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CONSTRUCTION OF AN ISOTHERMAL BALANCE WITH TWO SYMMETRICAL PANS FOR OPERATION UNDER PRESSURE

M. GHODSI, R. DERIE AND J. P. LEMPEREUR
Service de Chimie Industrielle et de Chimie des Solides, Université Libre de Bruxelles (Belgium)
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ABSTRACT

A thermobalance with two symmetrical pans was constructed in order to avoid thermogravimetry errors under pressure. The balance functions at 1000°C under 50 atm of hydrogen. The influence of parameters such as pressure, temperature and gas flow rate on the baseline deviation was studied. An example is given of the application of this balance to the hydrogenation of lignite char.

INTRODUCTION

Thermobalances under pressure have been used increasingly in many fields of research over the last decade; a particular case is the gasification of coals. The design or the utilization of thermobalances for use under pressure have been the object of several recent publications. Williams et al.[1] transformed a 950 Dupont model to carry out experiments at either 450°C under 133 atm, or 1000°C under 30 atm. Johnson[3] studied the kinetics of coke gasification in a thermobalance working under 70 atm at 1000°C. The balance built by Gardner et al.[4] can reach 140 atm at 1000°C. Biermann and Heinrichs[5] studied the pyrolysis of calcium oxalate at 1000°C under 70 atm. All these balances have only one pan; this leads to disturbances, especially under dynamic operation. Sasaki et al.[6] developed an electrical compensation system in order to minimize the thrust errors due to variations of the gas density with temperature.

The main thermogravimetry causes of error under pressure, namely Archimedes' forces, viscosity forces arising from the gas flow along mobile parts, and thermal gradient forces, may be avoided, or at least minimized, in a two-pan balance. The symmetrical balance described in the present work operates at 1000°C under a pressure of 50 atm and was designed for the study of the hydrogenation of carbons.

DESCRIPTION OF THE BALANCE

The installation is shown diagrammatically in Fig. 1.

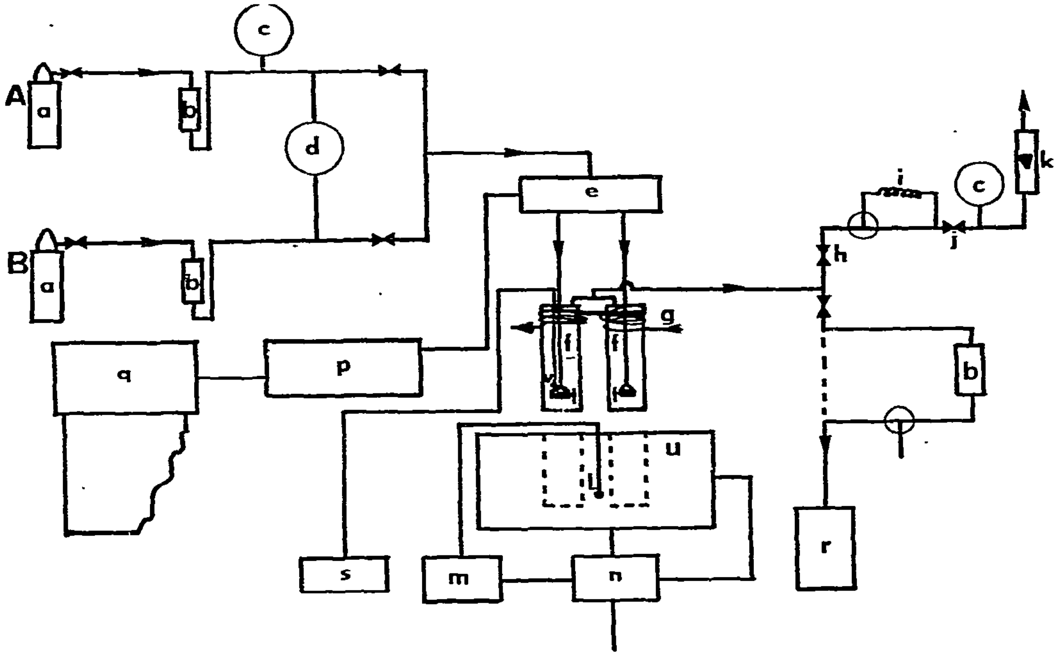


Fig. 1. Schematic diagram of the installation. (a) Gas cylinders; (b) liquid nitrogen traps; (c) manometer; (d) differential manometer; (e) balance head; (f) vessels; (g) flanges cooling circuit; (h) expansion valve; (i) chromatograph; (j) flow regulation valve; (k) flowmeter; (l) regulation thermocouple; (m) PDPI t° regulator; (n) triacs; (p) balance regulation panel; (q) recorder; (r) vacuum pump; (s) thermocouple tension/t° transformer; (t) crucibles (tare + sample holder); (u) furnace; (v) coaxial thermocouple.

Balance head

The Sartorius 4406 thermobalance measurement head was adapted for our installation. It is of the symmetrical type: the balance beam articulates on a torsion ribbon, and functions according to the automatic compensation principle. Masses or mass differences generate a mechanical moment which activates an opposite electromagnetic moment so as to return the arm to equilibrium. The necessary compensation current is regulated automatically; its intensity is a measure of the weight. The balance head can withstand a maximum pressure of 150 atm, and a maximum temperature of 110 °C.

Vessels submitted to high temperatures

The two vessels (f) in which alumina crucibles are suspended by means of thin molybdenum steel wires 5/100 mm in diameter, are of HT3 refractory steel composed as follows: Ni: 34–36%; Cr: 18–20%; Mn: $<$ 2%; Si: $<$ 1%; P: $<$ 0.045%; S: $<$ 0.030%; C: $>$ 0.15%. These vessels were built to conform to the following measurements: wall thickness, 12 mm; inside height, 340 mm; inner diameter, 34.5 mm. Figure 2 shows the cross-section of a vessel.

The upper part of these vessels is linked to the cold-part through a system of flanges and a Viton "O" ring. It was therefore necessary to cool the upper part of the vessels (g). This led to convection currents which disturb the measurements, as there

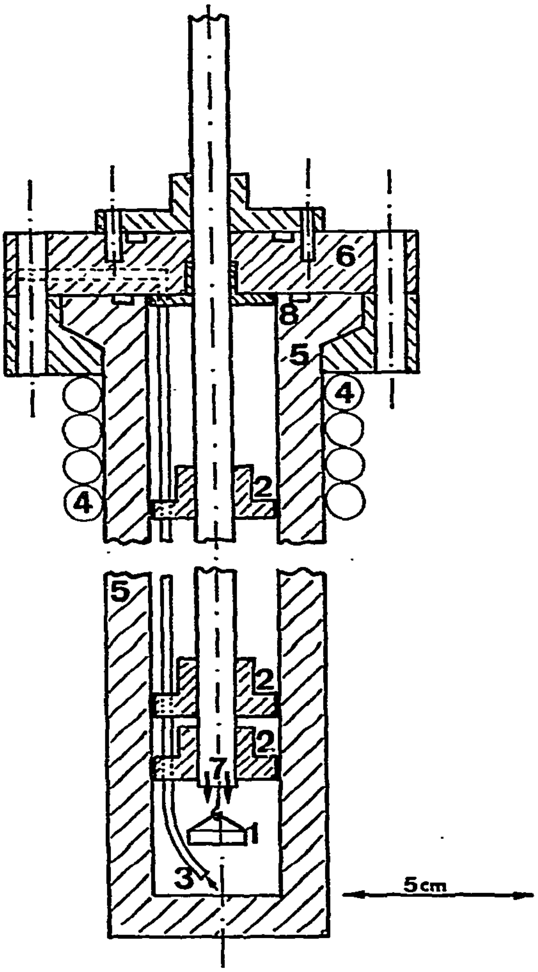


Fig. 2. Cross-section of a heating vessel. 1, Alumina crucibles; 2, diaphragms; 3, output; 4, cooling circuit; 5, vessel; 6, flange; 7, input; 8, Viton "O"-ring.

is an appreciable temperature difference between both parts of the vessels. This disturbance was reduced substantially by means of three diaphragms located near the crucibles.

Gas circuits

The installation can operate either with a confined or a dynamic atmosphere. In the latter case a gas A and/or a gas B is introduced through the balance head and is directed on both crucibles. It is easy to pass from a flow of A gas to a flow of B gas under pressure without perceptible disturbances; the pressures of A and B are equalized to ± 0.05 kg cm^{-2} beforehand by means of a differential manometer (d). The gases that are forwarded through the upper part of the "high temperature" vessels are expanded by two valves and expelled after passing through the flowmeter; part can be diverted to a gaseous phase chromatograph (i).

Regulating

A regulator acts on the power triacs trigger through integrated circuits; the regulation thermocouple is located inside the furnace. Temperature measurements are carried out by means of a coaxial thermocouple placed at the level of the sample.

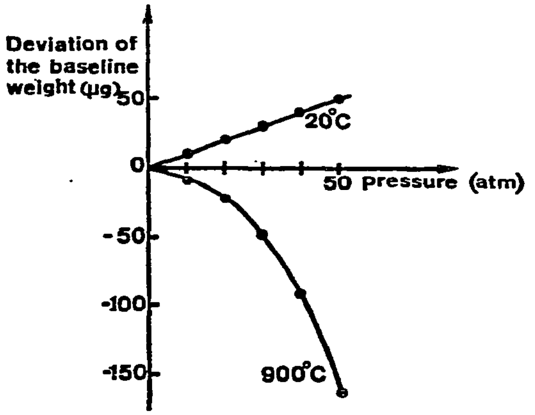
BALANCE PERFORMANCE

The maximum load per crucible is 25 g; the greatest weight variations are, according to the chosen sensitivity range setting, 1000, 100 or 10 mg. The balance's sensitivity under the best operation conditions is 1 μg.

THE INFLUENCE OF EXPERIMENTAL PARAMETERS ON BASELINE DEVIATION

Pressure

Baseline variation as a function of pressure at 20 atm and 900 °C is shown in Fig. 3. At 20 °C the shift is linear and stands at 50 μg under 50 atm; it is 165 μg at 900 °C under 50 atm. Dobner et al.[2] observed a baseline shift of 530 μg at 20 °C under 20 atm; under the same temperature and pressure conditions, we have only a 20 μg shift.



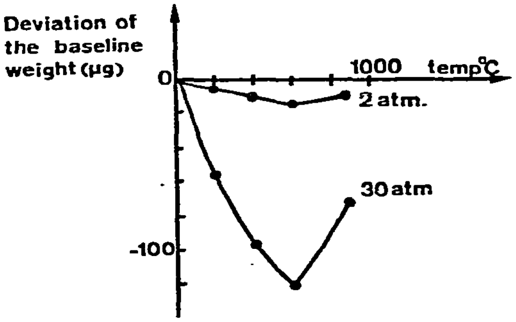


Fig. 3. Baseline variation as a function of pressure at 20 and 900 °C.

Fig. 4. Baseline variation as a function of temperature.

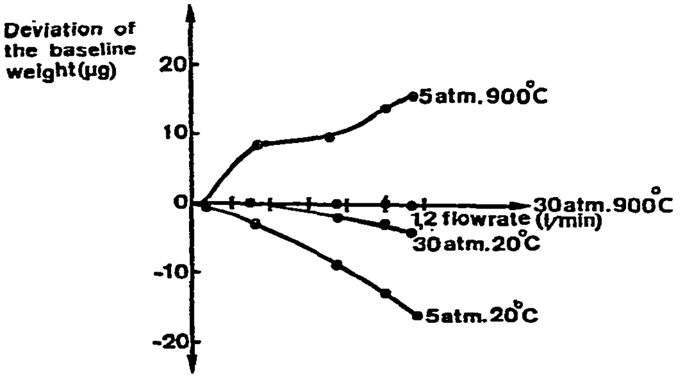


Fig. 5. Baseline variation as a function of flow.

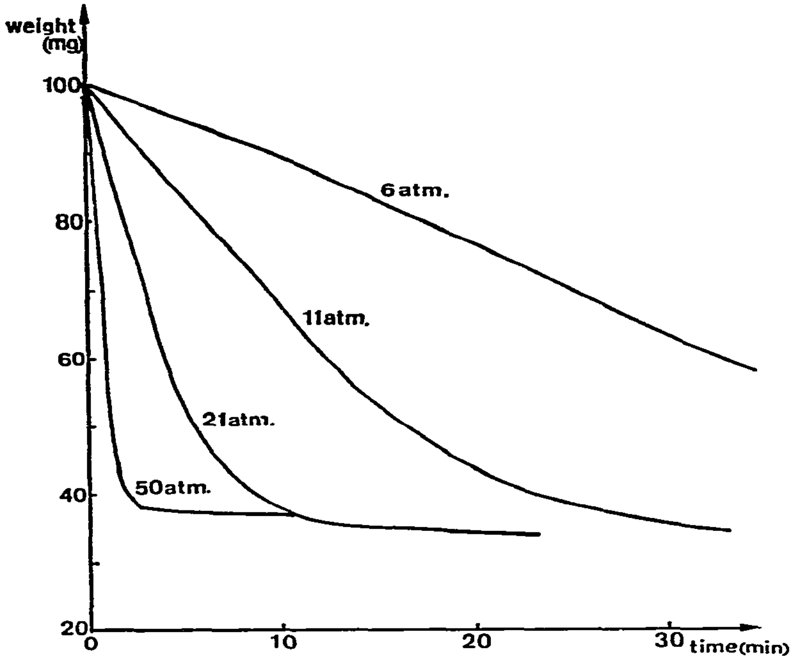


Fig. 6. Lignite char hydrogenation thermogram at 900 °C and under various pressures.

Temperature

The graphs shown in Fig. 4 show maximum deviation around 600 °C for both pressures considered. The deviation is highest under 30 atm where it reaches 120 μg. Dobner et al.[2] measured a 750 μg deviation under 21 atm at 600 °C.

Gas flow rate

The baseline deviation for helium flows reaching up to 1.2 l min^{-1} is shown in Fig. 5. The graphs were set up for two temperatures (20 and 900 °C) and for two pressures (5 and 30 atm). At maximum flow the highest deviation is observed under a pressure of 5 atm at 20 °C. The gas flow has hardly any influence under higher pressures.

APPLICATION OF THE THERMOBALANCE FOR USE UNDER PRESSURE

The first application of the balance for use under pressure thus developed is the study of the hydrogenation of lignite char. This work is part of a whole research work now underway. The kinetic curves obtained at 900 °C under hydrogen pressures ranging from 6 to 50 atm are given as illustration examples fitting the scope of the present publication (Fig. 6). These curves reveal the existence of a non-hydrogenable residue apart from the ashes. This extremely important problem for coal gasification is under investigation at the present time.

CONCLUSIONS

A two-pan thermobalance was produced which functions under 50 atm hydrogen pressure at 1000°C. The symmetry of the installation allows the main causes of thermogravimetry error, such as Archimedes' forces, the viscosity forces from flowing along the mobile parts and those forces stemming from thermal gradients, to be avoided; we thus obtained performances that were appreciably superior to those described previously for one-pan balances. This thermobalance was used for the study of the hydrogenation under pressure of lignite and pitch chars.

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