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## NOVEL CHROMATOGRAPHIC METHOD FOR THE EQUILIBRIUM STUDY OF HETEROGENEOUS REACTIONS IN GAS-CONDENSED PHASE SYSTEMS

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### SUMMARY

Dynamic and impulse chromatographic methods were developed for the equilibrium study of heterogeneous chemical reactions for gas-condensed phase systems. The special features and advantages of these methods for studying chromium sulphate and ammonium phosphate thermal dissociation reactions and zinc oxide recovery by carbon monoxide are discussed.

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### INTRODUCTION

Gas chromatography has been widely applied in physico-chemical investigations. The application of gas chromatographic methods, based on a reactor in direct combination with the chromatograph, to the study of heterogeneous reaction kinetics has been described<sup>1-3</sup>. Other studies<sup>4-6</sup> were concerned with the application of gas chromatography in the study of the kinetics of processes of the type



where C is a condensed (solid or liquid) phase and G a gaseous phase. Gas chromatography has usually been applied in thermodynamic studies to investigate processes in the absence of chemical reactions<sup>7</sup>.

The scope of the gas chromatographic applications in physico-chemical investigations may be extended, provided it is used for the equilibrium study of complex chemical reactions, carried out in the condensed and gaseous phases of types 1 and 2.



The method has been used to explore the equilibrium of non-organic reactions with the formation of condensed and gaseous phases of alternating composition.

## EXPERIMENTAL

The method proposed here includes a U-shaped reactor, samples being inserted into the gas chromatograph before the measuring cell of the differential detector.

For reactions of type 1 (chromium sulphate and ammonium phosphate decomposition), saturation of the carrier gas (helium) flow with evolving volatile components was applied until equilibrium was attained. A constant height of the detector step signal and its independence on the contact conditions of the carrier gas and the condensed phase was the criterion for equilibrium being attained.

To determine equilibrium of type 2 (zinc oxide recovery) a gaseous component (carbon monoxide) was introduced into the reactor in the form of an impulse of rectangular shape, and the amount of the gaseous product (carbon dioxide) formed was measured. It was found that when  $\geq 10$  ml of carbon monoxide are injected, the degree of conversion does not depend on the contact conditions of the impulse and the solid phase.

To confirm that equilibrium had been attained, the sample weight, sample dispersity and gas carrier velocity were varied over wide ranges in preliminary experiments.

When working with phosphate melts in order to increase and stabilize the contact surface, we placed a coating of phosphate on an inert support and the thickness of the melt layer was varied.

The combination of the reactor, the chromatograph thermal conductivity measurements of the concentration of volatile components in the flow in the form of a stepped chromatogram provides a significant increase in detection sensitivity compared with conventional chromatographic analysis; for instance, the limit of determination of oxygen is  $1 \cdot 10^{-3}\%$ , the relative standard deviation for the ranges  $10^{-3}$ – $10^{-1}\%$  and  $10^{-1}$ – $5\%$  being 7 and 3% (relative), respectively.

## RESULTS AND DISCUSSION

In the temperature range 763–933 K the decomposition of chromium sulphate may be described as follows:



$$K_1 = P_{\text{SO}_3}^3$$



$$K_2 = \frac{P_{\text{SO}_2} \cdot P_{\text{O}_2}^{0.5}}{P_{\text{SO}_3}}$$

Data on the temperature dependence of  $K_{\text{equil}}$  of the sulphur dioxide oxidation reaction have been published<sup>8</sup>, but literature data on the dissociation of chromium sulphate are absent.

Fig. 1 shows the step chromatogram that describes the change in oxygen concentration with a stepwise increase in temperature. From the experimental data we

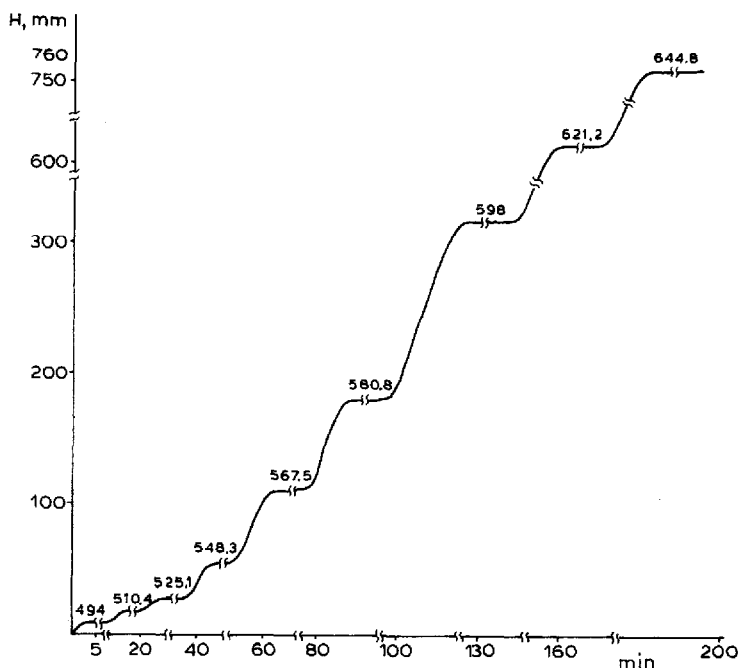


Fig. 1. Step output oxygen curve (sample weight, 3 g; helium velocity, 27 ml/min).  $H$  = value of the detector signal.

we calculated the oxygen partial pressure, taking into account the changes in the concentration as a result of sulphur tri- and dioxide removal from the carrier gas flow. The equilibrium constant of the dissociation of chromium sulphate was defined by the equation

$$K = P_{\text{SO}_3}^3 = \left( \frac{2P_{\text{O}_2}^{1.5}}{K_2} \right)^3 \quad (5)$$

where  $K$  is the equilibrium constant for the system  $\text{Cr}_2(\text{SO}_4)_3\text{-Cr}_2\text{O}_3\text{-SO}_3\text{-SO}_2\text{-O}_2$ ,  $P_{\text{SO}_3}$  is the sulphur trioxide partial pressure and  $P_{\text{O}_2}$  is the oxygen partial pressure.

The experimental data thus obtained were approximated by linear equation

$$\ln K = 54.38917 - \frac{0.4893275 \cdot 10^5}{T} \quad (6)$$

( $K$  in kPa). The residue dispersion is  $0.5655238 \cdot 10^{-11}$ , the Fischer criterion is 2.16 and the root-mean-square variation is  $2.378 \cdot 10^{-5}$ .

Fig. 2 presents a typical gas evolution curve for the decomposition of diammonium phosphate under equilibrium conditions. In the first stage ammonia alone is evolved (AB region). In the region BC equilibrium saturation of the carrier gas with ammonia is not achieved, as a result of nearly complete dissociation of  $(\text{NH}_4)_2\text{HPO}_4$  with the formation of  $\text{NH}_4\text{H}_2\text{PO}_4$ ; in the region CD the equilibrium

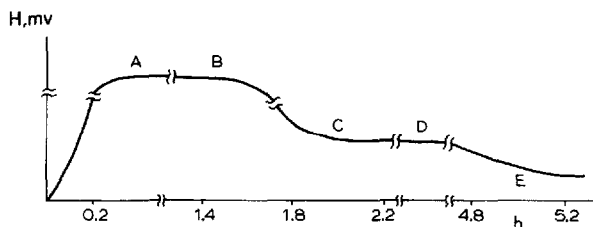


Fig. 2. Gas evolution curve for diammonium phosphate decomposition under equilibrium conditions at 442 K.  $H$  = value of the detector signal.

vapour pressure is registered above the ammonium phosphate formed and decomposition of the latter occurs with evolution of ammonia and water. The dependence of the vapour pressure of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  on temperature is complex. In the range 418–438 K the decomposition of solid  $\text{NH}_4\text{H}_2\text{PO}_4$  takes place; the ratio of the volumes of ammonia and water evolved in close to unity. In view of the low process velocities, the change in the composition of the solid phase is insignificant, and the pressure of the gaseous products is nearly constant. Fig. 3 (curve I) shows the temperature dependence of the equilibrium data of the solid-phase decomposition of monoammonium phosphate. An increase in the decomposition temperature is accompanied by melting of the reaction mixture. Under these conditions a decrease in the concentration of the components in the flow of carrier gas with time was observed (Fig. 2, region DE), which reflects the phosphate polycondensation process, *i.e.*, the vapour pressure above the liquid phase of alternating composition is registered. The amount of gaseous components evolved is determined by integrating the equilibrium output curve, thus permitting data on the composition of the gaseous phase to be related to the condensed phase composition and to avoid labour-consuming chemical analysis. The temperature dependence of the ammonia and water vapour pressures in the decomposition of monoammonium phosphate in the melt is also shown in Fig. 3 (curves II and III). The enthalpy values for the first stage of the process, calculated

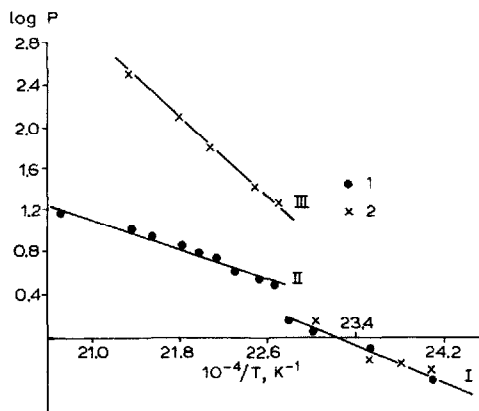


Fig. 3. Vapour pressure ( $P$ ) of (1)  $\text{NH}_3$  and (2)  $\text{H}_2\text{O}$  versus temperature ( $T$ ) in the thermal dissociation of monoammonium phosphate. I, Solid-phase decomposition; II and III, decomposition in the melt.

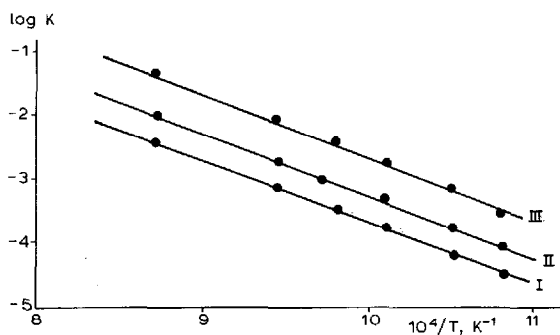


Fig. 4. Dependence of equilibrium constant ( $K$ ) on temperature ( $T$ ) in the zinc recovery reaction by carbon monoxide: I and III, literature data; II, this work.

from the experimental data, agree satisfactorily with the literature data<sup>9</sup>; there are no literature data for the other stages.

Fig. 4 shows the dependence of the equilibrium constant on the temperature for the reaction



As can be seen, the values of  $K$  calculated from the data obtained by the impulse method are within the range of the data obtained by the conventional methods<sup>10</sup>.

The above examples show that the use of these dynamic and impulse chromatographic methods for the study of the equilibrium state affords in a single apparatus a scheme for thorough investigations of the equilibrium state of complex multi-stage processes to be carried out over a wide range of temperatures within a reasonable experiment time on a single sample and for demonstrating a number of advantages of the application of gas chromatography in investigations of the equilibrium state of non-organic chemical reactions.

To prove that equilibrium is attained, temperature programming, including heating, cooling and isothermal conditions, is used in the same experiment. A combination of saturation of the carrier gas flow with volatile components and its impulse introduction into the reaction zone is also useful.

The absence of a temperature gradient between the reaction zone and the concentration measuring zone removes the limitations of the flow method related to the distortion of the data owing to thermal diffusion. Methods such as stream splitting after the reactor, a combination of detectors, reaction conversion and selective subtraction of some components give a significant increase in the accuracy of the experimental data.

The conditions for the impulse micromethod are much more favourable for the attainment of equilibrium; as a relatively small impulse passes through a significant layer of the condensed phase, prolonged stabilization of temperature is not required. The change in the reaction zone temperature due to thermal effects is negligibly small. The high sensitivity of the chromatographic measurements enables reactions to be studied with conversion to only an insignificant extent, thus removing

some kinetic complications, which hamper the attainment of equilibrium (for instance, slowing of the reaction by the solid product layer).

The above-mentioned data shows the advantages of the application of gas chromatography in the study of the equilibrium of heterogeneous reactions in gas-condensed phase systems.

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