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# EQUIPMENT DESIGN FOR INVESTIGATION OF SUBSTANCES DECOMPOSED UNDER THE PRESSURE OF SELF-GENERATED ATMOSPHERE BY MEANS OF THERMAL ANALYSIS

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## ABSTRACT

A thermal method to investigate decomposition reactions in a self-generated atmosphere is proposed. A sample having 3-70 mg mass was charged through a branch pipe into an ampoule which was a cylinder with 10 mm height and 0,9 ml volume. Such stainless steel ampoules could bear internal pressure up to 15 MPa. Before the experiment the ampoule branch pipe was sealed in the air or in an inert gas medium. Sizes and the design of the ampoule allowed to conduct investigations using a triple heat bridge dynamic calorimeter, designed before (ref.1). We studied a wide range of substances decomposed with the formation of gaseous products. As an example we provide brief results of investigation of ammonium carbamate and copper formate.

## INTRODUCTION

In the existing methods of thermal analysis of substances, the thermolysis of which is accompanied by gassing a sample holder is frequently open. It leads to an uncertainty when determining chemical transitions enthalpies at the expense of heat and mass exchange of the sample with the environment (ref.2). Difficulties also arise when determining the pyrolysis products composition. We used an isochoric method of investigations. It allowed to obtain reliable values of transitions enthalpies as well as to determine a reversibility degree of the studied reactions and the pyrolysis products composition by means of precooling and reheating. Besides, application of the triple heat bridge dynamic calorimeter allows not to conduct the cell calibration for quantitative evaluations.

## RESULTS AND DISCUSSION

The design of the triple heat bridge dynamic calorimeter, in which we used our sealed ampoule as a sample holder, as well the principle of its operation are described in (ref.1). A basic idea of "the heat bridge" is in the concentration of heat flux in a

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narrow section. To implement this idea three cups (a thin-walled hollow cylinder) are connected with a heater (a massive copper plate) through heat-conducting copel rods. Into one of the cups we place a sealed ampoule with a sample. The second cup containes a reference material (copper having 99,95% purity) with a well-known heat capacity temperature dependence. The third cup remains empty during the experiment. The cups, the rods and the heater form three differential thermocouples. In case of linear heating with the rate of 2 K/min these thermocouples measure temperature differences between the cups. Application of the third empty comparison cup considerably rises the measurements accuracy. The sample temperature is measured by a copper-constantan thermocouple. For any temperature heat value of the ampoule with a sample is calculated by the following equation:

$$W = \frac{\Delta T_1}{\Delta T_2} \cdot M_2 \cdot C_{p,2}$$

where $W$ is a heat value of the ampoule with a sample at $T_x$ temperature (J/K)

$\Delta T_1$ is temperature difference between a sample and the empty cup

$\Delta T_2$ is temperature difference between the reference material and the empty cup

$M_2$ is the reference material mass (mol)

$C_{p,2}$ is the reference material heat capacity at $T_x$ temperature (J/mol·K)

The substances thermolysis under self-generated atmosphere pressure was carried out in ampoules made of X18H9T-type stainless steel. The ampoule was a hollow cylinder, the walls thickness of which amounted to 0,5 mm. A cap with a branch pipe was sealed to the upper part of the cylinder and through this branch pipe the sample was placed into the ampoule. The charge density amounted to 3-75 mg/ml. Experimentally it was found out that such ampoules could bear internal pressure up to 15 MPa. In our experiments usual working pressure amounted to 4-8 MPa. If necessary, the ampoule could be filled with any gas before sealing the branch pipe. Application of closed sample holders allowed to determine some pyrolysis products by reheating the ampoule. In order to calculate chemical transitions enthalpies and the quantity of the forming products we conducted a numerical integration of the obtained

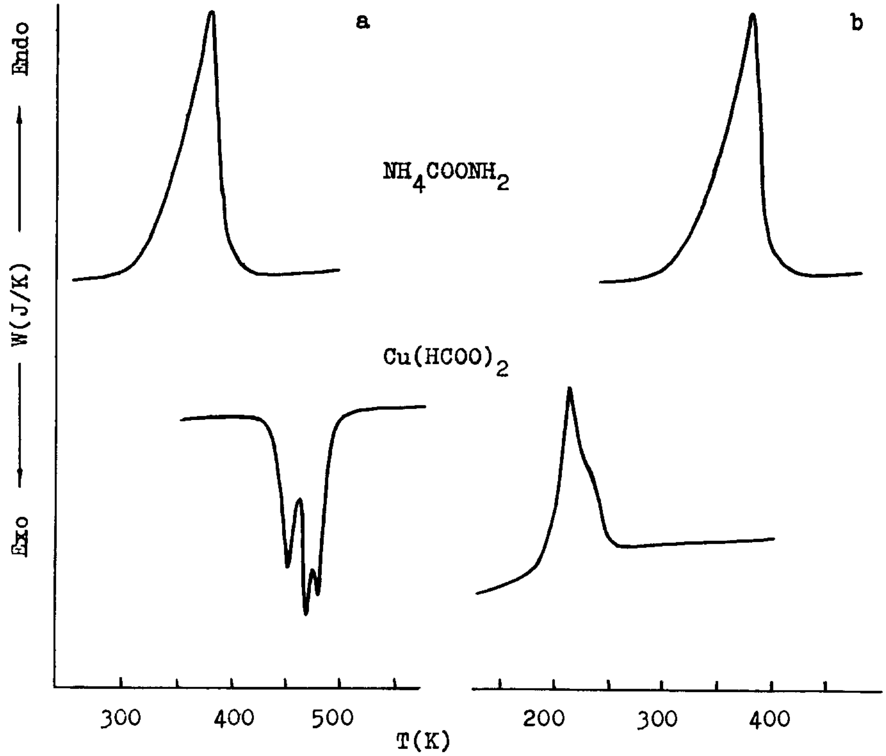

Fig.1 Thermal curves of decomposition of ammonium carbamate and copper formate in sealed ampoules.
a - initial substances, b - their decomposition products

thermal curves in coordinates W from.T.

Fig.1 shows the decomposition thermal curves in the self-generated atmosphere of initial samples (a) and their pyrolysis products (b).

Ammonium carbamate ($NH_4COONH_2$) is decomposed within 300-420 K with the peak at 400 K. At constant volume its decomposition enthalpy amounted to +145±7 kJ/mol and recalculated for constant pressure it was +155±7 kJ/mol. The obtained value well agrees with the literature data, i.e. 157,3 (ref.3) and 162,2 (ref.4). After cooling and reheating of the ampoule at the same conditions we obtained a thermal curve (b), which completely resembles the one of the initial sample. As one could expect this means that ammonium carbamate decomposition reaction is a reversible one and the decomposition products ($NH_3$ and $CO_2$) do not interact with the ampoule material at temperatures up to 700 K.

Study of copper formate thermal decomposition reactions clearly shows how thermal analysis under the self-generated atmosphere pressure allows to determine and quantitatively define some gaseous products. In this case it concerns $CO_2$ content. Copper formate decomposes within 430-500 K with heat liberation. Decomposition enthalpy recalculated for constant pressure (after gaseous products composition had been determined) amounted to -15±2 kJ/mol. On the thermal curve of reheating (Fig.1 curve "b") there is only one peak within 170-250 K, which is due to $CO_2$ sublimation. The content of the latter found on the peak area corresponded to the following reaction of copper formate decomposition

$$Cu(HCOO)_2 = Cu + H_2 + 2CO_2$$

After the experiments the ampoule was opened in a special device and the gaseous products were analyzed on a mass-spectrometer and a chromatograph. The results of these analyses confirmed that copper formate decomposed according to the above equation.

## REFERENCES

1 A.A.Vecher, A.G.Gusakov, A.A.Kozyro, Russ. J. Phys. Chem. 53 (1979) 783
2 W.W.Wendlandt, Therm. Acta 9 (1974) 101
3 R.N.Bennet, P.D.Ritchie, D.Roxburg, J.Tomson, Trans. Farad. Soc. 49 (1953) 925
4 D.Janjic, Helv. Chem. acta 47 (1964) 1879