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SIMULTANEOUS THERMOGRAVIMETRY /TG/ AND MASS SPECTROMETRY /EGA/ FOR STUDIES OF PARTIAL REACTIONS OF COMPLEX PROCESSES IN SOLID - GAS SYSTEM

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ABSTRACT

Some quantitative methods of analysis of mass-spectrometry results in combination with simultaneous thermogravimetric analysis results are proposed. The studies were performed by means of Universal Mettler Thermoanalyser with a Balzers Quadrupole Mass Spectrometer for complex reactions in solid - gas system. The suggested method enabled to draw some TG curves for partial reactions of a complex process as a basis for kinetic analysis.

INTRODUCTION

Simultaneous analyses TG-EGA are of special use when two or more gases simultaneously evolve from an examined sample. It is known that quantitative analysis of mass-spectrometry results is very difficult. The combination of thermogravimetry with mass-spectrometry should enable to analyse the EGA curves quantitatively. Knowing the courses of the TG curves for one of the products of each partial reactions one can make kinetic analysis of a complex process.

The aim of our work was to propose a method of plotting quantitative curves for gas evolution in partial reactions of complex processes on the basis of simultaneous thermogravimetric and mass-spectrometric analyses.

We have been concerned with the following type of thermal decomposition reaction :

$$A_s \longrightarrow B_s + C_g \longrightarrow D_s + E_g \quad . \qquad /1/$$

MEASURING METHODS

The experiments were carried out with a Mettler Thermoanalyser TA-1 equipped with a quadrupole Balzers mass spectrometer QMG - 101. The results of thermogravimetric analysis, TG, with the temperature, T, and pressure, P_o, curves and mass-spectrometric analysis, EGA, were recorded. The measurements were taken

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within the temperature range from 298 K to 1850 K under vacuum $1{,}33.10^{-6}$ kPa at the following heating rates : 6,8,10 and 12^{o}/min. The mass spectra were registered at the analysis rate 1M/s for the mass range of 1 - 50 M/e; the ionic current was 10^{-9} A. Samples of iron /II/ carbonate monocrystal were examined.

RESULTS AND DISCUSSION

The TG - EGA curves and the P_c curve for the thermal decomposition of iron /II/ carbonate were used with the purpose of plotting curves of gaseous products evolution for the complex reaction of the type /1/. This carbonate decomposes, as our previous studies showed (1) , according to the reaction network :

$$FeCO_3 \longrightarrow FeO + CO_2 \longrightarrow Fe_3O_4 + CO \ ,$$

when is heated under vacuum.

The curves of partial pressures of CO and CO_2 gases evolved were drawn on the basis of the EGA results obtained at the heating rate 10^{o}/min. The standard value of the partial pressure was calculated using the P_c curve and the value of the ionic current. Next, the values of p_{CO}/p_{CO_2} relation for the narrow time intervals were estimated and the mass loss corresponded was read from the TG curve. The mass of the CO_2 evolved, m_{CO_2}, was computed using the following formula :

$$m_C = m\left[\left(p_E M_E / p_C M_C\right) + 1\right]^{-1} \ , \qquad /2/$$

which has been derived (1) , according to the reaction network /1/. The mass of the CO evolved, m_{CO}, for each mass spektrum was evaluated by subtracting the m_{CO_2} values from the m values. Summing up the m_{CO} and m_{CO_2} values within the whole temperature range, the quantitative curves of CO and CO_2 evolution and the kinetic curves were plotted. The initial EGA curves and the curves of gases evolution for the reaction coursing at the heating rate 10^{o}/min are presented on Fig.1. The same calculation procedure was applied successively to the heating rates 6, 8 and 12^{o}/min. It enabled to make an analysis of the kinetics of the studied process because, as shown in the paper (2) , one can use the simple and general methods of calculating of the kinetic values based on the separate thermogravimetric analysis as a result of separating of simultaneous reactions.

As a matter of fact the above method is time-consuming. Therefore we have made an attempt to elaborate a method which would make use of the same experimental results but be quick-calcula-

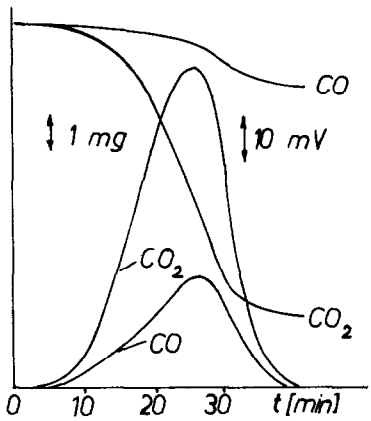

Fig. 1.
The EGA and TG curves for CO and CO_2.

ting. It is known that the mixture ratio may be determined by comparing the courses of the EGA curves and the amount of the gas is proportional to the area under the EGA curve. Thus, the integration of the EGA curves for each mixture components over the selected time intervals creates curves which, after summing up and recalculating, should give a summary curve conformed to the summary TG curve. Identity of both the summary curves within the whole temperature range is to advantage the method proposed. The integration of the EGA curves for the CO and CO_2 gases / at the heating rate 10^{o}/min / over ten-minutes intervals and plotting the dependence I=f/T/ were performed with a Hewlett - Packard computer. Taking into account the difference in the molecular masses of the gases evolved the summation of the curves obtained was curried out and the summary curve was compared with the TG curve. The quantitative curves of the CO and CO_2 gases evolved and the summary curve are compared with the TG curve at the heating rate 10^{o}/min in Fig.2. As shown the courses of the TG and summary curves are in good agreement to an accuracy of measuring error within the whole temperature range. It verifies the suggested method. The same procedure of calculation was repeated for the other analyses at the heating rates 6, 8 and 12^{o}/min and also the satisfactory agreement was obtained. In addition the above curves corresponded to the results of the method applied previously.

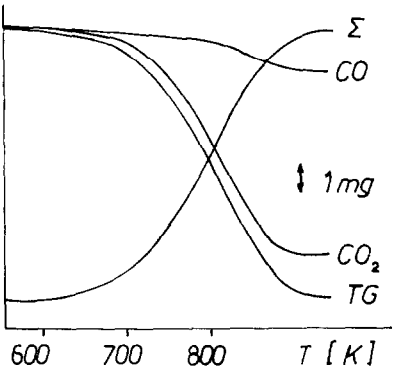

Fig. 2.
The comparison of the summary curve /Σ / with the TG curves.

CONCLUSIONS

In the case of thermal decomposition of $FeCO_3$ both the suggested methods yield good results. Besides, the method of integration of the TG curves is less time-consuming. The separation of simultaneous partial reactions of a complex process studied enables to make use of relatively simple and general methods of evaluating of kinetic quantities taking advantage of the separate TG curves. The quantitative curves obtained in our work,which corresponded to the TG curves for the partial reactions, were applied to kinetic characteristic of the studied process.

REFERENCES

1 Z.Kubas and M.Szalkowicz, Thermal Analysis,vol.2, Proceedings Third ICTA Davos /1971/ 447
2 Z.Kubas and M.Szalkowicz, ZN AGH 367, Met-Odl. z.51 /1973/ 123