

THERMOANALYTICAL STUDIES OF SUBSTANCES LIBERATING AGGRESSIVE GASES*

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A modification to the derivatograph has been designed that allows thermoanalytical investigations of chemical compounds, including sulphides and acids, that evolve aggressive gases such as CO, SO₂, S, etc. during warming. Application of this modification is exemplified by studies on the thermal dehydrogenation of titanium hydride (TiH_{1.85}) and on the interaction of rhenium disulphide (ReS₂) with concentrated sulphuric acid.

Thermoanalytical investigations of samples which are sensitive to air or generate aggressive gases need special apparatus precautions to protect the sample and/or the weighing mechanism. This paper deals with a sample holder and equipment adapted to the derivatograph to allow for reactions in a self-generated atmosphere, and the removal and analysis of the evolved gases, without disturbance of the weighing system.

Experimental

A detailed description of the changes to the conventional derivatograph and the technique of investigation has been given previously [1]. The most important features are (Fig. 1): The sample holder is a cylindrical crucible of optical silica glass with a cavity in its bottom. The crucible is covered by a tightly fitting ground-glass stopper through which the gas outlet tube is led. This container is placed as usual on the measuring thermocouple on the movable arm of the balance. The gas outlet tube ends without mechanical touching in the axis of a nozzle. By means of this movable seal, a vapour outlet is provided, a rigid fixture is excluded, and movability of the balance beam is preserved.

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Prior to heating, the container was evacuated by a water-jet pump with controllable speed. Argon was then pumped into the furnace volume. The vapour pressure in the container, generated by the heating of the dissociating substances, produces a directed gas stream because of the differences in pressure between the container and the channel. The flow of a neutral gas, argon, fed into the inner space

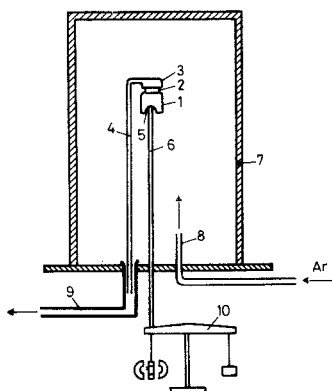


Fig. 1 Outline of the device for derivatographic analysis: 1. cylinder, 2. polished section, 3. ground-glass stopper, 4. gas-deflecting channel, 5. hole in bottom of cylinder, 6. thermocouple, 7. furnaces, 8. nozzle for argon introduction, 9. outlet nozzle, 10. balance

of the furnace, carries away vapour going from the outlet tube into the nozzle. Thus, the penetration of aggressive gases into the furnace and onto the thermocouple and balance, and also the thermodiffusion of vapour into the reaction zone, are avoided. The ejecting force of the gas flow on the sample and on the movable arm of balance is small (less than 0.2% at 360° [2]).

To check the apparatus and the technique, we studied the dissociation of compounds with known thermoanalytical properties: calcium oxalate, evolving CO and CO₂ and pyrite, evolving S. The results were well reproducible and agreed with literature data [3]. In order to characterize the chemical nature of the processes, the composition of the evolved gases was investigated concurrently by IR spectroscopy with the use of a separate attachment to the UR-20 instrument.

Results and discussion

The above-described attachment to the derivatograph was used for thermoanalytical studies of certain substances, chemical reactions, and condensed phases existing only in neutral atmosphere. Thermogravimetric data were handled

according to the equations of non-isothermal kinetics [4]. As an example, we shall consider the experimental data on the thermal dehydrogenation of titanium hydride, and on the interaction of rhenium disulphide with concentrated sulphuric acid.

1) Thermal decomposition of titanium hydride

The thermal dehydrogenation of titanium hydride is known to be highly sensible to "traces" of oxygen. Therefore, it must be studied in vacuum or in neutral atmosphere [5]. In this case, under the conditions of an autogenerated atmosphere without air access, the compound with composition $\text{TiH}_{1.85}$ dissociated in two stages, indicated by two sharp endothermic effects with peaks at 530° and 650° (Fig. 2). During the first stage up to 30% H is removed, and 68% H is lost during the second stage; the dehydrogenation degree attained in vacuum is 98% [6]. The apparent activation energies for stages I and II are 115 and 27 kJ/mol, respectively, and are close to the formation heats of the hydrides with the corresponding compositions [6]. The latter is convincing evidence that the suggested technique may be utilized for investigations of the thermal dissociations of such compounds.

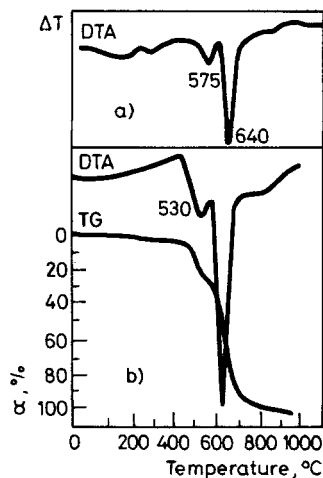


Fig. 2 Thermoanalytical curves of titanium hydride decomposition a) TiH_2 [7], b) $\text{TiH}_{1.85}$

2) Study of rhenium disulphide (ReS_2) oxidation

The oxidation of rhenium disulphide was studied both at high oxidant pressure (H_2SO_4) and upon heating in air.

It is known that, when heated to the roasting temperature of 500° in neutral

atmosphere or in vacuum, rhenium disulphide does not exhibit structural or chemical changes. In an oxidizing atmosphere at 200–500°, the oxidation of rhenium disulphide is thermodynamically possible, with the formation mostly of Re_2O_7 [8]. However, the possibility of the formation of certain other oxides, e.g. ReO_2 and ReO_3 , is not excluded, depending on conditions such as the oxygen partial pressure, the overall pressure of vapour components, and the temperature.

In the temperature range 200–500° and at oxygen pressures not less than 10^{-5} atm, mainly Re_2O_7 exists in the vapour [8]. During heating in the absence of oxygen, Re_2O_7 is reduced to ReO_2 , ReO_3 , etc., as confirmed by the values of the Gibbs energy of formation of oxides with different compositions: -374 kJ/mol for ReO_2 , -443 kJ/mol for ReO_3 , and -995 kJ/mol for Re_2O_7 [9].

The oxidation of ReS_2 in air begins at 300°, with the concurrent evaporation of the Re_2O_7 formed (Fig. 3a); the reaction proceeds in 2 stages. The mass loss at 500° comprises ≈ 20 mass%. The apparent activation energies for the weight loss are 38.5 kJ/mol and 87 kJ/mol, respectively.

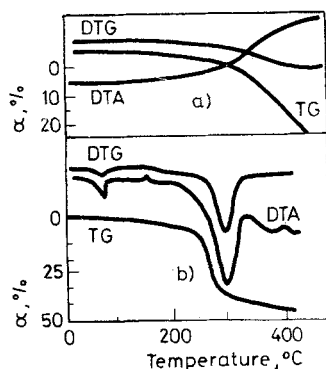
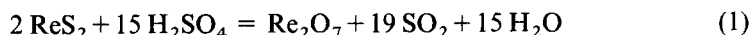


Fig. 3 Thermoanalytical characteristics of ReS_2 oxidation (a) in air and (b) in presence of acid

The reaction



is thermodynamically possible only at elevated temperature. It was found from the calculations that the Gibbs free energy has a positive value at room temperature, but above 100° it assumes negative values: $G_{473\text{K}} = -543.0$; $G_{673\text{K}} = -1698$ kJ/mol.

When ReS_2 is heated with H_2SO_4 , a reaction proceeds with evolution of gaseous SO_2 , H_2O and Re_2O_7 , accompanied by a strong endothermic effect with peak at 295° in the DTA curve and by a rapid mass loss due to the melting and evaporation of Re_2O_7 , respectively (Fig. 3b). This coincides with the thermodynamic data for

Re_2O_7 [8] and also with the thermoanalytical properties of evaporation of the rhenium oxides ReO_2 , ReO_3 and Re_2O_7 under the same experimental conditions.

Additional evidence of the completeness of the reaction is the absence of endothermic effects typical of the dissociative evaporation of HReO_4 (with maximum at 130°) and of sulphuric acid (with maximum at 380°) in the DTA curves

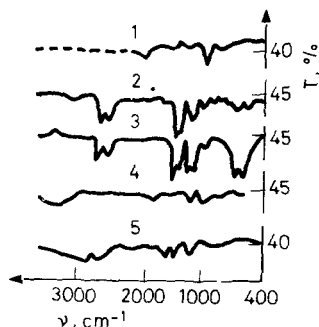


Fig. 4 IR spectra of (1) Re_2O_7 vapour, (2, 3) SO_2 and Re_2O_7 at 200 and 300°C , (4) HReO_4 and (5) H_2SO_4

of mixtures of ReS_2 and H_2SO_4 . It follows from the results that the oxygen partial pressure is sufficient for the formation of Re_2O_7 . In the presence of sulphuric acid, the greatest vapour extraction is reached at low temperatures. The apparent activation energy values are conditionally attributed to the overall processes: for the two stages they are 53.7 and 120 kJ/mol, respectively.

To confirm the chemical nature of the oxidation products of rhenium disulphide by sulphuric acid, the composition of the gas phase was studied by IR spectroscopy [10]. During the reaction, spectra of the gaseous products of oxidation were recorded (Fig. 4). Spectra of concentrated sulphuric acid vapour, condensed rhenic acid and rhenium oxide (Re_2O_7) vapour were taken for comparison.

The reaction products formulated in (1), viz. SO_2 , Re_2O_7 and H_2O , were identified by IR spectroscopy. Their band intensities in the spectra vary with their concentrations, which are dependent on the temperature.

Conclusions

The proposed device and the technique are demonstrated to extend the possibilities of application of the derivatograph for thermoanalytical studies of compounds evolving aggressive chemical compounds, such as acids and sulphides.

The directed outlet of gases from the reaction zone allows combination of the derivatograph with EGA techniques for the study of gas phase compositions.

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Zusammenfassung — Es wird über die Modifizierung eines Derivatografen berichtet, die die Thermoanalyse von Stoffen ermöglicht, die wie z. B. Sulfide oder Säuren beim Erhitzen aggressive Gase wie z. B. CO, SO₂, S usw. freisetzen. Als Beispiel für die Anwendung dieser Modifizierung dienten Untersuchungen der thermischen Dehydrogenierung von Titanhydrid (TiH_{1,85}) und des Einwirkens von konzentrierter Schwefelsäure auf Rheniumsulfid (ReS₂).

Резюме — Сконструировано устройство к дериватографу, позволяющее проводить термоаналитические исследования более широкого класса химических соединений, в том числе сульфидов, кислот, выделяющих при нагревании агрессивные газы CO, SO₂, S и т. д. Использование разработанного устройства продемонстрировано на 2-х примерах, исследованиях термического дегидрирования гидрида титана (TiH_{1,85}) и реакции взаимодействия дисульфида рения (ReS₂) с концентрированной серной кислотой (H₂SO₄).