

Determination of equilibrium quantities of the systems formed by thermal decomposition according to the reaction



I. Experimental equipment

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Dedicated to Corresponding Member M. Zikmund, in honour of his 65th birthday

Construction and function of the apparatus for measurement of the equilibrium values of temperature and pressure in heterogeneous systems containing gaseous phase including water vapour by a static method are described. The main parts of the equipment are the furnace with adjustable temperature gradient and adjustable pressure of the gaseous phase and the set of closable carriers of samples. The apparatus allows to measure the equilibrium temperatures in the range from 25 °C to 500 °C with the error of 2 °C. When the gaseous phase consists of water vapour the error in the determination of its equilibrium pressure changes from 0.02 kPa at the pressure of 1.7 kPa to 0.7 kPa at the pressure of 90 kPa.

Описаны конструкция и функционирование прибора для измерения равновесных величин температуры и давления в гетерогенных системах, содержащих газовую фазу, включающую пары воды, посредством статического метода. Главными частями прибора являются капельная печь с регулируемым градиентом температуры и регулируемым давлением газовой фазы, а также набор закрывающихся носителей для образцов. Прибор позволяет измерять равновесную температуру в промежутке от 25 °C до 500 °C с возможной ошибкой 2 °C. Если газовая фаза состоит из водного пара, ошибка в определении ее равновесного давления возрастает с 0,02 кПа при давлении 1,7 кПа до 0,7 кПа при давлении 90 кПа.

The equilibrium quantities are sometimes measured by dynamic methods which determine the beginning of the investigated process corresponding to the equilibrium state of the system in conditions when the values of quantities characterizing the equilibrium state, *e.g.* temperature [1], are changing. This approach is connected with a number of unaccuracies following from principle of the dynamic methods. Satisfactory results can be achieved only when the

investigated process is reversible and when it is studied in both directions. The static methods are more advantageous. In these methods the samples are kept for a long time (from several hours to several days) at given constant conditions and we investigate the changes in their composition. In this way, using 1/2—8 h isothermal heating at constant water vapour pressure, Pach [2] has determined the equilibria in the system $\text{CaO—H}_2\text{O}$. Statical methods allow an arbitrary close approach to the equilibrium state when the time of keeping sample at chosen conditions is sufficiently long. This can be time-consuming because determination of one point of the equilibrium dependence requires several long-term measurements. One of possible ways how to make these measurements more effective is using the apparatus described in this paper.

The equipment with adjustable gradient of temperature in the furnace and with adjustable pressure of gas component was developed. It is suitable for investigation of equilibrium quantities in heterogeneous systems of the type condensed phase—gaseous phase and it can be adapted also for the investigation of the systems with water vapour. It allows to make measurements in static atmosphere at the absolute pressure of pure water vapour or in the stream of inert gas with adjusted partial pressure of water vapour. In the latter case the total pressure of the gaseous phase equals atmospheric pressure. Several samples (maximum 17) of the investigated substance are kept in the apparatus for required time (from several hours to several days) at chosen constant absolute pressure or at chosen constant partial water vapour pressure and at different adjustable temperatures. Changes in mass, phase composition or another property (depending on the system) of the samples are investigated. Using these data the interpolation methods can be used for determination of the values of the equilibrium temperature corresponding to the adjusted water vapour pressure in the investigated system.

Description of the apparatus

Block scheme of the measuring apparatus arranged for measurements in the stream of carrier gas with adjustable partial water vapour pressure is presented in Fig. 1. The equipment consists of these main parts:

— Furnace with adjustable (unchangeable during experiment) nonlinear temperature gradient. Either a closed cell with adjustable water vapour pressure (the measurement with absolute water vapour pressure) or open tube with permanently flowing carrier gas with defined partial water vapour pressure (the measurements at the atmospheric pressure) are placed in the axis of the furnace. The cell or tube are equipped with carriers of samples with closing mechanism.

— Tempered box which prevents condensation of water vapour on colder parts of the apparatus.

— Manostat of water vapour with adjustable absolute pressure or the through-flow saturator where the carrier gas is saturated with water vapour at atmospheric pressure.

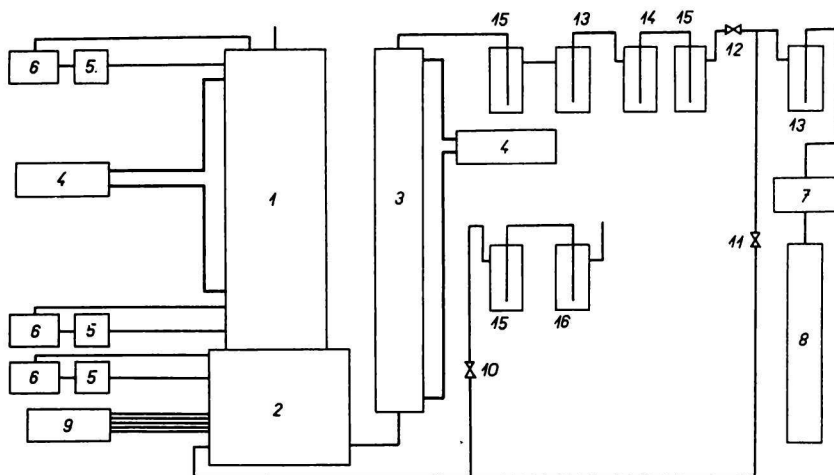


Fig. 1. Block scheme of the apparatus for measurement of the equilibrium values of temperature and pressure in heterogeneous systems formed by the reactions of the type $A_{\text{cond}} = B_{\text{cond}} + H_2O_{\text{g}}$. The arrangement of measurements in the stream of carrier gas with adjustable water vapour pressure is shown.

1. Furnace with controlled temperature gradient; 2. tempered box; 3. through-flow saturator of carrier gas with water vapour; 4. ultra-thermostat; 5. tyristor power supply; 6. electronic regulator of temperature; 7. manostat of carrier gas; 8. pressure bottle with nitrogen; 9. digital voltmeter; 10, 11, 12. valves; 13. purifying washing bottles; 14. washing bottle for purifying nitrogen of CO_2 ; 15. safety bottle; 16. washing bottle filled with water for following flow of carrier gas.

The main parts of the equipment are shown in Figs. 2—5. The most important part of the furnace (Figs. 2 and 3) consists of a thick-wall silver tube (26) having diameter 36 mm, 500 mm long which is fastened in steel mantle of the furnace by duralumin (29) and ceramic (20) flanges. The mantle is tempered by an ultra-thermostat. The upper part of the tube is equipped with 300 W resistor heating element (21) supplied from a tyristor power-supply. Constant temperature ($\pm 0.6^\circ C$) is maintained by an electronic regulator. The temperature is measured by a Fe—Const or NiCr—Ni thermocouple (22). Constant heating of the lower colder part of the tube is ensured by a resistor heating (28). The system

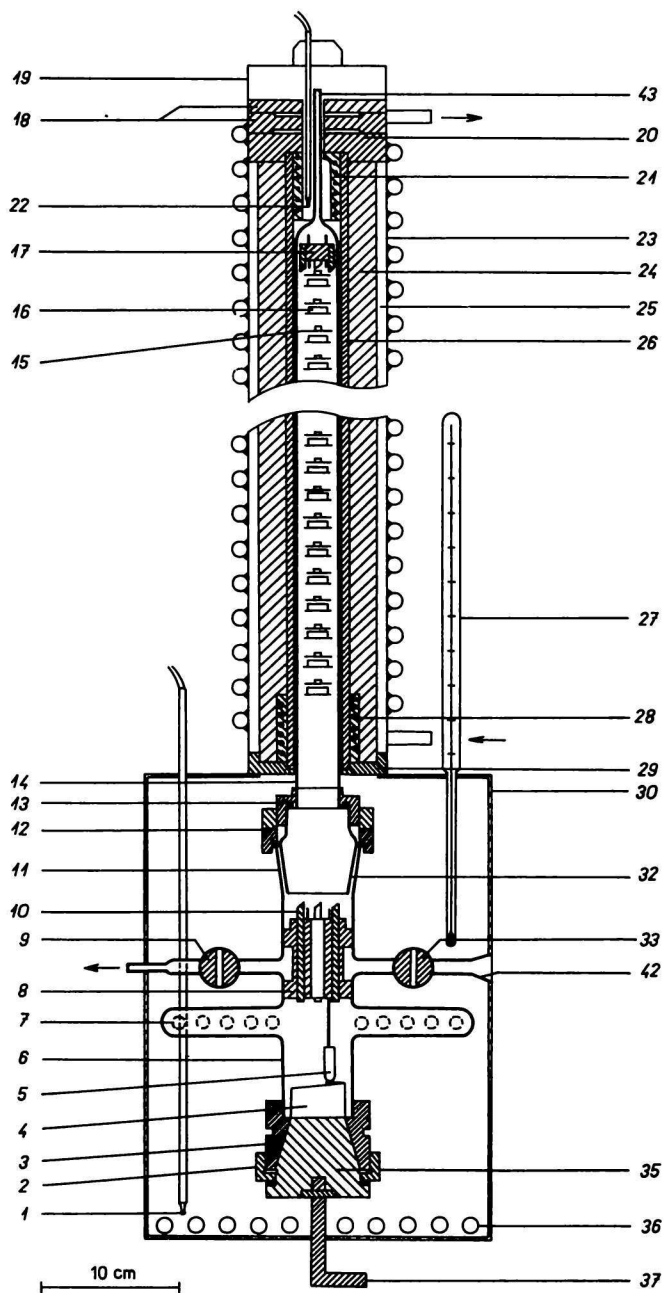


Fig. 2. Scheme of the furnace with controlled temperature gradient and of the tempered steel box (the items 1 and 2 in Fig. 1).

is similar to that in the upper part of the furnace. The heating element (28) can be replaced by the tube heat exchanger. Thermal insulation (24) of the tube (26) is formed by a layer of glass fibres made of silica oxide and by an air layer (25). This is separated from the tempered furnace mantle (23). In the upper part of the furnace there are placed insulating segments (18) and safety cover of electric heating (19). The furnace is fixed to a massive holder and it can be moved in

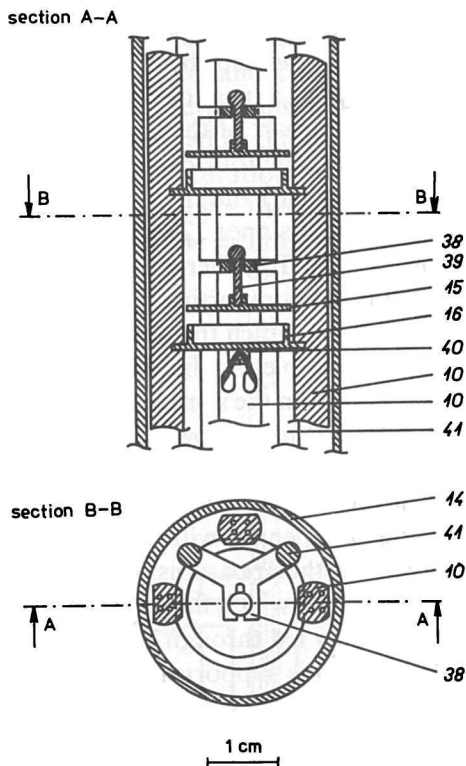


Fig. 3. Detail drawing of the carriers of samples placed in their supporting frame.

vertical direction by a rack jack. Next part of the equipment is a tempered steel box (30) with thermal insulation. Its task is to heat the parts of the apparatus between the manostat of water vapour (or the through-flow saturator) and the furnace in order to prevent condensation of water vapour. Constant temperature in the box (about 10—20°C higher than the temperature of manostat of water vapour or the through-flow saturator) is maintained by a resistor heating (36) connected with an electronic regulator. The temperature is measured by a Fe—Const thermocouple (1). Temperature in the box is measured by a thermometer (27). Glass tube (6) with defined partial water vapour pressure is placed in the constant temperature box as well. It is connected through the outer ground joint (11) and the inner ground joint (32) to the bottom part of

silica cell or tube (14). The furnace is shifted on this tube. The flange (13) makes possible connection of the bottom part of the cell (or tube) (14) with the inner ground joint (32) and simultaneously it bears the opening mechanism of the ground joint (12). The tube (6) is by means of the cock (9) connected to two washing bottles which, after closing the tube (43), serve to observation of the gas flow. Tube (6) is from opposite side connected through cock (33) and ground joint (42) to the manostat of water vapour or the saturator of carrier gas. The outer ground joint (3) is made of brass and it is cemented to the bottom part of tube (6). The joint bears a mechanical device which makes its opening easier (2). This joint is part of the closing mechanism of sample holders.

The main part of the supporting structure of the holder of samples consists of three ceramic four-capillaries (10) (see also Fig. 3). Their lower part is fixed in teflon base (8) and the upper part in nickel ring (17). Grooves in ceramic rods are made in distance 22 mm. Silver cups of the sample holders are slipped in the grooves (16). Together 17 sample holders, each having volume of 0.3 cm³, are placed in this supporting frame. Each fourth sample holder has in its bottom a recess (40) in which the weld of PtRh10—Pt thermocouple is placed. The welds of thermocouples are fixed in the recesses by platinum split pins. Thermocouple wires lead from the sample holders through ground orifices into ceramic capillaries (10) and in the lower part of the apparatus are led through vacuum-tight orifice (7) out of the space with adjustable partial water vapour pressure.

Closing and opening mechanism of the cups of sample holders allows their closing or opening with covers (15) at closed apparatus, without disturbing pressure in the apparatus. Covers of the sample holders (15) are equipped with pull rods (39) which fit in the slots of arms (38) of nickel rods (41). These rods are movably led through holes in teflon block base (8) and nickel disc (17) and one of them is supported by teflon extension piece (5) on the screw surface of teflon base (4) which is fixed in the inner brass ground joint (35). When this brass part is moved round by a handle (37) the whole mechanism moves in vertical direction and the covers are lifted or lowered. Total shift of the covers is about 3 mm.

The manostat of water vapours (Fig. 4) consists of a glass vessel (34) with double walls. Space above water level in the inner vessel is connected through cock (33) (Fig. 2) with measuring part of the apparatus. The jacket is tempered with water. Temperature of water in manostat is measured by a thermometer (31) (Fig. 4). Absolute water vapour pressure corresponding to the temperature of water in manostat of water vapours is stabilized in the cell (14) after evacuation of the measuring part of the apparatus.

In the through-flow saturator of carrier gas with water vapour (Fig. 5) the tempered carrier gas, divided into small bubbles, is in contact with tempered water. Partial pressure of water vapours corresponds to the temperature of

water. Jacket of the source of steam is formed by a glass tube (54) with thermal insulation (53). In the upper and lower part of the tube duralumin faces (52) with inlet (57) and outlet (51) of tempering medium are fixed. Carrier gas is led into the saturator by the tube (49) where it is also tempered. In the lower part of the saturation tube (47) a sintered disc (46) is fixed by melting. It ensures formation of bubbles with small diameter and homogeneous distribution of gas bubbles in the whole section of the inner saturation vessel. The saturation vessel (47) is filled with redistilled water. Space above water level is connected through tempered tube (55), outlet of saturated carrier gas (56) and cock (33) with measuring part of the apparatus. The outlet (56) with thermal insulation (44) is heated by a resistor heating (45). Temperature is controlled by thermocouple Fe—Const (58). Tempered water flows between the inner saturation vessel and the outer jacket. Temperature of the saturator is measured by a thermometer (50) placed in a test tube (48) situated in tempered water in the saturation tube (47).

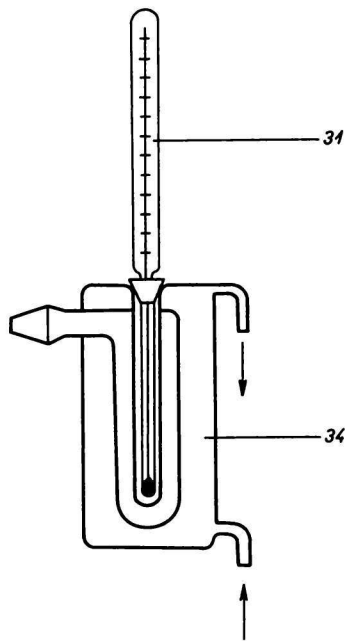
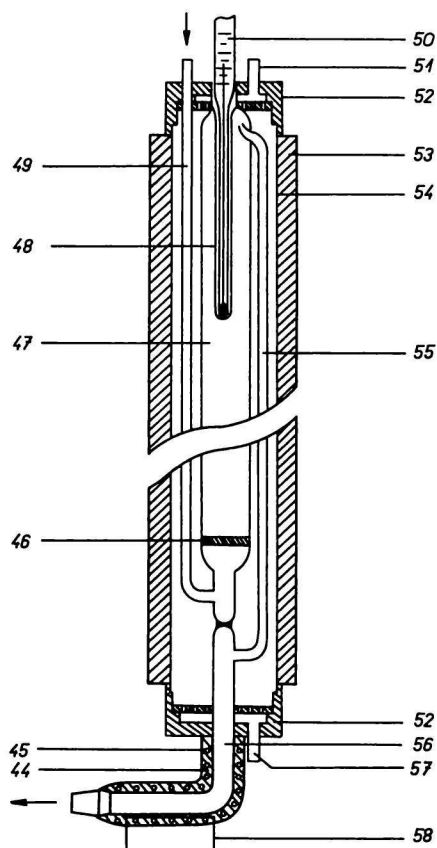


Fig. 4. Manostat of water vapours.

The described saturator of carrier gas allows to work with a partial pressure of water vapour ranging from 1.7 kPa to 90 kPa. The chosen temperature in the saturator in long-run measurements is kept constant within ± 0.05 °C. Nitrogen from pressure bottle was used as carrier gas. Its constant pressure is controlled by a manostat. Before entering the through-flow saturator the gas passes through a system of purifying washing bottles.

Fig. 5. Through-flow saturator of carrier gas
(the item 3 in Fig. 1).



Verification of function of the through-flow saturator

When the measurements in the stream of carrier gas were carried out the flow of carrier gas was $10\text{--}20\text{ cm}^3\text{ min}^{-1}$. At the beginning function of the through-flow saturator of carrier gas was tested. The aim of these experiments was to find out whether at given dynamic conditions the carrier gas is saturated to equilibrium with water vapour. If this is the case partial pressure of water vapours coming out of the saturator equals (in the limits of errors of measurement) the pressure of saturated water vapour at given temperature. For this purpose a direct method of optical observation of condensation and evaporation of water on a tempered plane-parallel glass plate of the thickness 1 mm was used. The plate was by-passed from one side by the stream of gas with water vapour flowing from the saturator and from the other side by tempered water. When the temperature of the plate is lower than the temperature corresponding

to the real pressure of water vapour in the gaseous mixture, water vapour condenses on the plate. When the temperature of the plate is higher than corresponding temperature of real pressure of saturated vapours in gaseous mixture, the film of liquid water (formed at lower temperature) evaporates. In this way one can measure the temperature corresponding to real pressure of saturated water vapours in gaseous mixture and compare it with the temperature of saturation. This allows to estimate quantitatively the measure of saturation of gas with water vapours.

Using this method pressures of water vapours in mixture with nitrogen at the temperatures ranging from 32.2 °C to 93.3 °C and flow of nitrogen ranging from 8 cm³ min⁻¹ to 30 cm³ min⁻¹ were determined. It was found that under these experimental conditions the arithmetic means of equilibrium temperatures of evaporation and condensation fall in the interval ± 0.2 °C around the temperature of saturation of nitrogen with water vapours. It follows that the apparatus saturates carrier gas with water vapour so that the real partial pressure of water vapour does not differ from the equilibrium pressure of saturated vapours more than by ± 0.7 % at 32.2 °C and ± 1.3 % at 93.3 °C.

Working procedure

The carriers of samples containing samples with closed covers (lids) are placed into the supporting frame. The measuring part of the apparatus is heated to the temperature which assures no condensation of water vapours. After several time evacuation of the apparatus and its purging with water vapour the temperatures of both ends of the furnace are stabilized at chosen values. Then the carriers of samples are opened by lifting lids (see the description of the opening and closing mechanism). In the course of measurement stability of temperature gradient in the furnace is checked by measuring the temperature at five carriers of samples. Also the water vapour pressure in the measuring part of the apparatus is checked by following the temperature of the manostat of water vapour or of the through-flow saturator. When the measurement is finished (the equilibrium is achieved) the sample carriers are closed and the furnace is shifted out of the cell (or of the tube). The cooled samples are analyzed (change in their mass, phase composition, *etc.* is determined).

References

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