torr, and the smallest one in carbon dioxide.

Table 1

TG data on kaolin
Sample weight: $\sim$ 25 mg $\pm$ 0.01 mg
$\sim$ 10 mg at 10^{-5} torr

Atmosphere	Heating rate °/min	Weight loss at 1200°, %
10^{-5} torr	4	15.86
N_2	4	12.11
	10	13.31
Synthetic air	10	11.23
CO_2	10	9.48

These results turned our attention to the possible interaction of carbon dioxide and kaolinite.

Kaolin is known to be a layer silicate. The specific area of this sample is about 20 m²/g. This value is not high compared to other types of layer silicates, but nevertheless adsorption processes were assumed in this case. However, the proof of this supposition needs great care in the thermoanalytical investigations, especially after beginning of heating [4].

The first aim of our research was to investigate the changes in the kaolinite structure below 400° and at 400−600° [5]. These processes were followed by parallel application of TG, IR and X-ray methods (Table 2) in order to determine the thermal changes of differently bonded and situated OH^- groups. After heat treatment the IR and X-ray spectra of samples were recorded. The weight loss up to 400° was very little in both gases, but it was greater in each case when the samples were heated in nitrogen.

Table 2

Low-temperature dehydroxylation of kaolin
Sample weight: ∼ 100 mg
Heating rate: 4°/min

Temper-ature°	Weight loss % after isothermal heating		Remarks
	N_2 ∼ 88 cm³min⁻¹	CO_2 ∼ 90 cm³min⁻¹	
250	0.68	0.57	
300	0.77	0.59	
350		1.34	IR
400	2.51	2.23	X-ray
425		4.24	IR
450	10.0	9.51	

Table 3

TG and DTA data on kaolin + NaCl reaction
Sample weight: ∼ 25 mg. Heating rate: 4°/min

Atmosphere	NaCl %	Weight loss at 1200°, %	DTA peak endo max. 800° (NaCl melting point)
10⁻⁵ torr	5	19.95	
N_2	5	15.15	—
	10	16.68	—
Synthetic air	5	13.97	—
CO_2	5	12.52	+
	10	12.84	+

Our experiments on the solid-phase reactions between kaolin and NaCl in carbon dioxide atmospheres resulted in very unexpected observations. Thermo-analytical investigations (Table 3) proved that the weight loss is the smallest in carbon dioxide gas. Furthermore, it was established by several analytical methods that a "high-temperature hydrolysis" occurs during the heating of kaolin and NaCl mixtures.

The DTA data show that carbon dioxide hinders the dehydroxylation of kaolin-ite and the subsequent hydrolysis of NaCl. The TG and DTA results after iso-thermal heating of the kaolin and NaCl mixture are rather surprising (Table 4): the weight loss in carbon dioxide was less than 3% up to $850-1050°$. The samples were cooled to room temperature and their high-temperature X-ray spectra then recorded.

Table 4

TG and DTA data on kaolin + NaCl reaction after isothermal heating

Atmosphere	Weight of sample mg	NaCl %	Highest tempera-ture°	Weight loss %	DTA peak, endo, max. 800° (NaCl melting point)	Remarks
CO_2	24.80	—	1200	9.48		Without iso-thermal heating
CO_2	10.07	—	1050	7.14		
CO_2	13.30	5	1050	2.71	+	
N_2	10.07	5	1050	10.33	—	
In Heraeus tube-furnace						
CO_2	1000	5	850	2.42		X-ray
	1000	10	850	0.90		

Table 5

High-temperature X-ray data on kaolin sample mixed with 10% NaCl and preheated in CO_2 up to 850°

Temperature °	Phases
25	kaolinite, nepheline, NaCl
530— 800	— nepheline, NaCl
800—1100	— nepheline, —
1100—1200	— nepheline, — mullite

From X-ray (Table 5), IR and DT data it is obvious that the kaolinite structure was preserved at 850° and the metakaolinite phase did not form.

It can be concluded that the effect of even a chemically "inactive" gas may be of great importance both in the study of the solid-state reactions and from a technological point of view.
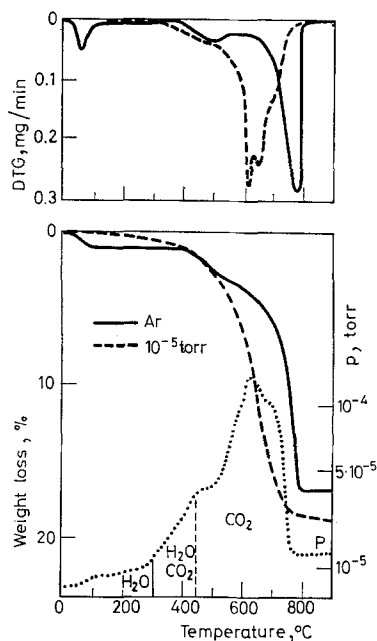

Fig. 6. Decomposition of a natural mixture of alkaline earth metal carbonates and clays. Sample weight: ~ 40 mg; crucible: 0.1 cm³, Pt; heating rate: 4°/min; flow-rate: 78 cm³/min

Figure 6 illustrates thermoanalytical investigations on a soil sample in argon and at 10^{-5} torr. The X-ray data prove that this sample contains a great amount of non-crystalline and very fine-crystalline compounds. In argon the TG and DTG curves indicate the loss of adsorbed water and the decomposition of various clays and alkaline earth metal carbonates. Under vacuum the loss of adsorbed water occurs even during the evacuation. Naturally, the substances decompose in a lower temperature range than at atmospheric pressure. Otherwise, the DTG curve also shows the two steps of decomposition of double carbonates. The reason is the higher thermal resolution at 10^{-5} torr.

The continuous weight loss of the soil sample is in agreement with the changes in the mass-spectra at the same temperature. The patterns prove carbon dioxide evolution too, its amount being the greatest within the temperature range of the decomposition of the alkaline earth metal carbonates.

Much valuable information was obtained from vacuum thermogravimetric investigations when supplemented with mass-spectra.

References

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Résumé — Les auteurs discutent l'influence de la composition de l'atmosphère (balayage de gaz inertes, gaz nobles, azote, diozyde la carbone, air synthétique ou vide de 10^{-2} et 10^{-5} torr) sur la décomposition thermique des substances inorganiques et organiques.

Plusieurs exemples montrent qu'il est nécessaire d'appliquer des atmosphères de gaz contrôlées depuis la préparation des échantillons jusqu'à l'étude du mécanisme des réactions dans l'état solide.

Les résultats de l'étude par TG—TGD—ATD—SM de la décomposition de l'oxalate d'argent(I), de l'acétate de potassium, d'un mélange natural d'argile et de carbonates alcalino-terreux, ainsi que du comportement de l'oxyde de manganèse(IV)-β et de la déshydroxylation du kaolin aux températures peu élevées, sont présentés.

Zusammenfassung — Der Einfluß von inaktiven strömenden Atmosphären (Edelgase, Stickstoff, Kohlendioxid, synth. Luft- und Vakuum (10^{-2} und 10^{-5} torr) auf die thermische Zersetzung anorganischer und organischer Substanzen wird auf Grund von Literatur- und eigennen Versuchsangaben erörtert.

Die Tatsache, daß es erforderlich ist geregelte Gasatmosphären angefangen von der Probenbereitigung bis zum Studium des Mechanismus von Festphasenreaktionen, anzuwenden, wird an Hand verschiedener Beispiele gezeigt.

Die Ergebnisse der besonders durch TG/DTG/DTA/MS-Methoden untersuchten Zersetzungen von Silber(I)-oxalat, Kaliumacetat, einem natürlichen Gemisch von Tonen und Erdalkalikarbonaten, bzw. des Verhaltens von β-Mangan(IV)-oxid und der Dehydroxylierung von Kaolin bei niedrigen Temperaturen, werden mitgeteilt.

Резюме — На основании литературных и собственных экспериментальных данных обсуждено влияние неактивной, проточной атмосферы (благородные газы, азот, двуокись углерода, искусственный воздух) и вакуума (10^{-2} и 10^{-5} торр) на термическое разложение неорганических и органических веществь. Несколькими примерами доказано, что необходимо использовать газо-контролируемую атмосферу, начиная от получения образцов до изучения механизма твердотельных реакций. Представлены результаты разложения оксалата серебра(I), ацетата калия, природной смеси минералов и карбонатов щелочно-земельных металлов, поведение β-двуокиси марганца(IV) и низко-температурное дегидроксилирование каолина, изученных главным образом методами ТГ, ДТГ, ДТА и масс-спектрометрически.