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A SIMPLE MICROBALANCE FOR INVESTIGATING THE REACTIONS OF SOLIDS WITH AMMONIA AND FREONS AT PRESSURES UP TO 10 BARS

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ABSTRACT

The authors have adapted a quartz-spring microbalance suitable for the study of the kinetics of reactions between solids and common gases such as freons or corrosive gases like ammonia. This equipment was built in order to investigate solid-freons and solid-ammonia systems for solar cooling. It can be used from -40 to 350 °C and at pressures from 10^{-5} to 10 bars. Results concerning kinetics and thermodynamics in the $CaCl_2$-NH_3 and 13X zeolite-R22 freon systems are given as examples of application.

INTRODUCTION

We have started research work in order to control the suitability of some solid-freon and solid-ammonia systems for refrigeration cycles in affinity thermal machines using solar heating (1)(2). The data on kinetics and thermodynamics concerning these systems need to be perfectly known, particularly in the experimental range of temperature and pressure imposed for the good working of these machines and dependent on the local climatic conditions.

Unfortunately these data often are not available or are incomplete, particularly when these systems are considered at pressures higher than one atmosphere. Thermogravimetry seems to be one of most powerful and direct techniques for obtaining these data. That is why we have built a spring Mac-Bain balance having specific technical characteristics well-adapted to the present requirements: high pressure and corrosive atmosphere.

In this paper we describe the features of this simple microbalance. Then some experimental results are given as examples of its utilization.

DESCRIPTION OF THE EXPERIMENTAL EQUIPMENT

The body of the microbalance was built from a stainless steel tube of 5mm in thickness and 38 mm in diameter in order to support a pressure of 50 bars. The junction of movable parts is made by stainless steel flanges clamping aluminium joints on their knife edges. The system of weighing is essentially constituted by a silica spring the movements of which are recorded by a displacement follo-

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wer (3). Due to the opacity of the body of balance, an optical passage for the beam of light is needed. Its realization was tricky because of the difficulty in obtaining a good gastightness for the glass-metal junction at high pressures after heating. The best adapted assembly (Fig. 1) consists of a pyrex-glass tube of 5 mm in thickness and of 20 mm in internal diameter, mechanically held by two stainless steel assemblies, of packing-box type, which make possible the clamping of teflon rings against the glass tube. The optical passage and the tube containing the silica-spring are enclosed in a caisson kept at constant temperature by air heating (Fig. 2). The temperature of the reaction tube was fixed either by a temperature regulated water bath or by an electrical furnace controlled by a power regulator. The minimum pressure possible from our vacuum system was $\sim 10^{-5}$ bar and the limiting maximum value of the pressure was evaluated at 15 bars for a good safety. The last value depends on the mechanical properties of the glass-tube and could be increased by modifying the dimensions of this tube.

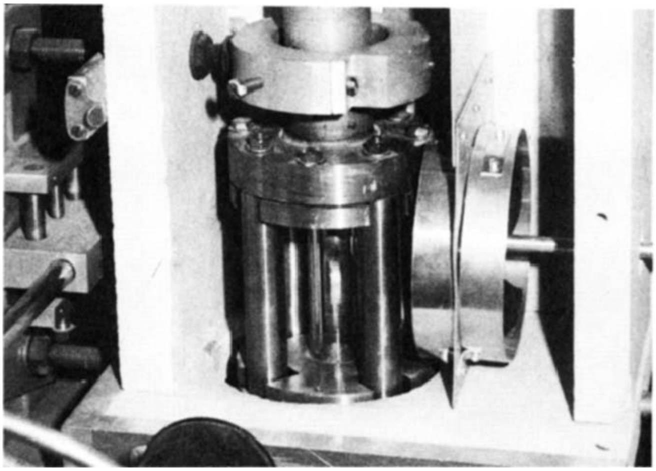

Fig. 1. The optical passage of the microbalance.

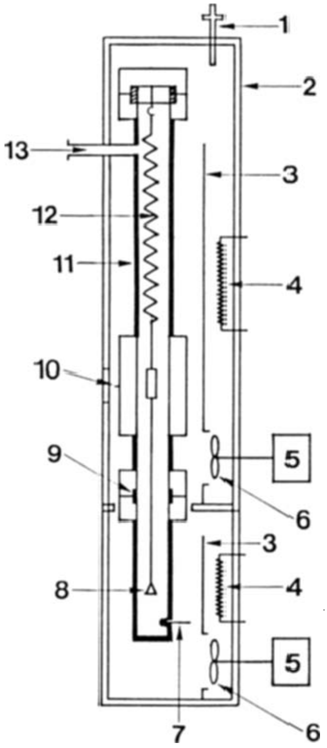

Fig. 2. The high pressure quartz-spring microbalance.
1/ Contact thermometer controlling the temperature in the upper compartment. 2/ Thermal insulator. 3/ Blowed air deflector. 4/ Electrical heaters. 5/ Electrical motors. 6/ Blowing screws. 7/ Measuring thermocouple. 8/ Sample holder. 9/ Knife-edge profiled flanges for aluminium joints. 10/ Optical passage. 11/ Stainless steel tubing. 12/ Quartz spring. 13/ Connection tubing for vacuum and gas inlet.

In order to cancel the chimney effects which bring about uncontrolled movements of the spring, the caisson surrounding the upper part of the microbalance including the quartz-spring, was heated to 170 °C, a temperature much higher than the maximum temperature of the reaction tube (100 °C). In these conditions, no disturbing effect was detected when the pressure was increased up to 10 bars. On the other hand, no correction of the value measured for the mass was needed when the temperature of the reactor was modified in the above range. But buoyancy correction was necessary (Fig. 3). For example, with a quartz-spring of 0.19 mm/mg sensitivity, the buoyancy correction was ∿1 mg/bar for R 22 freon and ∿0.25 mg/bar for ammonia. This correction might represent up to 20 % of the mass variation at 10 bars.

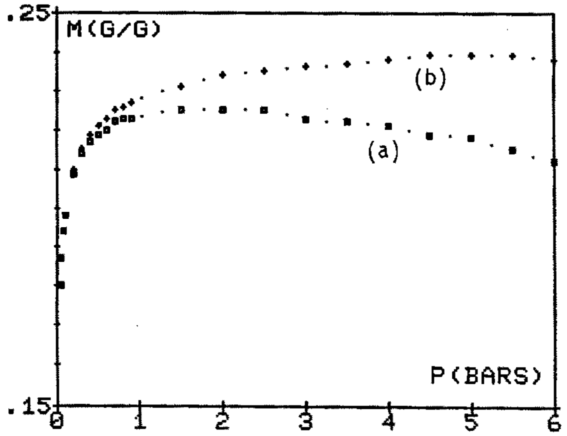

Fig. 3. Example showing the buoyancy effect as a function of pressure. The curves represent the amount of R 22 freon fixed on 13 X zeolite at 60 °C before correction (a) and after correction (b).

Lastly a processing by microcomputer could be used from the gravimetric data as recorded by the displacement follower.

SOME EXAMPLES OF USING THE MICROBALANCE

To illustrate this presentation and to show what types of information can be obtained by means of this microbalance, two examples of chemical reactions are reported.

First example: experimental investigation of the kinetics of formation and decomposition of $CaCl_2, 8\ NH_3$.

The chemical reaction:

$$CaCl_2, 4\ NH_3 + 4\ NH_3 \rightarrow CaCl_2, 8\ NH_3$$

and the reverse one were studied in the following conditions:

ammonia pressure: from 0 to 7 bars
temperature: from 40 to 80 °C

Pressure and temperature were kept constant during the reaction. All experiments were performed from the same sample of calcium chloride ($CaCl_2$) previously dehydrated under vacuum at 80 °C. The system $CaCl_2, 4\ NH_3 - NH_3 - CaCl_2, 8\ NH_3$ was found to be thermodynamically univariant in the experimental range investigated

(2 and therein).

Generally speaking, the system was found to behave as expected when referring to previous observations made from other metallic salt-ammonia-ammoniate systems studied at ammonia pressures below one bar. The following points have to be emphasized:

1/ When cyclic reactions of formation and decomposition were considered, kinetics were perfectly reproducible so long as the reaction preceding in the cycle was performed in standardized conditions.

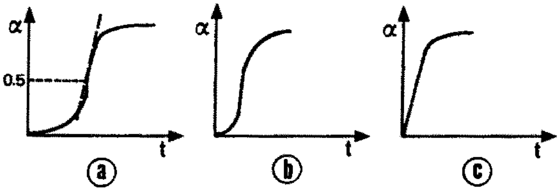

Fig. 4. The different α(t) curves observed for the kinetics of formation and decomposition of CaCl$_2$, 8 NH$_3$ when the experimental conditions were near (a), further (b) or furthest (c) from the equilibrium.

2/ The shape of the curves expressing the degree of conversion (α,fraction of reaction product) versus time was found to depend on the distance between the experimental conditions and the equilibrium conditions (Fig. 4).

3/ For a given temperature, the reaction rate for the degree of conversion α = 0.5 was strongly connected to ammonia pressure. This rate can be taken as characterizing the evolution of the reaction (Fig. 5).

4/ The "metastability" range, that is the pressure range surrounding the equilibrium pressure where the reaction rate is extremely low, appeared to be more limited at higher temperatures than at lower.

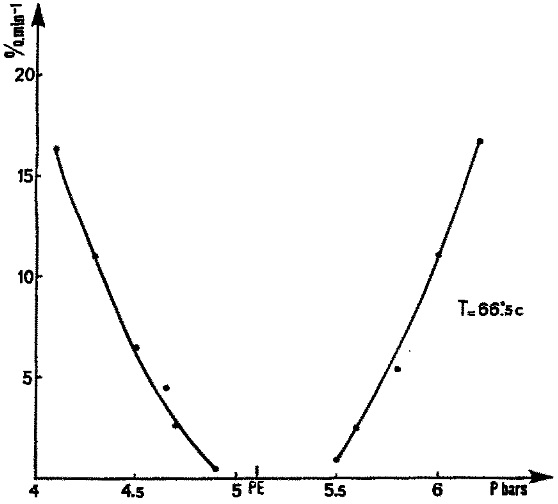

Fig. 5. Evolution of the reaction rate as a function of the ammonia pressure at 66.5 °C. (rate in percentage of reaction fraction per minute).

5/ From the experimental curves obtained at each temperature for both reactions of formation and decomposition, two sets of "isokinetic" curves could be deduced by plotting the couples P-T corresponding to a given value of the reaction rate. This network of curves makes possible to predict the reaction rate for any P-T values (2).

6/ An effect of "solid ageing" was evidenced (Fig. 6). This effect was detected when the reaction was performed in the same conditions but from initial solids differentiated only by their life time after formation. The time t_S passed between two consecutive reactions (see the figure 6) was selected for measuring the duration of ageing. The effect was inhibiting and the influence of ageing remained constant after t_S = 7 hours. It might be the consequence of the relaxation of defects in the initial solid.

Second example: thermodynamics of the adsorption of R 22 freon on 13 X zeolite.

All experiments were performed from samples dehydrated "in situ" under vacuum at 350 °C. The weight of these samples was continuously recorded in order to control the possible fixation of gaseous impurities by the solid during its cooling.

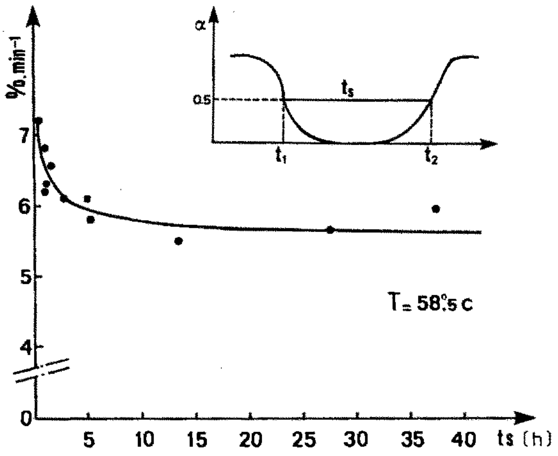

Fig. 6. Evolution of the reaction rate in the $CaCl_2$, 8 NH_3 formation as a function of t_S, the time selected to characterize the ageing of the initial ammoniate.

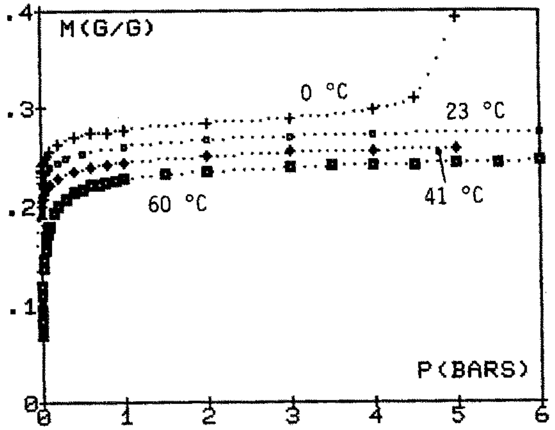

Fig. 7. Adsorption isotherms of R 22 freon on 13 X zeolite. The fixed mass is given in gram per gram of dehydrated solid.

The isotherms for the adsorption of R 22 freon were determined between 0 and 60 °C under pressures from 10^{-3} to 6 bars. They have the well-known shape characterizing the gas adsorption on this type of zeolites (Fig. 7). Using the classical Polanyi-Dubinin theory after introduction of the Clapeyron's equation leads to the linear form:

$$\text{Log } W/W_0 = \text{Log } \theta = - D'(T/T_0-1)^2$$

where:

W = volume of the adsorbate at P and T.

W_0= geometrical volume of micropores in zeolite.

D'= constant characterizing the gas-solid couple.

T_0= temperature of liquefaction of the gas under the considered pressure.

This function is very helpful for comparing the gas-zeolite couples in refrigeration (4). When Log $\frac{W_0}{W}$ is plotted as a function of $(T/T_0-1)^2$ for a given zeolite (here 13 X zeolite):

- the steeper is the slope of the

straight line, the larger is the amount of fluid cycled.

- the gas-zeolite couple represented by the straight line with the most gentle slope corresponds to the cooling production at the lowest temperature.

In the figure 8 the curves corresponding to four isotherms are plotted. When R 22 freon is compared with other fluids such as water, ethanol or methanol previously studied by Simonot-Grange and coworkers (4,5), it is obvious that this chemical compound is not interesting with regard to the question of the amount of fluid cycled, but it seems to be attractive as far as very low temperatures below 0 °C are required in refrigeration.

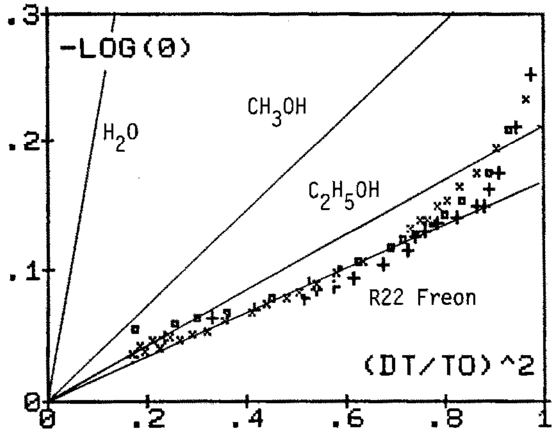

Fig. 8. Linear representation of the adsorption curves of R 22 freon on 13 X zeolite as compared with ethanol, methanol and water.

CONCLUSION

These two examples illustrate the possibilities of a very simple microbalance for exploring the characteristics of the corrosive gas - solid systems at pressures higher than one bar.

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