THERMOGRAVIMETRIC STUDY OF ALCOHOL ADSORPTION ON ACTIVE CHARCOAL

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ABSTRACT
    Interest of using the Mac Bain thermogravimetric balance in order to charac-
terize alcohol adsorption or desorption on various active charcoal is developed.
Precautions and peculiarities of proposed method are indicated. They result
from very good precision and reproducibility in the thermal range of 273.15
to 313.5 K, and in the pressure range of 666.6 Nm^{-2} to 26664 Nm^{-2}.
    Some results are given to illustrate the statics, and kinetics of adsorption
desorption process of alcohol on various active charcoals.
    These results are important to develop and optimize refrigerating machines,
or heat pumps, or physico-chemical storage using these systems.

I-INTRODUCTION

    To study vapor adsorption on active charcoal, thermogravimetry has been used
by A. METROT[1], and by J. RILLING, R. PERONNE and D. BALESDENT[2].

    The peculiarity of the present experiment consists in associating a MAC BAIN
microbalance with hot and cold ovens. The combination of these two allows us to
stabilize the reactor temperature between 273.15K and 313.15K, and to submit
the charcoal specimen to an alcohol vapour pressure varying between 666.6 Nm^{-2}
and 26664 Nm^{-2}. The vapour pressure is imposed by a cold surface on the boiler.

    Nickel thermosensors are placed on specified points of the laboratory tube
in order to determine the evolution of temperature gradients in the reactor, to
control the temperature of the cold surface on the boiler, and the constant
temperature of the microbalance. An optical device is used to determine the
length of the hangdown continuously and to deduce the alcohol-sorbed mass
variation.

II-APPARATUS DESCRIPTION AND CALIBRATION

    The thermogravimetric apparatus is shown schematically in Figure 1.

II.1. a microbalance

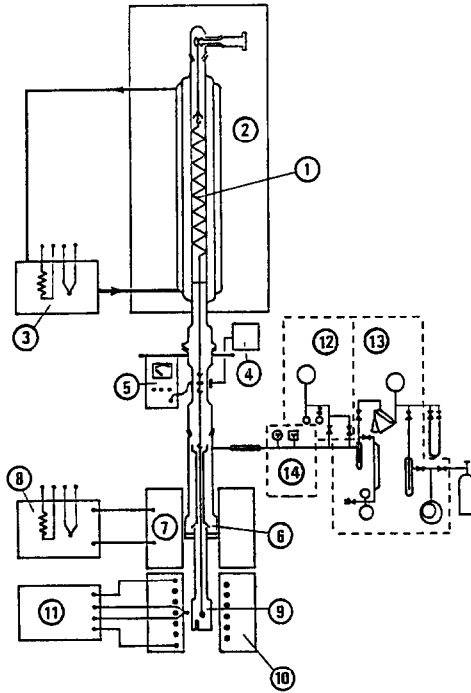   Microbalances used are furnished by Institut de Recherches en Chimie Appliquée
(IRCHA).

Fig. 1. Schematic view of thermogravimetric system.
1   Microbalance.
2   Thermostatic environment of microbalance.
3   Thermostatic reactor bath of microbalance.
4,5   Length measuring and amplifying system.
6   Boiler.
7   Boiler refrigerating system.
8   Cold thermostatic bath of boiler.
9   Reactor.
10   Reactor hot oven.
11   Regulated heating system for Reactor.
12   Alcohol introduction apparatus.
13   High vacuum pumping assembly
14   Pressure sensors.

These silica springs having a 20mm diameter are suspended within a 30mm diameter pyrex tube. The temperature in this tube is perfectly regulated.

calibration of microbalance

The microbalance sensitivity is expressed in a linear form :

$$\Delta M = K_t \cdot L \tag{1}$$

The K_t coefficient is determined by linear regression from results obtained with different temperatures Tp.

$$K_\ell / mg\ mm^{-1} = 3.5429\ (1 + 1.755\ 10^{-4}\ T_p/^\circ C) \tag{2}$$

The length corresponding to maximum weigth varies with temperature according to :

$$\frac{dL_m}{dT} = -0.1189\ mm\ K^{-1} \tag{3}$$

A $\pm$ 0.1mm variation of hangdown length corresponds to an absolute microbalance temperature variation of $\pm$ 0.1K. The constant temperature chosen is 318.15 K $\pm$ 0.1 K.

measurement of the length of the spring

The length of the spring is continuously measured by a SEFRAM-ST-GOBAIN apparatus. The displacement sensitivity of this apparatus is $\pm$ 10^{-2}mm for a total variation of spring length corresponding to 4.5 $\pm$ 0. 01mm. The total absolute error on the displacement is estimated to 10^{-2}mm.

calibration of SEFRAM-ST-GOBAIN apparatus

The calibration curve of SEFRAM-ST-GOBAIN apparatus is established with the aid of a cathetometer which measures length with a precision of $\pm$ 0.005mm. The observed length variation is a linear function of measured voltage. Linear regression applied to the previous results furnishes the following formula :

$$\Delta L = \alpha_\nu (u - u_o) \tag{4}$$

$(u-u_o)$ represents the voltage difference at the exit of the amplifier

$$\alpha_\nu = 0.904_{078} mm\ Volt^{-1}$$

To conclude, the maximum absolute error of all the measures performed is 4×10^{-4}mg for one mg of active charcoal tested.

II.2. the laboratory tube

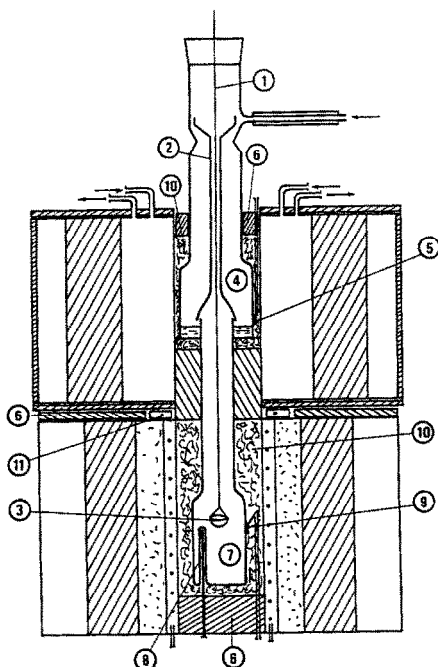It mainly consists in two parts : the boiler and the reactor linked with an intermediate tube (Figure 2).

Fig. 2. Laboratory tube.
1   Suspension filament.
2   Coaxial protecting tube.
3   Sample basket.
4   Boiler.
5   Control thermal nickel sensor.
6   Thermal insulation.
7   Reactor.
8,9   Platinum and nickel sensors for
      measures in reactor.
10   Metal sponge .
11   Heating element.

II.2.1. the boiler

The boiler is an annular cylindrical tank with an outer diameter of 60mm. The
inner diameter is the same as the one of the intermediate tube, with a diameter
of 30mm. The first stage of an experiment consists in filling the boiler with
alcohol by means of an evaporating-condensing process. The heat necessary to
evaporate the alcohol is furnished by a thermostat that delivers heat to an oven
via an ethyleneglycol circuit. The refrigerating and heating power are respecti-
vely delivered by a refrigerating machine of 200 Watt power at 233.15K, and
electrical resistance of 500 Watt; refrigerating and heating power is controled
by a PEGASE P.I.D. regulator.

The regulated temperature domain is from 258.15K to 313.15K. The lower tempe-
rature of the experimental apparatus corresponds to the colder point of the

thermogravimetric microbalance. A VISHAY-MICROMESURES nickel thermosensor on the cold surface of the boiler, at the level of the liquid alcohol, allows us to control the boiling temperature and therefore to follow the evolution of the corresponding vapor pressure.

Otherwise an absolute pressure sensor continuously measures the alcohol vapor pressure within the boiler; the adsorption thermal equilibrium is established when the pressure and the adsorbed alcohol mass remain constant whatever the time.

calibration of SEDEME pressure sensor

calibration with respect to an absolute mercury manometer has been performed in an argon inert gas atmosphere. The pressure is monitored via a variable leak valve. The height of the mercury column is determined by means of the previously described cathetometer.

After numerical treatments the calibration result can be set as follows :

$$P_v = \alpha_T \ (P_S - P_{S_o})$$ (5)

$(P_S - P_{S_o})$ correspond to the voltage difference in mV after amplification.
$\alpha_T/mbar \ mVolt^{-1} = 1,51_{83} - 8,4_{77} \ 10^{-4} \ . \ T_a/°C$

T_a represents the ambient temperature measured at the surface of the pressure sensor.

II.2.2. the reactor

The reactor is a cylindrical pyrex chamber whose diameter is 50mm, and whose height is 110mm. This cylindrical chamber possesses a flat bottom with a glass finger 66mm high and of 6mm diameter. This finger is specially designed to allow the measure of the charcoal sample temperature with a platinum thermal sensor. It also allows us to determine the temperature gradient existing between the finger and the outer surface of the reactor. The surface temperature is measured with a nickel thermal sensor.

The heat necessary to maintain a constant reactor temperature corresponding to the studied isotherm is furnished by another ethyleneglycol thermostat. This thermostat is refrigerated by a cooling machine of 320 Watts at - 263.15K heated by two heating resistances 250 Watts each. All this subsystem is controlled by a P.I.D. regulator. For temperatures higher than ambient temperature a thermocoax oven is used.

calibration of nickel thermal sensors

The different locations of nickel thermal sensors in the laboratory tube are indicated on figure 2. The calibration of STG-50B sensors has been performed with respect to a reference state (sensor placed on 10-18 steel). An experimental method called "by contact" has been used[3].

The numerical adjustement (least square method) gives the following polynomial form for the evolution of the resistance placed on pyrex glass with temperature:

$$R(T) \doteq 43.71_{22} + 0.24_{84}T + 2.56 \times 10^{-4} \ T^2 - 3.16 \times 10^{-9} \ T^4 \qquad (6)$$

with R in ohm, T in °C.

III-EXPERIMENTS

III.1. adjustement and correction of parameters

III.1.1. temperature gradient in the reactor

Temperatures in the finger that is in the vicinity of the charcoal sample, and on the external surface of the reactor are measured respectively by means of a platinum resistance and a nickel sensor (figure 2). These measures indicate that it is possible to have good stability of the corresponding temperature with a maximum gradient of 0.8K.

The standard thermal deviation of the two former thermometers is ± 0.1K. The maximum absolute error on t_R, the sample temperature, is estimated at ± 0.2K via a simple model[5]

III.1.2. time-constant to obtain boiler thermal equilibrium

Adsorption is performed by stages that correspond to various state points of the boiler regulator. The relative pressure variation indicated by the pressure sensor corresponds to the curve of figure 3. P_V^o, P_V, P_V^* represent respectively the pressure measured at $t = 0$, at time t, and at equilibrium. The average time constant associated with the equilibrium pressure is 32 minutes; it represents 5% of the total time to reach equilibrium.

A maximum absolute difference of two mbars is observed when comparing experimental pressure values with theoretical alcohol vapor pressures. The theoretical values are calculated with the aid of ANTOINE correlation and correc-ted alcohol boiling temperature.
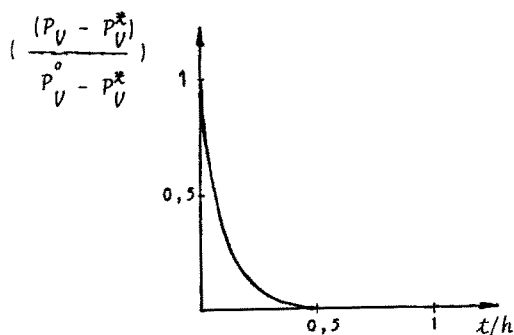
$$\left(\frac{(P_V - P_V^{\ast})}{P_V^{o} - P_V^{\ast}} \right)$$

Fig. 3

III.1.3. buoyancy forces

ARCHIMEDES' forces are   responsible for the main error when evaluating the adsorbed alcohol mass (reference[4] and experiments[5]). In the present study the upthrust acting on an inert silica sample in the presence of alcohol vapor has been measured. The corresponding results are in good agreement with calculated values.

When active charcoal is used, the value of the ARCHIMEDES' force acting on every element of the microbalance is calculated for each adsorbed mass. The corresponding values of the upthrust vary between 0.5 and 2mg depending on the isotherm studied.

IV. Examples of results obtained

Here are presented some thermostatic and thermokinetic experimental results on the system ethanol-active charcoal. These results have been obtained with the microbalance system previously described.

IV.1. thermostatic results

Figures 4, 5 and 6 represent adsorption and desorption isotherms of ethanol vapors on some active charcoal samples near the temperature of 313.15K. All the observed isotherms are practically of type I of the B.D.D.T. classification. A theoretical approach has been developped to have a model of these adsorption-desorption isotherms; the DUBININ-RADUSKEVITCH approach seems to be the most representative of all the results obtained. Maximum relative deviation of experimental results from the proposed model is 1%.
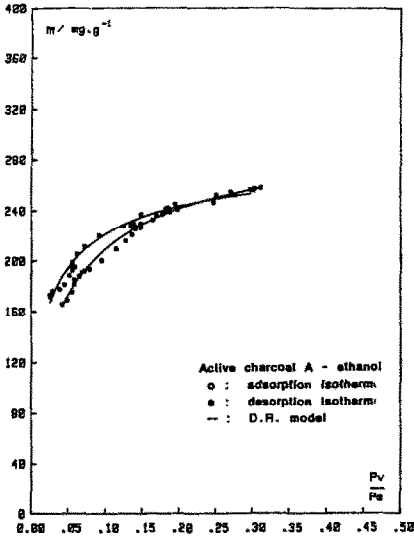
Fig. 4. sorption isotherms.
         active charcoal A - ethanol
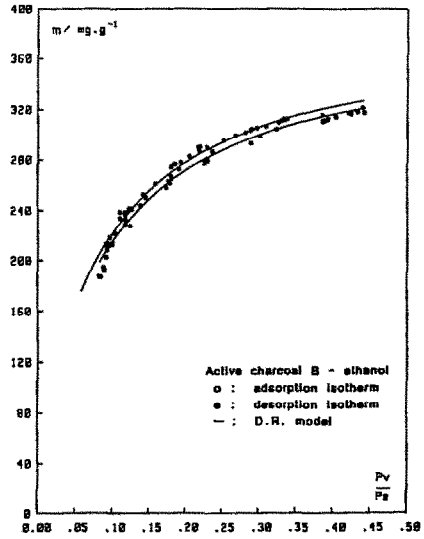

Fig. 5. sorption isotherms.
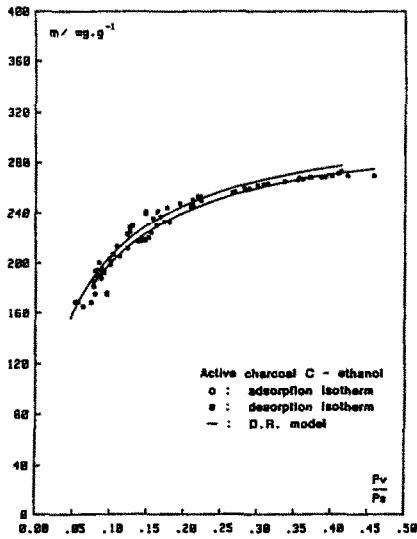   active charcoal B - ethanol

Fig. 6. sorption isotherms.
        active charcoal C - ethanol

IV.2. thermokinetic results

Figures 7 and 8 present some examples of adsorption-desorption kinetics for various sample mass filling, at 313.5K, and for the same samples as in IV.1. In figures 9 and 10, variation of $(\frac{D}{a^2})$ diffusion parameter in the adsorption and in the desorption case with the reference mass filling $m_{1/4}$ corresponds to 25% of M_t/M_∞. M_t and M_∞ are respectively the alcohol mass adsorbed or desorbed at time t, and at equilibrium. Maximum absolute error on the $(\frac{D}{a^2})$ values is $0.2 \times 10^{-6} s^{-1}$.
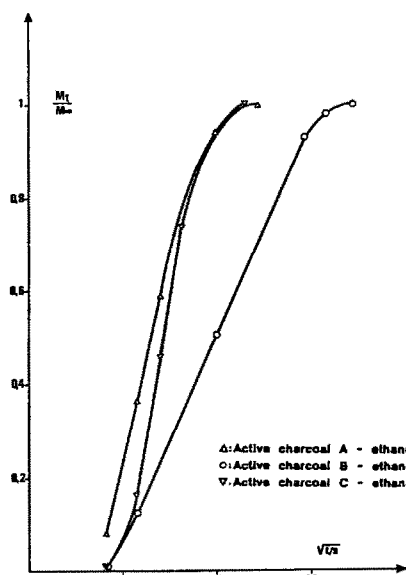

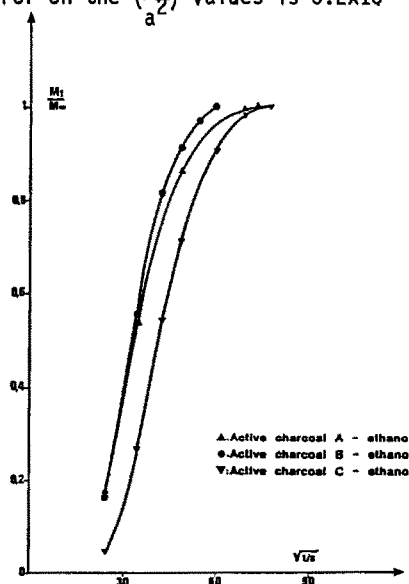Fig. 7. adsorption kinetic
         active charcoal i - ethanol

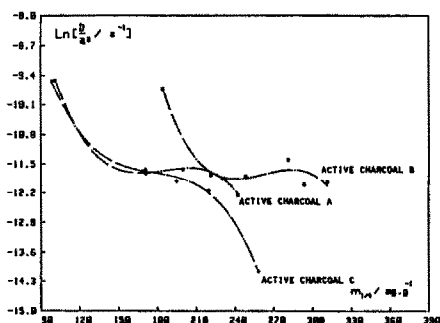Fig. 8. desorption kinetic
         active charcoal i - ethanol

Fig. 9. Variation of internal diffusion
        with alcohol mass filling $m_{1/4}$
        active charcoal i - ethanol
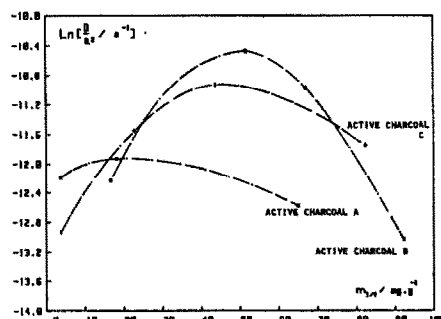   (adsorption case)

Fig. 10. Variation of internal
         diffusion parameter with
         alcohol mass filling $m_{1/4}$
         active charcoal i - ethanol
         (desorption case)

V- CONCLUSION

The reported study illustrates the interest of a thermogravimetric method to obtain thermostatic and thermokinetic characterization of alcohol-active charcoal samples.

Summarized are precautions that are necessary in order to get a fine characterization of alcohol-active charcoal samples. Optimization of thermal systems that use three heat sources becomes possible ↓ These systems can produce simultaneously refrigeration and heating, or also physico-chemical thermal heat storage.

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