Thermochimica Acta, 16 (1967) 197–211

CARBON DIOXIDE ADSORPTION BY SYNTHETIC MORDENITE

ISOTHERMS AND DIFFERENTIAL HEAT OF ADSORPTION

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(Received 12 November 1975)

ABSTRACT

Carbon dioxide adsorption isotherms by synthetic mordenite are determined over the ranges 10^{-5} atm$<P<$50 atm and -77°C$<T<+160$°C, differential heats of adsorption calorimetrically measured over 10^{-5} atm$<P<$1 atm and -77°C$<T<+120$°C.

Differential heat curves show two adsorption ranges with different energetic characteristics. At the transition a very marked maximum appears.

The integral molar entropy and specific heat of adsorbed phase are calculated.

Two methods for adsorbed phase density determination are proposed:

(i) The first, straight from maximal adsorbed amount at 50 atm. where adsorption isotherms level out.

(ii) The second, based on adsorption potential theory with an elementary graphical determination.

When the adsorbed phase density is so determined, Dubinin's equation can be successfully applied.

INTRODUCTION

During adsorption close to critical temperature, gas behaviour is a particularly interesting topic among adsorption phenomena by zeolites.

Owing to carbon dioxide characteristics, a broad range of temperature and pressure can be explored; thermal effects, calorimetrically measured, give information about adsorbent–adsorbate interactions. Consequently, adsorption isotherms have been set from 10^{-5} to 50 atm and thermal effects measured up to 1 atm.

EXPERIMENTAL

Apparatus

Sorption and thermal measurements are made at the same time between 10^{-2} and 5 Torr with a microcalorimeter connected with a classical volumetric system.

Adsorbed amounts are measured by varying the pressure knowing all different apparatus volumes. We use a flow-type differential microcalorimeter devised by Barberi[1] and commercialized by Arion-Electronique.

Thermal effects can also be measured up to 1 atm, when adsorbed amounts, which have been thermogravimetrically determined, are known.

Between 1 and 760 Torr, mass variations are measured with a Mac-Bain's type balance according to pressure and temperature.

A volumetric sorption system is perfected to measure adsorbed amounts from 1 atm up to 50 atm. For any measurement two manipulations are made: one with zeolite, the other with the same volume of inert solid instead of the sample. With both these experiments, absolute adsorption is obtained from pressure variations[2].

Experimental conditions and evaluations

Before each sorption set, the sample is evacuated by an oil diffusion pump to 10^{-5} Torr at +400°C for 10 h. The sample weight is 0.1 g or 0.2 g.

The accuracy in the amount adsorbed does not exceed 5% up to 1 atm and 10% above.

In calorimetry we are used to measuring the heat quantity ΔQ in relation to the adsorbed mole number Δn. The ratio $\Delta Q/\Delta n$ will be closer to differential adsorption heat dQ/dn as Δn is smaller.

The experimental process is such that it has a Δn value which is about 10^{-4} mol per gram of anhydrous zeolite, and ΔQ about 1 cal.

10% is the accuracy of thermal effect measurements, that we generally have with this type of apparatus[3].

Materials

The zeolite we study is synthetic mordenite with the formula: $Na_8(AlO_2)_8(SiO_2)_{40} \cdot 24H_2O$ for a unit cell. It is a powder produced by C.E.C.A. Society[4]. Its crystal structure has been studied by Meier[5].

The structure consists of infinite chains of (AlO_4) and (SiO_4) tetrahedra, so that a two-dimensional channel system appears. The main channels parallel to the c-axis are linked by small channels parallel to the a-axis. These channels have an approximately elliptical opening with a major and minor diameter of 6.95 and 5.81 Å for the main ones, 4.72 and 3.87 Å for the small ones. The volume of these channels is 0.156 cm^3 per gram of anhydrous zeolite. This number was calculated[6] and measured by adsorption of different gases[7].

DIFFERENTIAL HEATS OF ADSORPTION

Differential heat curves are plotted against the number of adsorbed moles over the range −77 to +120°C. Separate curves are obtained for each temperature. They have the same shape with three main features (Fig. 1):

The differential heat has a high value for the initial adsorbed molecules and then decreases.

It increases again and rises to a maximum.

Then it decreases continuously to a constant value. We will discuss these three points consecutively.

Initial range

Interaction between zeolitic carbon dioxide and the crystal has four components: dispersion and short-range repulsion energies ϕ_D and ϕ_R, polarization energy ϕ_P, and quadrupole energy ϕ_{FQ}. Interaction energy between pairs of carbon dioxide molecules may be omitted, because we shall be concerned only with the determination of initial heats (i.e., heats as the adsorbed amount approaches zero).

Barrer and Gibbons[8] have calculated these energies for CO_2 sorbed by ion-exchanged faujasite. Their results indicate that the most important part is played by quadrupole energy ϕ_{FQ}. These interactions, which seem to be connected more with the quadrupole moment of the CO_2 molecule than with the solid nature, may be related to the very high initial values observed. So, this first range is characteristic of a strong adsorbent–adsorbate interaction. The internal electrostatic field is stronger near sodium ions ensuring crystal-electroneutrality. Consequently, these ions may be energetic active centres leading to a strongly localized adsorption.

Taking important relative variations of q_D into account, the surface is heterogeneous for the initial adsorbed molecules and at the highest temperatures.

Maximum range

When the most energetic centres are occupied, interactions between adsorbed molecules and q_D increase. Curves show very marked maxima. This may be the consequence of increasing interactions up to the set of a new kind of sorption with different energetic features. Such a pronounced maximum at high temperatures is unusual. However, Kington and Mc Leod[9] have also noted it with carbon dioxide sorption by chabazite at 0°C. This range would be typical of strong adsorbate–adsorbate interactions with a new arrangement of adsorbed molecules leading to a new kind of sorption with different energetic features.

Terminal range

In this terminal curve part, the differential heat has small variations against the number of adsorbed moles. At any temperature the solid shows a homogeneous surface in this range; q_D values have the magnitude of liquefaction heat corresponding to the transition of molecules from the gaseous to the liquid phase. For each temperature, the differential heat tends toward a constant value. In the first range, centres have very different and high energies, in the last one, centres have lower energies, but similar to each other. This change in the sorption energy features can be seen from the important maximum noted on the curves.

Temperature influence

The important point as evidenced in Fig. 1 is that the curves are characteristic for each temperature. Few studies gave us information about temperature influence around the critical point. We can refer to Huang and Wiebel about CO_2 and SO_2 with H-mordenite[10]. For ammonia adsorption by NaA zeolite there are also different curves for each temperature[11]. On the other hand indistinguishable curves are found

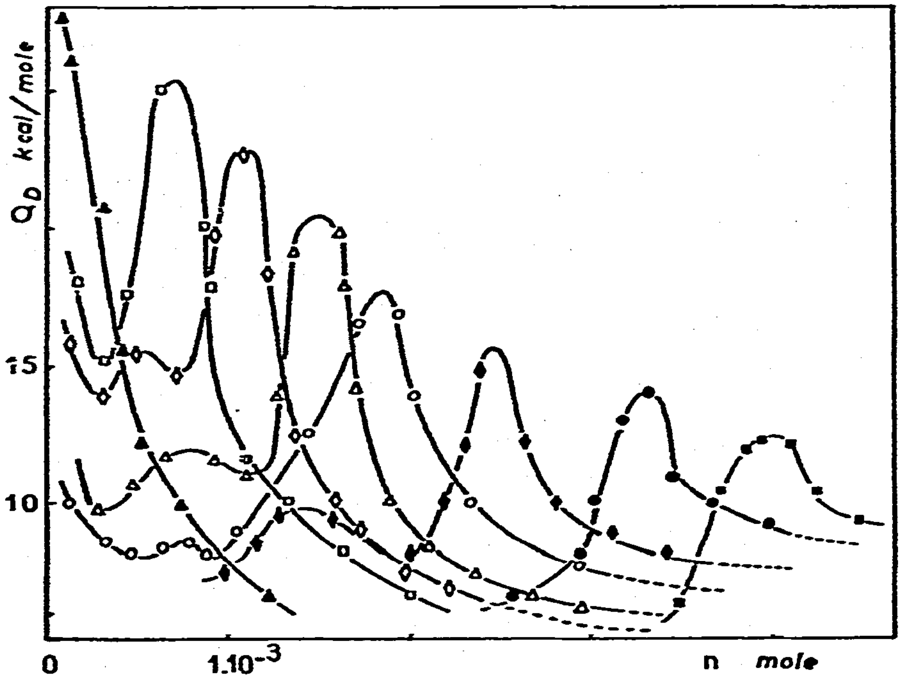

Fig. 1. Differential heat of adsorption. ■, −77°C; ●, −30°C; ◆, 0°C; ○, +20°C; △, +40°C; ◇, +60°C; □, +80°C; ▲, +120°C.

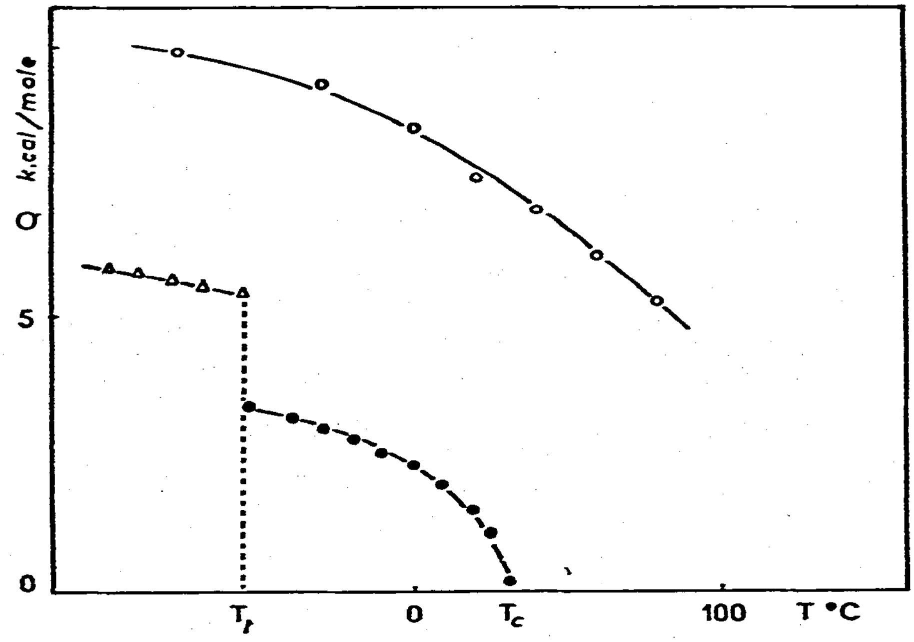

Fig. 2. Variations of differential heat q_{DL} (○), sublimation heat (△), and liquefaction heat (●) against temperature.

for nitrogen adsorption by silicagels. However, the temperature variation is small and the temperature itself is near the adsorbate boiling point[12].

Many authors speak about "initial heat". Most of the time, this value is obtained by extrapolation of the q_D versus the n curve for $n = 0$. In our case, differential heats show important variations for initial adsorbed molecules and it is difficult to extrapolate such curves. Qualitatively, it appears that the initial value is more important as the temperature is higher. Adsorption centres seem to have higher energies at high temperatures and the surface appears more heterogeneous.

The maximum intensity q_D is more important as the temperature rises. This curve range characterises strong interactions of the adsorbate-adsorbate type.Thus, motions of molecules are more intense as the temperature increases, limited by degrees of freedom let by adsorption; so interactions are all the stronger.

In the last range, the differential heat approaches a constant value q_{DL} when the number of adsorbed molecules increases. q_{DL} variations are plotted against the temperature in Fig. 2. The liquefaction heat curve and the q_{DL} curve have the same shape. It is important to note that no discontinuity appears at triple point and critical point temperature. In this range, where the number of adsorbed molecules is the most important, we can conclude that no change occurs in adsorption over the entire temperature range.

Instead of plotting differential heats against n, it is possible to plot q_D against coverage degree or filling degree θ:

$$\theta = \frac{n}{n_0}$$

n_0 is the maximal number of adsorbed molecules at temperature T, experimentally determined with isotherms set up to 50 atm, when the saturation vapor pressure is reached or when adsorption isotherms level out, above critical point.

Knowing n_0, Table 1 lists θ values in relation to the number n_M of adsorbed moles at the observed maxima of differential heat curves.

TABLE 1

DEGREES OF FILLING AT THE MAXIMUM OF DIFFERENTIAL HEAT CURVES

T (°C)	−77	−30	0	+20	+40	+60	+80	+120
$n_0 \cdot 10^{+3}$ (mol g^{-1})	4.39	3.98	3.77	3.64	3.45	3.30	3.11	2.73
$n_M \cdot 10^{+3}$ (mol g^{-1})	4.00	3.30	2.50	1.90	1.50	1.10	0.70	0.15
θ	0.91	0.83	0.66	0.51	0.43	0.33	0.22	0.05

These maxima are lower for θ values as the temperature is raised. If we assume that formation of a condensed phase is at the maximum, this would appear at degree of filling, much more important at high temperatures, and much lower at low temperatures, i.e., contrary to observations.

At the opposite, an energy distribution of the sites produced by temperature, superposed upon a numerical distribution in relation to their respective energies can explain such curves of differential heats.

At temperature T, the number of sites N_i of E_i energy is generally an exponential function of this energy:

$$N_i = C \exp\left[-\frac{E_i}{RT}\right] \tag{1}$$

C is a constant.

Sites number N_i of E_i energy is lower as this energy is higher. A sites distribution against temperature where E_i would also be a function of temperature has not been formulated. In our case, increasing temperature would lead to the formation of very energy-rich sites. So, initial q_D values would be more important as the temperature is higher. As the energy of these sites increases their number decreases, according to the exponential law of distribution (relation (1)). And so, these sites are completely occupied for rather low degrees of filling ($\theta = 0.05$ at +120°C, $\theta = 0.22$ at +80°C) where the maximum appears.

At low temperatures, the energy of the sites is low and their number much higher. So, the initial values of q_D are lower and the maximum appears for higher values of θ ($\theta = 0.66$ at 0°C, $\theta = 0.83$ at −30°C). This double distribution of sites allows us to explain the separate curves and their evolution with temperature.

THERMODYNAMIC DATA FOR ADSORBED PHASE

The molar integral entropy S_a of adsorbed phase is calculated from the relation:

$$S_a = \frac{1}{n}\int_0^n \bar{S}_a \, dn \tag{2}$$

n is the number of adsorbed moles, $\bar{S}_a$ the molar differential entropy:

$$\bar{S}_a = S_g - \frac{q_{st}}{T} \tag{3}$$

S_g is the molar integral entropy of gas and the isosteric heat q_{st} can be calculated from the experimental values of differential heat q_D:

$$q_{st} = q_D + RT \tag{4}$$

The molar integral entropy of the adsorbed phase is calculated by graphical integration of the area under the $\bar{S}_a$ versus n curve. These calculations can be made from +20 to +120°C (Fig. 3). For initial adsorbed molecules, the molar integral

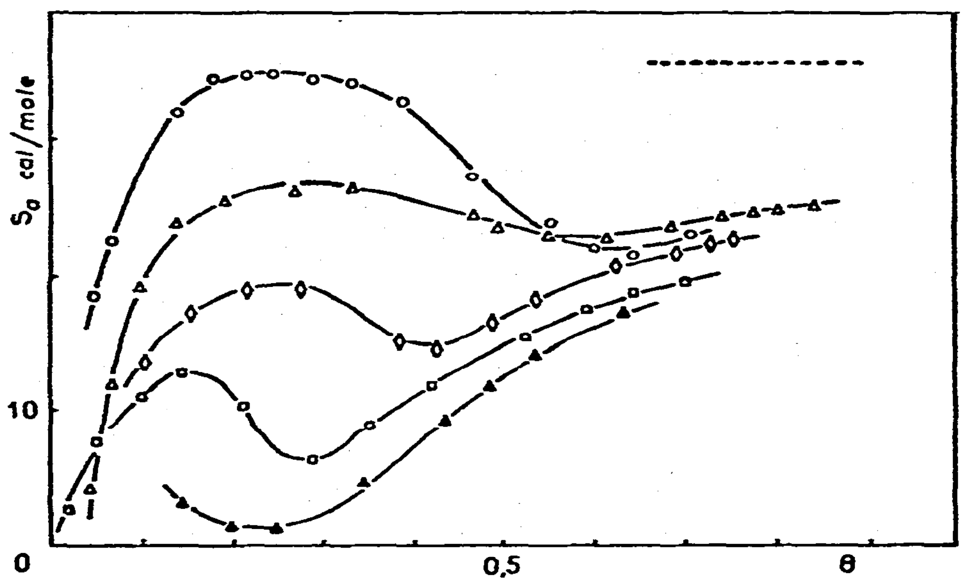

Fig. 3. Molar integral entropy of adsorbed phase. ○, +20°C; △, +40°C; ◇, +60°C; □, +80°C; ▲, +120°C; and molar entropy of liquid phase at +30°C (— — —).

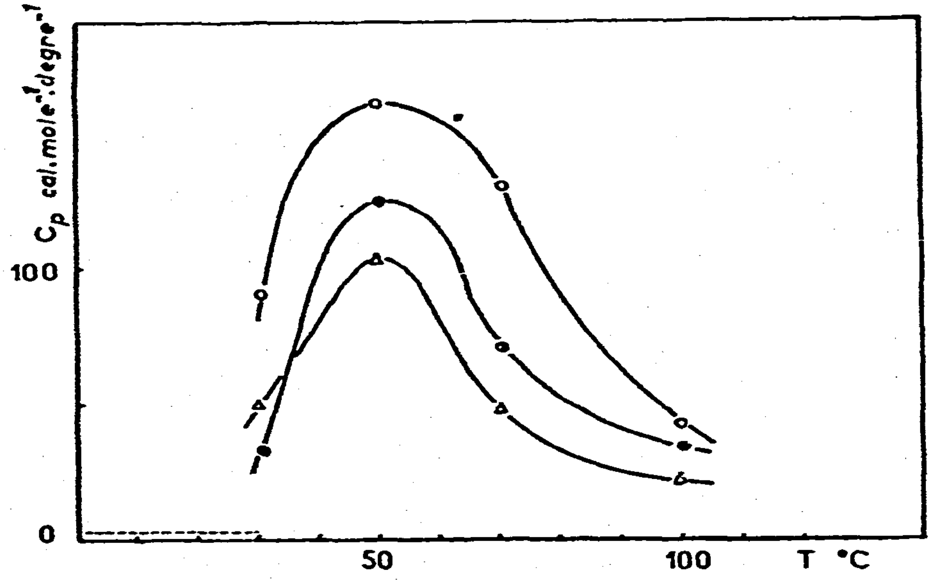

Fig. 4. Specific heat of adsorbed phase. (○) $\theta = 0.35$; (●) $\theta = 0.40$; (△) $\theta = 0.50$; and specific heat of liquid phase (— — —).

entropy is very low in relation to the well-ordered state characteristic of strongly localized adsorption. Then S_a increases and goes through a maximum, after curves approximately approach a constant value when the degree of filling becomes important. Barrer and Gibbons[8] have noted maximum and minimum on integral entropy curves for CO_2 sorption by faujasite. According to them, such curves would be characteristic of heterogeneous surfaces.

For the same degree of filling θ, the integral entropy is all the lower as the temperature is higher. This supports the assumption of formation of very energy-rich sites at high temperature in relation to the well-ordered state of adsorbed molecules.

The specific heat C_p of adsorbed phase can be calculated from the relation:

$$C_p = T\frac{dS_a}{dT} \tag{5}$$

Integral entropy curves plotted for several temperatures, ratios $\Delta S_a/\Delta T$ are calculated for each couple of similar temperatures and for several degrees of filling (Fig. 4).

Specific heat goes through a maximum between +40 and +60°C rising to values much higher than can be attributed to the liquid phase.

Similar curves are found with methane adsorption by CaA[13] and with n-heptane by the same zeolite[11]. In the first case, measurements are carried out with a drop calorimeter allowing a direct measurement of the specific heat of adsorbed phase.

Hill[14] suggested that transition between a localized and mobile sorption type could be seen by a maximum of specific heat C_p. He showed that this transition might appear at rather low temperatures (50 K), but is all the higher as the energy barrier between the sites was large. As we showed that mordenite has a heterogeneous surface from intermediate temperatures (+40°C), the observed maximum near +50°C on specific heat curves could exhibit a similar change in the adsorption. This would agree with the appearance of two adsorption ranges on differential heat and integral entropy curves: a first strongly localized type and a second with much less energy-rich sites.

On the other hand, the shape of the curves is the same as the one representing variations of specific heat during the second order Λ transformation. The main character of this transformation is that we never find two phases together, the phenomenon occurs in a single phase where the system goes through an order–disorder transformation.

Such an evolution of adsorption characteristics against temperature and number of adsorbed molecules seems difficult to be translated by an isotherm equation requiring a physical detailed representation of the phenomena.

On the other hand, Polanyi's potential theory[15], which is based on thermodynamics and where layers, mobility, interactions and energetic uniformity ideas are not considered, may be satisfactory.

ADSORPTION ISOTHERMS

Adsorption isotherms are set from 10^{-5} atm up to 50 atm and in the temperature range −77°C to +160°C with the three experimental techniques we have described before. The data are plotted in Fig. 5 in a semi-log diagram. Adsorbed amounts are given in grams per gram of anhydrous zeolite. Depending on the temperature, isotherms are like sigmoïd curves or straight lines in these coordinates, which seems to be a general characteristic for microporous materials[16]. However, in the usual m versus P diagram, these isotherms are like type I of Brunauer et al.'s classification[17]. Adsorption and desorption isotherms perfectly coïncide.

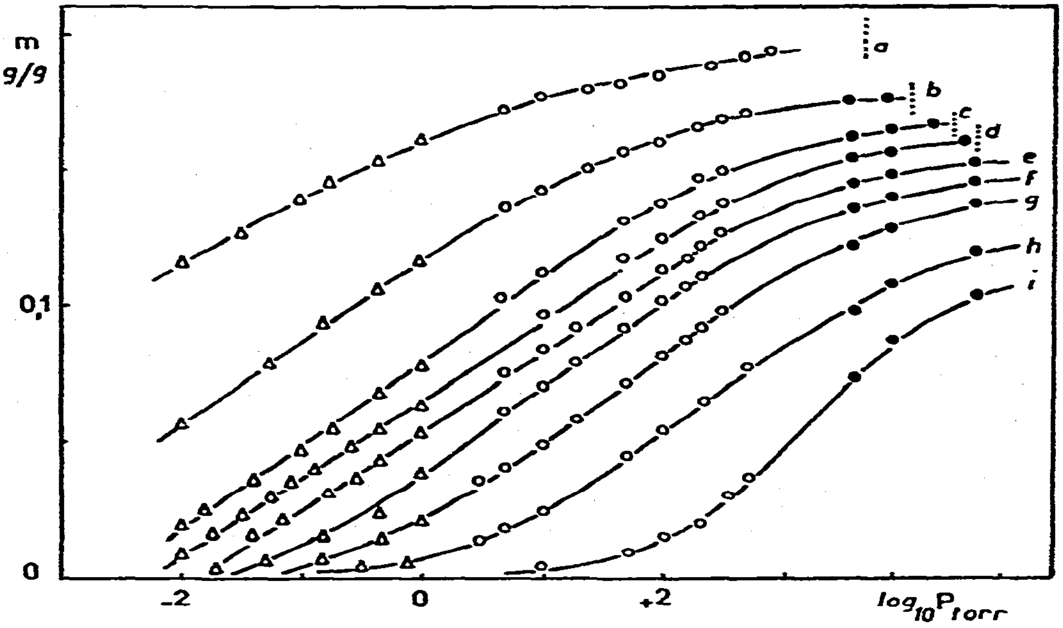

Fig. 5. Adsorption isotherms. a: −77°C; b: −30°C; c: 0°C; d: +20°C; e: +40°C; f: +60°C; g: +80°C; h: +120°C; i: +160°C. Data coming from different processes: (△) volumetry-calorimetry, (O) thermogravimetry, high pressure volumetry (●).

Isotherms have the same shape on both sides of the critical point; differential heat curves have the same property; this leads us to think that no change appears in adsorption on either side of this temperature[18,19].

ADSORBED PHASE DENSITY

Polanyi has defined the adsorption potential ε as free energy change in transferring the molecules from the gaseous to the adsorbed state:

$$\varepsilon = RT \log_e \frac{P_0}{P} \qquad (6)$$

where P is the equilibrium pressure of gas and P_0 its saturation vapor pressure at temperature T.

Let W be the adsorbed volume and m the mass adsorbed, then the adsorbed phase density can be written as:

$$\rho = \frac{m}{W} \tag{7}$$

This theory states basically that W versus ε curve, i.e., the so-called characteristic curve, is temperature independent. Its universality has been widely proved.

When the isotherm temperature is much lower than the critical point of the adsorbate, it is known that adsorbed phase density ρ can be taken equal to the density of the liquid at the same temperature. When the temperature is higher than the critical point, P_0 and ρ have no existence.

According to Lewis et al.[20] the $\log_e P_0$ versus T^{-1} curve is linearly extrapolated at temperatures above the critical point and we replace P by its fugacity at any temperature. This assumption has been widely used and is satisfactory[21,22].

When micropores filling is important, adsorbed phase is like a condensed phase similar to a liquid in many points of view, even above the critical point. This is the reason why we can assume the density idea in this filling range. Molecule area in B.E.T. theory is substituted by adsorbed phase density for microporous materials.

We propose two processes to determine density: a purely experimental one[2], and another called equipotential curves process based on potential theory and using an easy graphical method[22].

Experimental determination

Isotherms set up to 50 atm, saturation vapor pressure is reached at +15°C. At this pressure, the adsorbed amount m_0 represents the whole micropore filling W_0. We can so determine the adsorbed phase density:

$$\rho = \frac{m_0}{W_0} \tag{8}$$

W_0 was determined before[7]. The adsorbed amount on external surfaces of crystallites can be neglected in comparison with the amount adsorbed in the micropores[23].

Above the critical point, from +40 to +120°C, isotherms level out corresponding to saturation of micropores. Table 2 lists m_0 and ρ values so determined.

TABLE 2

m_0 AND ρ VALUES AT THE SATURATION OF MICROPORES

T (°C)	−30	0	+20	+40	+60	+80	+120
m_0 (g g^{-1})	0.175	0.166	0.160	0.152	0.145	0.137	0.120
ρ (g cm^{-3})	1.12	1.06	1.02	0.97	0.93	0.88	0.77

Equipotential curves

Initial assumptions are:

Characteristic curve $W = f(\varepsilon)$ exists.

Dependence of ρ on amount adsorbed is neglected relative to the dependence of ρ on temperature.

ρ is taken equal to liquid density ρ_L at equal or lower temperatures than triple point.

The curves plotting the logarithm of the adsorbed amount m against the temperature at constant adsorption potential are called equipotential curves:

$$(\log_{10} m)_\varepsilon = f(T)$$

We proved these curves must translate one from the others along y-axis, at various adsorption potential values[22].

On the other hand, the main interest of these curves is that in $\log_{10} \rho$ and $(\log_{10} m)_\varepsilon$ follow the same variations law against temperature on each equipotential curve. To obtain the real curve we only need a ρ value at T, which is given by the third assumption.

Figure 6 shows equipotential curves at various ε values. Translation is well confirmed in the whole temperature range and these curves allow to determine ρ

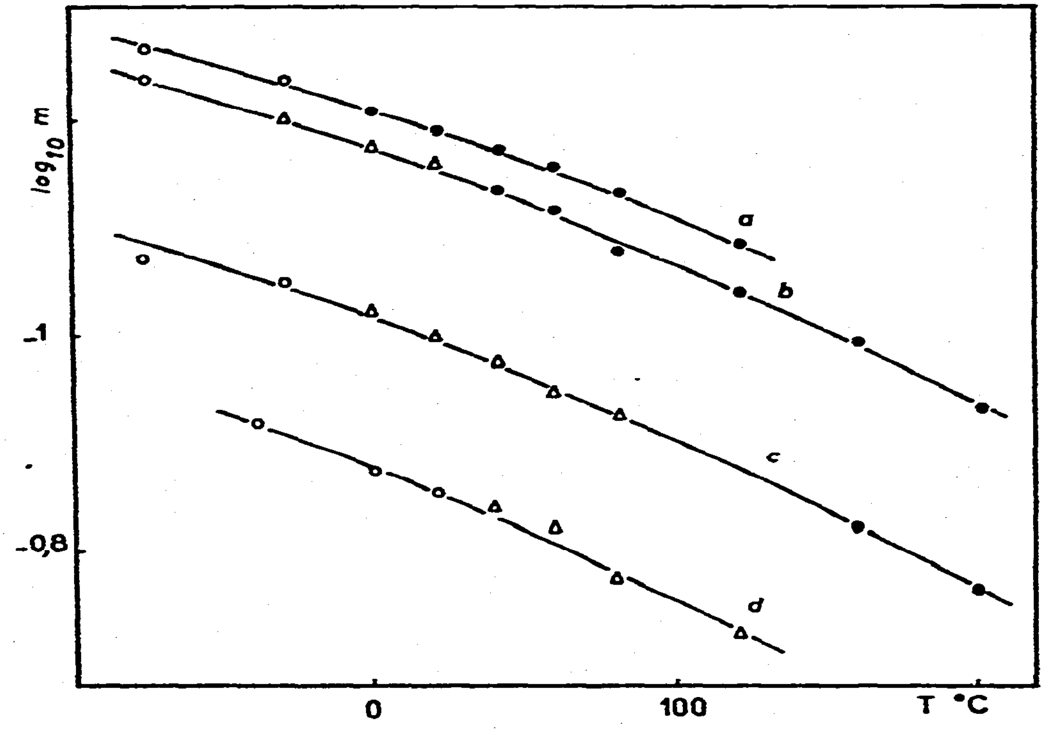

Fig. 6. Equipotential curves. a: $\varepsilon = 1.150$ cal; b: $\varepsilon = 2.300$ cal; c: $\varepsilon = 4.600$ cal; d: $\varepsilon = 5.750$ cal. Data coming from different processes: (△) volumetry-calorimetry, (○) thermogravimetry, high pressure volumetry (●).

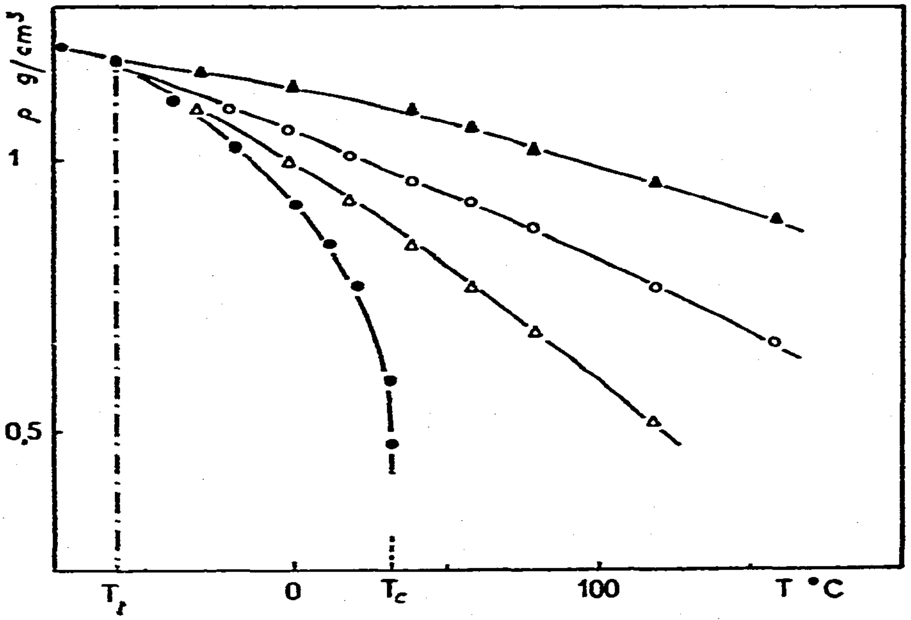

Fig. 7. Density variations against temperature, of liquid phase (●), of adsorbed phase by acid mordenite (△), sodic mordenite (○), and a 22% strontium exchanged form (▲).

variations against temperature (Fig. 7). In this figure the curves obtained with H-mordenite and a 22% strontium exchanged form are also plotted[2,24].

Discussion

According to the two processes, values obtained are in very good agreement. The following three remarks can be noted:

(i) No discontinuity appears in the plot of adsorbed phase density through critical point.

(ii) Above the critical temperature, the adsorbed phase density has the same magnitude as the liquid phase density. But at the same temperature, the adsorbed phase appears always more dense than the liquid phase. This last remark was often made[25,26].

(iii) Separate curves are obtained for each adsorbent, and separate from the liquid phase curve. According to several works, this aspect seems to be general[22,27,28].

CHARACTERISTIC CURVE

Knowing the adsorbed phase density, the characteristic curve $W = f(\varepsilon)$ can be plotted (Fig. 8). A single curve is obtained, even at the lowest fillings and it presents the general shape of a Gaussian curve.

Polanyi's potential theory, which translates by a single characteristic curve, is perfectly confirmed. It would be evident if the adsorbed phase density was only determined by equipotential curves as this process assumes that the characteristic curve exists. But the purely experimental process does not require any equation; thus, it proves that the adsorption potential theory is successfully applied.

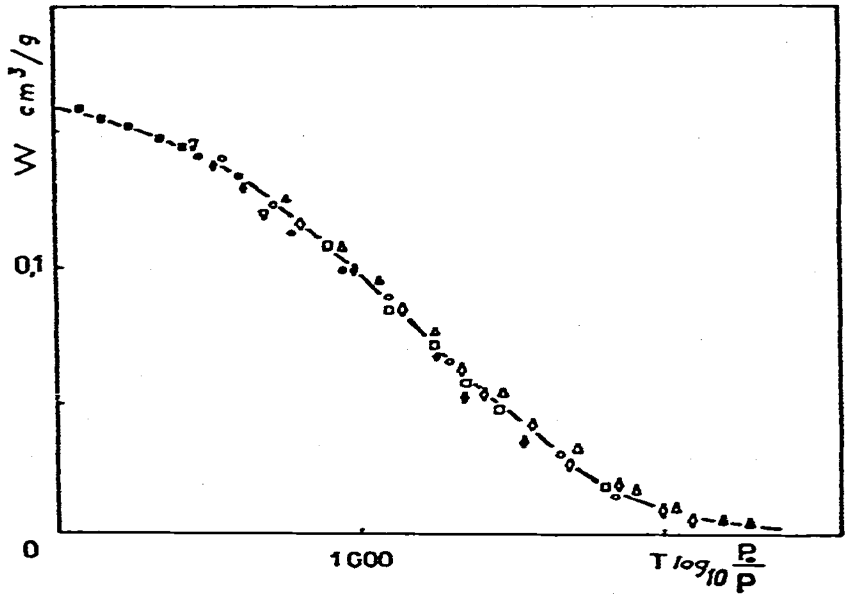

Fig. 8. Characteristic curve. ■, −77°C; ●, −30°C; ◆, 0°C; △, +40°C; ◇, +60°C; □, +80°C; ▲, +120°C; ▽, +160°C.

For high degrees of filling, the density idea is grounded for the adsorbed phase. A single characteristic curve is also obtained at the lowest degrees of filling; so, it can be assumed this density idea is useful to yield experimental isotherms very well, even if it has no physical reality.

ISOTHERM EQUATION

According to Gaussian shape of the characteristic curve, Dubinin[29] proposed the following analytical equation:

$$W = W_0 \exp(-k\,\varepsilon^2) \tag{9}$$

where k is a constant depending upon the adsorbent–adsorbate system.

From relations (6) (7) and (8) we can write:

$$\log_{10} W = \log_{10} W_0 - D\left[T \log_{10} \frac{P_0}{P}\right]^2 \tag{10}$$

where $D = 2.3R^2k$

When plotting $\log_{10} W$ against $(T \log_{10} P_0/P)^2$ a single straight line must be obtained. This test is successfully carried out (Fig. 9) using the ρ values we have determined.

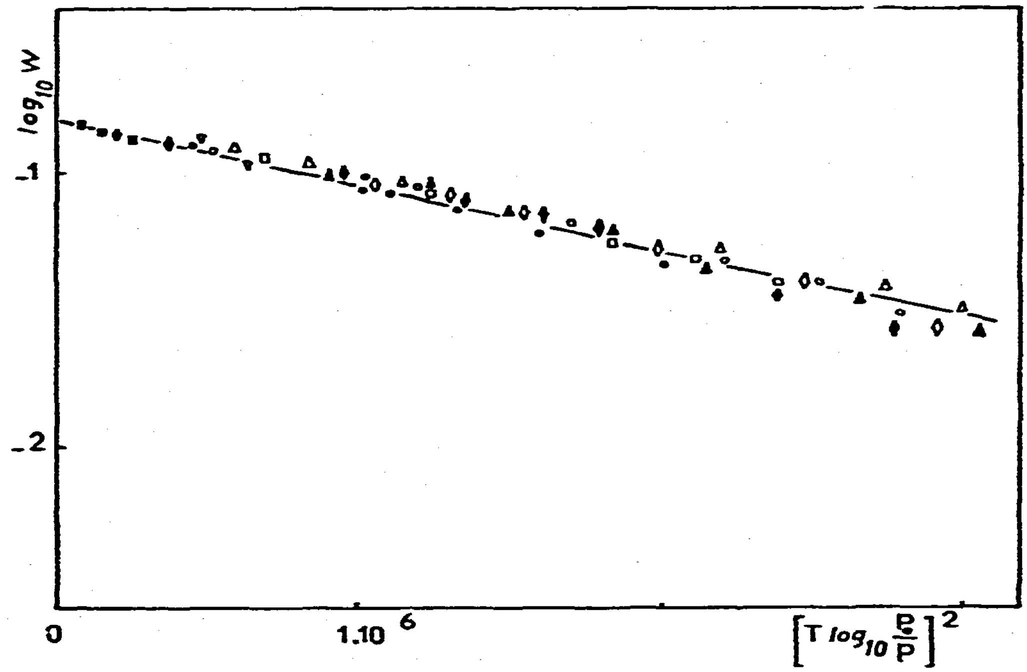

Fig. 9. Dubinin's plot of characteristic curve. ■, −77°C; ●, −30°C; ◆, 0°C; △, +40°C; ◇, +60°C; □, +80°C; ▲, +120°C; ▽, +160°C.

CONCLUSION

Thermal effects calorimetrically measured have given important information about the nature of interactions between carbon dioxide and synthetic mordenite. They are not so elementary as theoreticians would like.

The data show two adsorption ranges:

(i) The first, related to strongly localized adsorption and a heterogeneous surface; the more so the higher temperature.

(ii) The second is characterized by sites of identic and low energies.

The differential heat curves go through a pronounced maximum between the two ranges, indicating strong interactions between adsorbed molecules. The temperature dependence of maxima and curves themselves lead to the assumption that there is a double distribution of sites:

one, as a function of temperature: its increasing leads to formation of very energy-rich sites;

the other, as a function of the respective energies of these sites: the most energetic are fewer.

The shape of the integral entropy experimental curves and that of the specific heat of adsorbed phase curves both support these assumptions.

Two methods for determining adsorbed phase density were used:

an experimental one which consists in measuring the maximal adsorbed amount from adsorption isotherms set up to 50 atm;

equipotential curves method, graphical and elementary, based on generally admitted assumptions.

When the adsorbed phase density is so determined, the adsorption potential theory is successfully applied, as the isotherms equation proposed by M. M. Dubinin.

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