

# UNIT FOR SIMULTANEOUS MEASUREMENT OF ISOTHERMS AND ADSORPTION HEATS

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## Abstract

This work presents the design of a station for the simultaneous measuring of adsorption isotherms and heats of adsorption. A Calvet heat-flux calorimeter is developed, specially designed and built for this purpose, and it is connected to a volumetric unit to register adsorption isotherms. The calorimeter is previously calibrated, electrically obtaining a  $K=15,12$  and  $\pm 0,32 \text{ W.V}^{-1}$  and chemically, with the system THAM-HCL, obtaining  $\Delta H = -47,41 \pm 0,01 \text{ kJ.mol}^{-1}$ .

The system is connected to obtain the adsorption isotherms and the corresponding heats from which Gibb's Free Energy is deduced.

Key words: adsorption heat, adsorption microcalorimetry, adsorption thermodynamic variables, adsorption free energy.

## INTRODUCTION

Today porous solids are very useful adsorbents because of their wide range of use in different areas of the knowledge, from basic to applied sciences. During the last decades, such materials have gained importance due to their application in environmental chemistry and in the development of new materials for various applications in removals and purification [1-3]. Given their diversity in various fields of application, in the processes for obtaining porous solids, among which activated carbons and zeolites stand out, variables like temperature and carbonization and/or activation time, activating agents, etc. should be controlled, thus obtaining solids with diverse superficial characteristics. On these superficial characteristics will depend the application and final effectiveness of the solid obtained, which is then used in the design of adsorption engineering processes like PSA, USA, TSA and their combinations, storage of gases, heavy metal retention, etc [4-6]. For this reason, it is important to know with precision certain parameters which characterize the solid, like superficial area, pore distribution, pore volume and the heat adsorption which they permit, among others [7,8]:

a) to characterize the adsorbent material from the energetic point of view.

b) to provide data to learn about adsorption equilibrium and its kinetics.

Literature presents some possibilities to determine adsorption heats from experimental data: calculation of adsorption heats from adsorption heat data, taken at different

temperatures, e.g. adsorption isotherms or adsorption isotheres. Calorimetric Methods: These are usually classified as adiabatic or Tian-Calvet isothermal methods, immersion calorimeters, etc. The present work is the result of combining the different developments in the area of calorimetric instrumentation during the last 18 years and the modification of conventional volumetric equipments to obtain adsorption isotherms, thus obtaining a compact and semi-automatic equipment to take experimental isotherms and adsorption heats.

#### Thermodynamic aspects of Dubinin's theory [9]

The formulation of the universal equation for adsorption isotherms in the 1950s allowed Dubinin's school to endow new life into the idea of Erich Hückel, i.e. that it would be possible to calculate the differential molar heat of adsorption at a particular temperature from an isotherm measured at this temperature alone. Generally, it is necessary to have at least two isotherms at two adjacent temperatures to achieve this result. In his paper delivered to the 56<sup>th</sup> General Discussion organized by the Faraday Society at Oxford University in January 1932. Hückel analysed Zsigmondy's capillarity theory and, anticipating some of the ideas used later by Kubelka, derived the equation for the evaluation of the heat for capillary condensation from a single adsorption isotherm. He attributed a clear physical meaning to all the terms in his equation.

Changes in thermodynamic quantities, such as enthalpy, entropy and free energy, may be subtracted from the standard values which correspond to the state of the normal liquid adsorptive at a temperature T for the adsorption isotherm  $a = a(P,T)$ , where a is the amount adsorbed. In agreement with above-mentioned equation (1), the maximal work of adsorption A of 1 mol of the adsorptive from the liquid phase on to an infinitely large amount of adsorbent is:

$$A = -\Delta G = RT \ln(P_g^o / P_g) \quad (1)$$

where  $\Delta G$  is the change in the Gibbs free energy. This relationship and all others involving non ideal phases employ the use of fugacities rather than pressures. The differential molar entropy based on the same standard state is given by the well-known expression:

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_a = \left(\frac{\partial A}{\partial T}\right)_a \quad (2)$$

and the change in enthalpy  $\Delta H$ , which is equal to the net adsorption heat q taken with a minus sign, is evidently:

$$\Delta H = -q = \Delta G + T\Delta S = -A + T\left(\frac{\partial A}{\partial T}\right)_a \quad (3)$$

Along with the amount adsorbed, a, the new independent variable  $\theta$ , i.e. the degree of filling, defined by equation (4) may be introduced:

$$\theta = a/a_0 \quad (4)$$

where  $a_0$  is the limiting amount adsorbed.

The partial derivatives  $(\partial A / \partial T)_a$  can be expressed as:

$$\left(\frac{\partial A}{\partial T}\right)_a = -\left(\frac{\partial a}{\partial T}\right)_A \left(\frac{\partial A}{\partial a}\right)_T \quad (5)$$

where the partial derivative  $(\partial a / \partial T)_A$  may be further evaluated by partial differentiation with respect to temperature (at constant A) of the expression for  $\theta$  [equation (4)]. This differentiation gives:

$$\left(\frac{\partial \theta}{\partial T}\right)_A = \left[\frac{\partial(a/a_o)}{\partial T}\right]_A = \frac{1}{a_o} \left[ \left(\frac{\partial a}{\partial T}\right)_A + \alpha a \right] \quad (6)$$

where

$$\alpha = -\frac{\partial \ln(a_o)}{\partial T} \quad (7)$$

the final equation for the evaluation of the differential molar entropy is obtained:

$$\Delta S = \left(\frac{\partial A}{\partial T}\right)_a = \left(\frac{\partial A}{\partial T}\right)_o + \left(\frac{\partial A}{\partial \ln a}\right)_T \quad (8)$$

The so-called net heat of adsorption  $q$  which is less than the isostheric heat of adsorption  $Q$  by the heat of condensation  $\lambda$  is

$$q = Q - \lambda \quad (9)$$

From equations (3), (8) and (9), the expression for the evaluation of the adsorption heat  $Q$  from the adsorption isotherm follows as:

$$Q = \lambda + A - T \left(\frac{\partial A}{\partial T}\right)_o - \alpha T \left(\frac{\partial A}{\partial \ln a}\right)_T \quad (10)$$

The fundamental postulate of the potential theory which is valid for adsorption on activated carbons may then be written as:

$$\left(\frac{\partial A}{\partial T}\right)_o = 0 \quad (11)$$

By substituting the value of A from equation DA into equation (8), through the use of postulate for the differential molar entropy of adsorption subtracted from the standard state, we obtain:

$$\Delta S = -\frac{\alpha E}{n} [\ln(a_o/a)]^{1/n} \quad (12)$$

Similarly, by assuming the validity of this equation with the value of A from equation the DA into equation (14), it is also possible to obtain the equation for the net heat of adsorption  $q$  as:

$$q = E \left\{ [\ln(a_o/a)]^{1/n} + \frac{\partial T}{n} [\ln(a_o/a)]^{1/n-1} \right\} \quad (13)$$

where  $a_o$ , the limiting amount adsorbed, is given by the expression:

$$a_o = a_o^o \exp[-\alpha(T - T_o)] \quad (14)$$

The quantity  $a_o^o$  is the limiting amount adsorbed as determined from the adsorption isotherm measured at  $T_o$  which was used for the determination of the characteristic energy  $E$  as well as of the exponent  $n$ . By elimination of  $E$  from equations (13) and (14), the relationship between the entropy and the net heat of adsorption follows as:

$$\Delta S = -\alpha q \left[ \ln(a_o/a) + \frac{\alpha T}{n} \right]^{-1} \quad (15)$$

which is applicable when postulate (12) and the DA equation. Equation (15) is an expression of the well-known “compensation principle” between the heat of adsorption and the entropy. Its physical meaning is clear. The more strongly adsorbed molecules are the less mobile.

## EXPERIMENTAL

### Description of the Tian-Calvet micro calorimeter

Figure 1 shows the complete “explosion” diagram of the micro calorimeter built, which can work as an immersion calorimeter and as an adsorption calorimeter. In the figure, details are shown inside out. The part identified as 1 is the macro calorimetric cell made of stainless steel, which is embedded inside a large block which acts as heat deposit, made of aluminum, which because of its large thermal diffusion coefficient permits a rapid heat conduction to the surroundings which, in this calorimeter, consists of a Nylon block to stabilize the equipment temperature. The thermal effects are sensed through the four thermo elements connected in series to increase the sensibility of the micro calorimeter. These thermo elements, by the Seebeck effect, generate a voltage signal which is proportional to the heat flow produced from the cell. This thermoelectric potential is measured by means of a 6<sup>1/2</sup> digits Agilent multimeter, model 34349, connected to a PC through a RS-232 interface. The upper part of the adsorption micro calorimeter consists of a system made of Nylon, which acts as lid and, at the same time, has a conic device split into two parts, which permits the reception of the small vial what the porous solid has, without leaving any empty space towards the inner part.

### Electric calibration of the adsorption micro calorimeter

To establish the correct working of the micro calorimeter built to connect it to the volumetric adsorption unit, its thermal stability and sensibility were evaluated determining the constant of the calorimeter. The calibration constant relates to the voltage generated by the micro calorimeter when a heat flow is emitted from inside the micro calorimetric cell. There are two methods to determine the calibration constant (K):

#### - Determination of the calibration constant by application of electric power

This method is based on the fact that, when dispersing an energy ( $W_e$ ) through an electric resistor, the micro calorimeter is generated in voltage ( $V_t$ ), which is measured. According to Steckler, Goldberg, Tewari and Buckley [10], the micro calorimeter calibration constant (K) is given by:

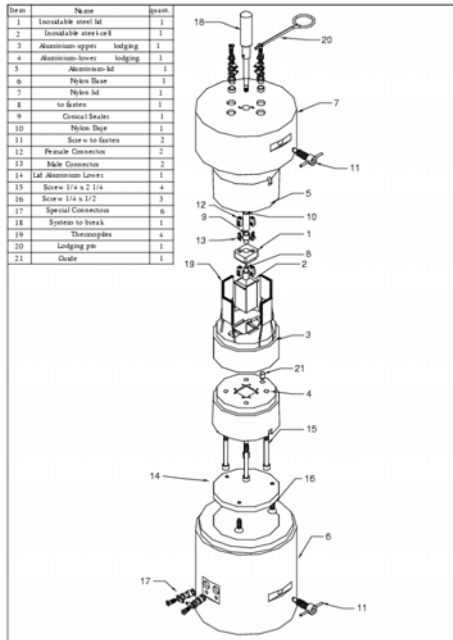


Figure 1. "Explosion" diagram of the microcalorimeter built.

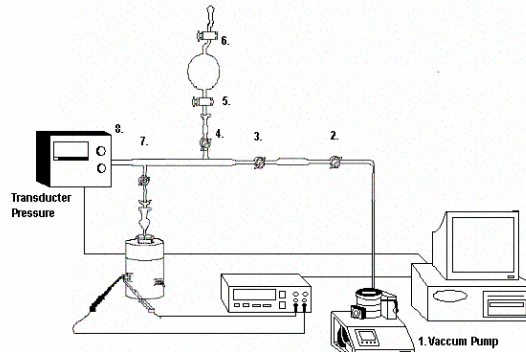


Figure 2 General diagram of USMIAH.

$$K = \frac{We}{\int V_t dt} = \frac{VIt_c}{\int V_t dt} \quad (1)$$

where  $V_c$  is the voltage provided to the resistor,  $I$  is the current that flows through it and  $t$  is the time expressed in seconds.

- Determination of the constant by stationary state method.

This is an alternate method to the one above which is used to compare and evaluate whether constant ( $K$ ) evaluated with the method above is correct. The method consists on applying a constant voltage ( $V_c$ ) through the electric resistor of the micro calorimeter until the voltage generated by the calorimeter ( $V_t$ ) reaches the condition of stationary state. Under these conditions,  $K$  is given by:

$$K = \left( \frac{V_c}{V_t} \right) \quad (2)$$

### Micro calorimeter accuracy

In order to determine the accuracy of the equipment built and according to recommendations from Kegeles, Richards, Bender, Pitzer and Moreno, Giraldo and Gómez [10-18], the accuracy of the equipment is monitored by determining the heat of neutralization THAM-HCl. For this purpose, 0,5 grams of THAM are placed in the vial and 10,0 mL of HCl 0.1 N in the microcalometric cell. Once the signal is stabilized, the vial is broken to finally obtain the thermogram. This procedure is repeated several times.

Description of the unit to simultaneously measure isotherm and adsorption heats.

Figure 2 shows a general diagram of USMIAH; the pump for ultra high vacuum (Pfeiffer Vacuum Reference TSH 071E ) is shown in part a, which is previously connected to an oil revolving pump, which permits to have a previous vacuum in all the system, so that once the system reaches a pressure of  $10^{-3}$  Torr, an ultra high vacuum pump is placed, and is allowed to act until the pressure reaches at least  $10^{-5}$  Torr.

- The porous solid (Zeolite or activated carbon) is placed and then the glass wool to prevent the solid from being dragged when vacuum is made.
- The vial is carefully mounted again.
- Then, it is placed in the oven, so that the whole body of the vial is inside and its temperature is programmed at  $250^{\circ}\text{C}$  for 24 hours, to carry out the desertion of solid impurities.
- The system is left, making sure that it reaches  $250^{\circ}\text{C}$  and  $10^{-5}$  mbar.

Taking of isotherms and adsorption heats.

- The oven is removed and, then, the MicroCal-Ad is assembled, in order to continue the simultaneous process.
- The feeding tube is dismantled to charge it with the corresponding inert gas, e.g.  $\text{CO}_2$ . Once the CFT (Calorimetric Feeding Tube) is filled
- The reading from the manometer (which consists on a pressure transducer Teledyne Hastings Instruments Model 2002) is recorded in the PC; simultaneously, the calorimetric signal resulting from the adsorption of the corresponding gas dose injected to the sample is registered in another PC.
- When the manometer's reading has stabilized vacuum is already made in all the system; this continues until 10 more points are completed, which permit to obtain isotherm and adsorption heats.

## RESULTS.

- Electric calibration of the Micro-Cal-Ad: (by applying electric power)[18] .

Table 1 measures the calibration constants obtained for the operation conditions of the micro calorimeter built. The values reported at different voltage levels are shown. It shows that the values range between  $12.34 \pm 0.12 \text{ WV}^{-1}$  and  $16.67 \pm 0.32 \text{ WV}^{-1}$ . It is shown that a higher sensitivity to equipment reported in literature is obtained and a similar one to those built in our laboratory.

Table 1 Calibration constants obtained for the manufactured heat conduction micro calorimeter obtained applying a known electrical power

Total electrical energy (J)	Electrical power (mW )	Calibration constant, K ( $\text{W}\cdot\text{V}^{-1}$ )*
4.500	25.00	$12.37 \pm 0.47$
3.000	16.00	$12.34 \pm 0.12$
2.000	9.000	$13.66 \pm 0.08$
0.700	4.000	$14.45 \pm 0.19$
0.180	1.000	$15.36 \pm 0.37$
0.045	0.250	$16.67 \pm 0.32$

\* Each reported value corresponds to the mean value of 20 measures and a certainty of 95%

Figure 3 shows a typical thermogram, which corresponds to having an electric power of 1 joule inside the cell, which contains distilled water. Form this type of thermo gram the calibration constant (K) can be obtained. It is worth pointing out the stability of the base

line before and after the thermal effect. Figure 7. A typical thermogram of electric calibration by input electric

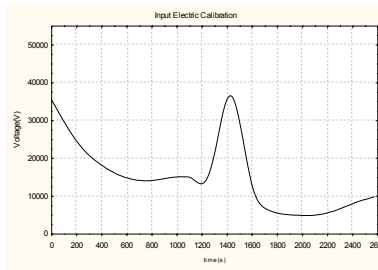


Figure 3 A typical thermogram applying electric power .

- By stationary state method.

Table 2 shows the calibration constants obtained for the equipment built. These results match those of the previous methodology and of previous laboratory works.

Table 2 Steady state calibration constants obtained for the manufactured heat conduction micro calorimeter

Applied voltage (V)	Electrical power (Mw )	Calibration constant, K ( $W \cdot V^{-1}$ )*
0.254	0.060	$14.23 \pm 0.29$
0.567	0.230	$14.45 \pm 0.25$
1.009	0.980	$13.23 \pm 0.54$
2.084	3.920	$13.28 \pm 0.34$
3.096	8.860	$12.57 \pm 0.34$
4.084	15.92	$13.98 \pm 0.34$
5.096	24.75	$12.21 \pm 0.34$

\* Each reported value corresponds to the mean value of 20 measures and a certainty of 95%

Figure 4 illustrates a thermo gram obtained when an electric power of approximately 6 mW is dispersed inside the micro calorimetric cell.

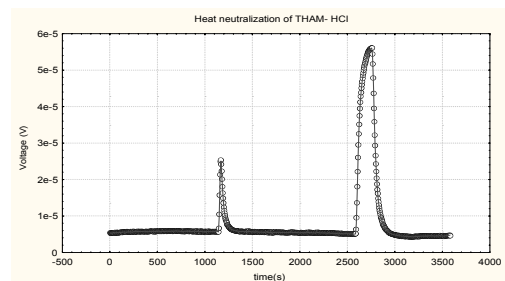
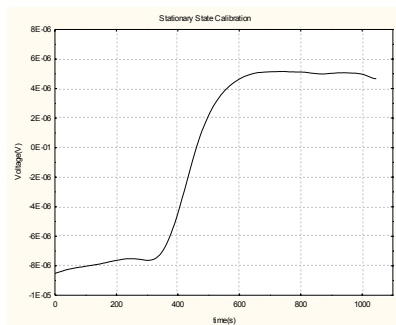


Figure 4. A typical thermogram of electric calibration by state stationary. Figure 5. Thermogram THAM-HCl heat of neutralization

\*Chemical calibration of the Microcal - Ad

Figure 5 shows a thermogram where the first sign represents THAM-HCl neutralization heat and the second corresponds to the electric calibration sign, which is made in each measurement.





during the peach pit physical activation process are shown. Figure 6 shows the isotherms obtained for the four samples analyzed, showing that these carbons have certain degree of heterogeneity; they show a different micro porosity development according to the thermal treatment to which the sample was subjected, to present later a mesopores development. Figure 7 shows some of the thermometric signs recorded, taken after each adsorbent addition; with these results and according to what was exposed in the introduction, one of the thermodynamic parameters, in this case free energy  $\Delta G$  corresponding to the adsorption for each of the activated carbon samples, is calculated. Figure 8 shows these changes in differential energy of adsorption. Only Gibbs free energy corresponding to the carbons obtained in the laboratory are shown, where a continued increase of this parameter according to the degree of coverage is observed, which can be associated to the possible tendency to a greater

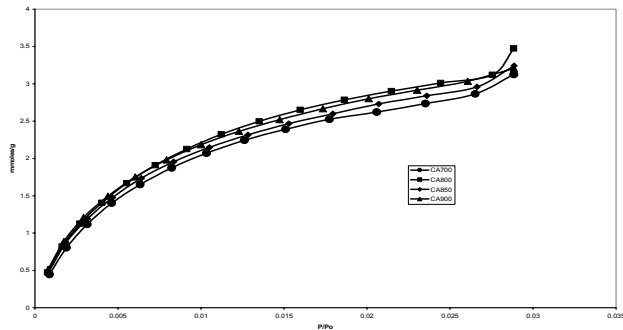


Figure 6. The isotherms obtained for the activated carbon analyzed.

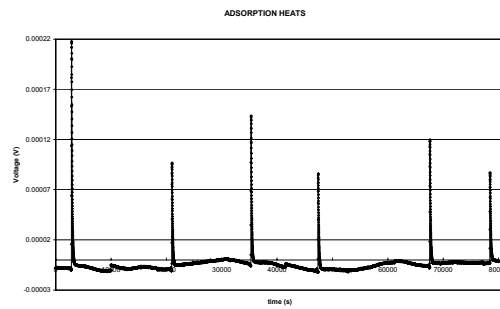


Figure 7. The thermometric signs recorded: adsorption heats.

Table No 4 Superficial characteristics of activated carbon analyzed. These values are calculated from the CO<sub>2</sub> adsorption at 298 K.

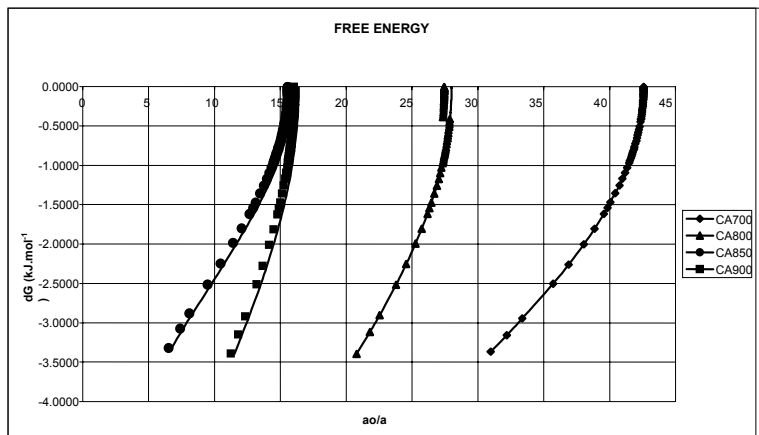


Figure 8 shows these changes in differential energy of adsorption. mobility during the adsorption process, as it is completed with the adsorbate and lateral interactions gain importance

	Vo (DR)	Eo	L
Simple	(cm <sup>3</sup> .g <sup>-1</sup> )	(kJ / mol )	( nm)
CA-750	0,289	36,48	0,432
CA-800	0,323	33,78	0,443
CA-850	0,342	35,67	0,449
CA-900	0,344	36,54	0,553

## CONCLUSIONS

USMIAH is designed and constructed, establishing its correct functioning, through the calibration of the Micro-Cal-Ad and the volumetric adsorption equipment.

For this purpose, the calibration constant for the Micro-Cal-Ad was found with values that range from  $12.34 \pm 0.12 \text{ WV}^{-1}$  to  $16.67 \pm 0.32 \text{ WV}^{-1}$  and chemically through the THAM-HCl system where the value obtained was  $-30,92 \text{ kJ.mol}^{-1}$ . Adsorption isotherms are determined for four activated carbon samples and micro pore volume value is established, with values between 0.432 and 0.553 nm, characteristic energy and average pore length. Finally, adsorption heat is directly determined microcalorimetrically for each of the samples whose values are between 25,34 and 45,34  $\text{kJ.mol}^{-1}$ .

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