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## Reaction-gas chromatography for physico-chemical investigations on aggressive gases

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### ABSTRACT

Reaction-gas chromatographic methods for determining aggressive gases such as  $\text{HClO}_4$ , HF and  $\text{NH}_3$  were developed. The methods were used for examining thermal decomposition processes of  $\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ . The additional requirements arising when using reaction conversions in physico-chemical investigations were examined.

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### INTRODUCTION

Chromatography is widely used for physico-chemical investigations [1,2]. In previous papers [3–5] we have proposed a number chromatographic methods for studying the kinetics and equilibrium of heterogeneous chemical processes that proceed with gaseous components present. The methods are based on direct insertion of a chemical reactor into the gas line of a chromatograph. The conditions of the application of gas chromatography to studies of the kinetics and equilibria of heterogeneous reactions in gas-condensed phase systems have been substantiated. It was shown [3] that with thermal conductivity detection (TCD) the signal height is directly proportional to the rate of gas evolution in the process being studied. By increasing the amount of condensed phase in the reactor, a maximum constant concentration, *viz.*, partial equilibrium pressure, of volatile product in the carrier gas was attained [4].

With a multi-component composition of gaseous products, it is proposed to use schemes with the flow being split after the reactor and two detectors, and to use selective absorption (removal) of some components from the gas stream.

In the chromatographic analysis of gases, the determination of aggressive and hardly detectable species is a real and often difficult problem. In the chromatographic methods described above, it is proposed to use reaction conversion of such gases into other gases that easily detected by TCD. For this purpose, into the gas line of the chromatograph after the main reactor where the process being studied takes place is introduced an additional reactor for reaction conversion of aggressive component.

In order to apply reaction-gas chromatography to kinetic studies, it is necessary

to establish the following specific conditions. In kinetic experiments, conversion of a reaction component should proceed faster than its rate of formation in the process being studied. Quantitative conversion of a component should be provided over a wide range of concentrations in accordance with minimum and maximum rates of its formation in the main process. The reactor volume for analytical conversion (and amounts of chemical reagents) should be sufficiently small that the broadening in the additional volume does not distort the shape of the evolving product zone. The volume of the reactor is selected in preliminary tests.

In this paper, reaction-gas chromatographic methods for determining the aggressive gaseous compounds  $\text{HClO}_4$ ,  $\text{HF}$  and  $\text{NH}_3$  are described. The peculiarities of the application of the methods to physico-chemical investigations are considered using the following examples: (i) thermal decomposition of  $\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ; (ii) kinetics and equilibrium of the  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$  dehydration process; and (iii) equilibrium of ammonium phosphate decomposition.

## EXPERIMENTAL

The thermal decomposition of  $\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  proceeds with the evolution of water and highly aggressive, thermally labile  $\text{HClO}_4$ . Thermolysis of this salt was studied at 130–350°C in a carrier gas (helium) flow. For the detection of  $\text{HClO}_4$  evolved during thermolysis of the perchlorate, an exchange reaction method (eqn. 1) involving the formation and subsequent detection of  $\text{CO}_2$  was employed:



A schematic diagram of the apparatus used for this purpose is presented in Fig. 1. A mixture of anhydrous potassium carbonate (granular) and quartz particles (diameter between 0.25 and 0.5 mm) was placed on a glass porous partition (Schott No. 1 standard filter) in the hot zone of reactor 1 above the weighed perchlorate sample 9. The reactor was placed in a preliminary heated (to a given temperature) oil-bath.

To establish the accuracy and precision of the procedure, the following aspects were established.

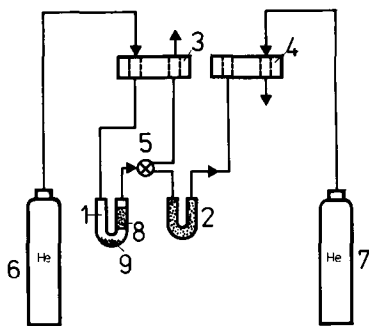


Fig. 1. Schematic diagram of apparatus for reaction exchange and detection of  $\text{HClO}_4$ : 1 = reactor; 2 = absorber for water; 3,4 = katharometers; 5 = flow-dividing valve; 6,7 = carrier gas tanks; 8 = potassium carbonate; 9 = perchlorate sample.

(1) The perchloric acid evolved does not decompose until it comes into contact with the potassium carbonate. No acid decomposition products (oxygen, chlorine or chlorine oxides) were apparently formed. This conclusion was made based on the following special experiments. After the reactor for  $K_2CO_3$ ,  $H_2O$  and  $CO_2$  from the gaseous phase were absorbed (in the cartridge containing granular KOH); with TCD recording no gas evolution at all was observed. Moreover, the absence of chlorine and chlorine oxides in the off-gases was confirmed by a chemical iodimetric method.

(2) The primary potassium carbonate and potassium perchlorate formed are thermally resistant under the test conditions. This was confirmed by the absence of gas evolution in the primary potassium carbonate and perchlorate formed (in the absence of an exchange reaction) at  $350^\circ C$ .

(3) The quantitative aspects of the exchange reaction in eqn. 1 were controlled on the basis of the stoichiometry, proceeding from the known  $ClO_4^-$  ion content in the perchlorate sample of known weight. The exchange reaction proceeds quantitatively over the entire range of concentrations corresponding to the initial perchlorate decomposition rate of  $0.05\%/min$  and a maximum rate of  $8\%/min$ .

(4) The exchange reaction is not rate limiting, and the determination of carbon dioxide evolution rate reflects the perchlorate decomposition kinetics. To establish this, tests were conducted in a special reactor, in which in the process of perchlorate decomposition a carrier gas flow was fed below the net partition by switching a valve; delivery of  $HClO_4$  to carbonate was stopped and no  $CO_2$  was registered by the detector. Therefore, perchloric acid in the potassium carbonate layer is not accumulated, *i.e.*, the exchange reaction proceeds faster than the decomposition being studied.

In the process of  $Be(ClO_4)_2 \cdot 4H_2O$  decomposition, water is evolved together with perchloric acid; moreover, 1 mol of water per mole of compound is evolved as a result of the exchange reaction.

To record the kinetics of  $CO_2$  and  $H_2O$  evolution simultaneously, an installation (Fig. 1) with two thermal conductivity detectors was used, the flow after the reactor being split into two streams. In one stream, water vapour was absorbed in the cartridge containing anhydrous magnesium perchlorate (2), and detector 4 recorded the concentration of  $CO_2$  formed in the exchange reaction (see Fig. 3, curve a); in the other stream, detector 3 measured combined  $H_2O$  and  $CO_2$  evolution. The rate and amount of water evolved were determined by the differences in heights and areas on the basis of  $H_2O$  and  $CO_2$  detector calibrations, each made separately (differences with stoichiometric quantities for  $CO_2$  and  $H_2O$  did not exceed 3 and 4%, respectively).

To detect HF evolved from the thermolysis of  $AlF_3 \cdot 3H_2O$ , reaction of the former with  $CaCO_3$ , leading to the formation of  $CO_2$ , was used.

Analytical validation of the above procedure was accomplished in the following way: HF equilibrium partial pressures above hydrofluoric acid solutions of known concentration were measured and the values obtained were compared with literature data [6]. Details of the procedure are as follows: The hydrofluoric acid solution was coated on to the quartz layer in the reactor and a carrier gas (helium) flow, saturated with water vapours and HF, was passed through the  $CaCO_3$  layer. Water vapour was absorbed in the cartridge containing anhydrous magnesium perchlorate and the  $CO_2$  concentration in this flow was detected. In Fig. 2 the data obtained are presented in

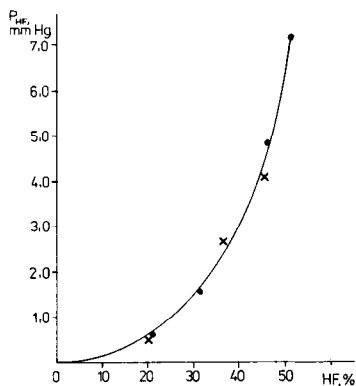


Fig. 2. Partial pressure of HF vapour ( $P_{HF}$ ) versus HF concentration in solution at 25°C. ●, Literature data; ×, experimental data.

comparison with the literature data. The maximum deviation does not exceed 10% relative.

To control ammonia and water evolution in the initial stages of ammonium dihydrogenphosphate decomposition, the data on which are contradictory, a method was used based on ammonia oxidation with potassium hyperbromite solution in accordance with the reaction



The characteristics of the method have been presented previously [7].

It was shown, however, that the reaction conversion proceeds slowly owing to diffusive retardation in the solution, and is rate-limiting with regard to the kinetics of ammonium dihydrogenphosphate decomposition. Consequently, the dynamic (flow) modification of the method described was used only to study equilibrium of ammonium dihydrogenphosphate decomposition at low temperature.

## RESULTS AND DISCUSSION

In Fig. 3, kinetic curves for gaseous product evolution under conditions of heating at a constant rate of  $\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  are presented as examples. The de-

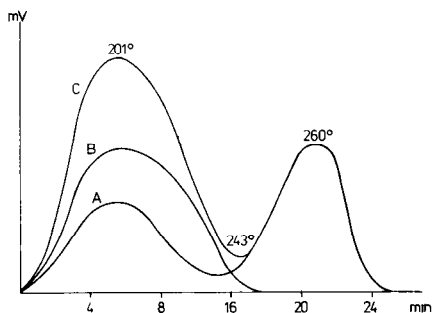
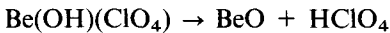
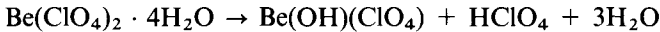


Fig. 3. Kinetic curves of  $\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  decomposition: (a)  $\text{HClO}_4(\text{CO}_2)$  evolution; (b)  $\text{H}_2\text{O}$  evolution; (c)  $\text{HClO}_4(\text{CO}_2) + \text{H}_2\text{O}$  evolution.

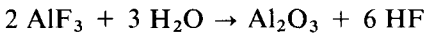
composition starts at 140°C and proceeds with splitting of the process into two macrostages. Perchloric acid (as CO<sub>2</sub>) and water appear in the gaseous phase simultaneously, *i.e.*, evolution of the water of hydration does not occur as a preliminary process. In the first stage 3 mol of water are removed, 1 mol of which takes part in the pyrohydrolysis with the formation of HClO<sub>4</sub>. The perchloric acid (CO<sub>2</sub>) is evolved in two stages; the degree of decomposition in the minimum of the kinetic curve a in Fig. 3 is 50%.

On the basis of kinetic data for the reaction mixture formed in the minimum of the kinetic curve, the decomposition scheme of perchlorate is considered to be



The formation of the intermediate product was ascertained by NMR and X-ray diffraction analysis.

It was found that the dehydration of AlF<sub>3</sub> · 3H<sub>2</sub>O occurs in one macrostage, the main amount of water being evolved at 100–160°C; however, 0.2–0.25 mol of water per mole of salt is held in the aluminium fluoride lattice; the removal of residual water occurs on further heating to 400–450°C and is accompanied by a pyrohydrolysis process:



The respective kinetic curves are presented in Fig. 4.

The carrier gas flow was saturated with water when passing through the AlF<sub>3</sub> · 3H<sub>2</sub>O layer and equilibrium water vapour pressures were determined (1.7, 4.3, 12.1, 57.1, 160.7 and 598.8 mmHg at 89.6, 100.4, 113.8, 127.5, 134.5 and 150.7°C, respectively).

Fig. 5 represents the dependence of  $P_{\text{NH}_3}$  on the temperature of the ammonium

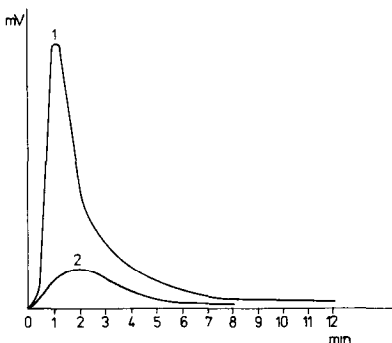


Fig. 4. Evolution kinetic curves: HF: curve 1,  $n = 1$ , maximum detection for sensitivity. H<sub>2</sub>O: curve 2,  $n = 10$ , detector response attenuated by a factor of 10.

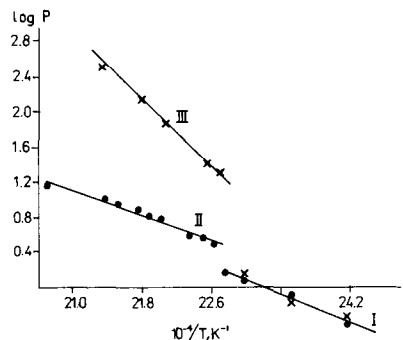


Fig. 5. Vapour pressure ( $P$ ) of (●) NH<sub>3</sub> and (×) H<sub>2</sub>O versus temperature ( $T$ ) in the thermal decomposition of ammonium dihydrogenphosphate. I, solid phase decomposition; II and III decomposition in the melt.

dihydrogenphosphate thermal decomposition process obtained by the above-mentioned procedure involving ammonia oxidation to elemental nitrogen.

In conclusion, the examples presented demonstrate the use of reaction gas chromatographic methods for detecting the reactive gases  $\text{HClO}_4$ ,  $\text{HF}$  and  $\text{NH}_3$  in physico-chemical investigations. Similar methods may be suitable for other reactive gases.

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