



Determination of the Kinetic and Thermodynamic Parameters of Adsorption Processes by a Volume Step Thermal Method

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Abstract. A volume step method measuring the pressure and the adsorbent temperature of an adsorbent-adsorbate system has been developed. It is shown that this method allows the determination of all the relevant parameters of an adsorption process, kinetic as well as thermodynamic in case of Linear Driving Force mass transfer. The method for determining the parameters can be extended to the case of diffusive mass transfer if the mass transfer kinetics is faster than the heat transfer kinetics. An example is given, showing the determination of the diffusion coefficient of carbon dioxide in NaX zeolite pellets and the change of the diffusion coefficient and of the isosteric heat of adsorption when the adsorbent is not fully dehydrated.

Keywords: diffusion, kinetics, adsorption heat, measurement method, NaX, carbon dioxide

Introduction

The constant-volume-variable-pressure method has been widely used for a long time for uptake measurements (for instance: Brandt and Rudloff, 1964; Riekert, 1971; Kärger et al., 1982; Bülow et al., 1980). It consists in a sudden change of the adsorbate concentration by opening and closing shortly a valve between the sorption vessel and a dosing volume. The pressure is recorded after the concentration step allowing, in principle, the determination of the sorption kinetics.

The sample under study consists of adsorbent particles, which can be either monodispersed (for instance zeolite crystals) or bidisperse (for instance pellets of zeolite crystals agglomerated by a binder). In the general case, the mass transfer is limited by Fickian diffusion or by surface barrier resistance at both levels of porosity. The internal heat transfer is limited by the thermal conductivity of the particles and the sample exchanges heat with the surroundings through a finite heat transfer conductance. Many models have been developed to account for uptake of such adsorbent particles under

constant pressure or constant volume conditions. Because the complete process is complex, an analytical solution is obtained only in simplified cases:

- Monodispersed, isothermal (Crank, 1956)
- Bidisperse, isothermal (Ruckenstein et al., 1971; Dubinin et al., 1975; Ma and Lee, 1976)
- Monodispersed, non-isothermal (Ruthven and Lee, 1981; Haul and Stremming, 1983; Kocirik et al., 1984)
- Monodispersed, isothermal, surface barrier resistance (Marutovskii and Bülow, 1984)
- Monodispersed, non-isothermal, surface barrier resistance (LDF) (Sircar, 1983; Sircar and Kumar, 1984)

The complete model: bidisperse, non-isothermal, taking into account the Fickian diffusion and surface barrier and the thermal conductivity of the particles, can be solved numerically. (Sun and Meunier, 1987).

Due to the heat of adsorption, the adsorbent temperature is not constant: it increases at the beginning and returns to its initial value at the end of the process.

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The mass transfer kinetics and the heat transfer kinetics are coupled and are difficult to separate, when only the pressure is measured.

To improve the efficiency of the method, an apparatus has been developed at LIMSI which allows the measurement of the sample temperature as well as the pressure after the concentration step (Bourdin et al., 1998). The temperature is measured by infrared detection, insuring that no perturbation of the sample temperature occurs during the course of the experiment, and that the measured temperature is effectively the sample temperature, whatever the steepness of the temperature change. Moreover the concentration step is obtained without a valve, by reducing the volume of the experimental chamber which is closed by bellows. That allows very steep changes of the concentration, the bellows being compressed in less than 20 ms, and thus it is possible to measure fast kinetics. This is the basis of the “Volume Step Thermal Method” (VSTM) for adsorbent-adsorbate system characterisation. VSTM may be considered as an improvement of the “Single Step Frequency Response method” (Van-Den-Begin et al., 1989) where only the pressure is measured.

The aim of this paper is to show that the simultaneous measurement of the sample temperature and of the pressure allows the determination of all the relevant parameters of the system, and thus the clear separation of the mass transfer kinetics from the heat transfer kinetics.

Theory

A volume step experiment is carried out as follows: the sample of adsorbent particles is placed in a variable-volume chamber of initial volume V_0 filled with the adsorbate gas at pressure P_0 . The wall temperature T_0 is maintained constant during the experiment. When the system is at equilibrium, the chamber volume is suddenly reduced to V_e by compression of the bellows. A typical recording of the pressure and of the temperature is shown on Fig. 1. The pressure rises suddenly during the bellows compression, afterwards it begins to decrease as a result of the adsorption. The sample temperature rises as a consequence of the heat released by the adsorption. It reaches a maximum and decreases afterwards until it returns to the equilibrium temperature T_0 . When, at the end of the experiment, the new equilibrium is reached, the pressure stays at a final pressure, P_f .

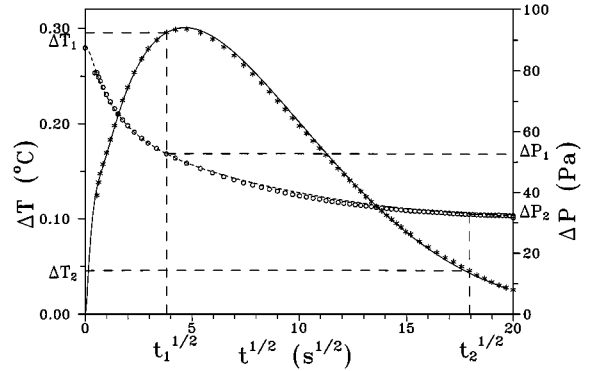


Figure 1. Anhydrous NaX zeolite experiment at 302 K and 105 kg m^{-3} CO_2 loading. (*), (—) temperature and (○), (---) pressure experimental and calculated responses respectively. The calculated curves has been obtained knowing the heat of sorption a priori. The dotted straight lines indicate the points for calculating the partial integrals.

Monodispersed Model

We will at first examine the case of monodispersed particles. All the particles are assumed to be identical, of regular geometrical shape (plane, cylindrical or spherical) and in identical physical conditions.¹ It will be assumed that only the following parameters are known before the experiment:

- Chamber volume before and after bellows compression, V_0 and V_e respectively.
- Sample volume, V_s .
- Radius of the particles, R_c .

The other relevant parameters of the process are the following:

- Differential heat of sorption, $|\Delta H|$.
- Slopes of the isotherm, $K_P = (\frac{\partial q}{\partial P})_{T_0, P_0}$ and of the isobar, $K_T = -(\frac{\partial q}{\partial T})_{P_0, T_0}$.
- Overall volumic heat capacity of the sample, C_s , which is the sum of the heat capacity of the adsorbent and the heat capacity of the adsorbed phase, per volume unit of the adsorbent.
- Heat transfer coefficient, h , between the sample and its surroundings.
- Mass transfer characteristic time, τ_m which can be split into diffusion characteristic time τ_D and surface barrier characteristic time τ_s .

The equations governing the adsorption process are:

Overall mass balance:

$$\frac{PV_e}{R_e T_0} + V_s \bar{q} = \frac{P_M V_e}{R_e T_0} + V_s q_0 \quad (1)$$

where P is the pressure and P_M is the calculated maximum pressure after the step and before any adsorption. q_0 is the (uniform) adsorbate concentration in the initial state and \bar{q} is the average adsorbate concentration in a crystal. R_e is the specific constant of the gas. The maximum pressure P_M is calculated assuming that the gas remains isotherm² and assuming an instantaneous compression:

$$P_M = P_0(1+k) \quad \text{with} \quad k = (V_0 - V_e)/V_e \quad (2-3)$$

The compression factor k is reduced to a small value in order to insure the linearity of the system: all the parameters will be considered constant during the whole process.

Heat balance:

$$C_s \frac{dT}{dt} + \frac{(\sigma + 1)h}{R_c}(T - T_0) = |\Delta H| \frac{d\bar{q}}{dt} \quad (4)$$

R_c is the crystal radius and σ is a shape factor (0, 1 or 2 for a plane, cylinder or sphere respectively). All crystals are assumed to have the same regular geometry and to be in identical physical conditions.

Because zeolite crystals are always small (mostly less than 100 μm in the larger dimension) the heat diffusion in the crystals is very fast and the sample temperature, T , can be considered uniform ($\text{Bi} \ll 1$ and $\text{Le} \gg 1$ (Sun and Meunier, 1987)).

State equation:

The adsorbate concentration at thermodynamical equilibrium, q^* , is given by the state equation

$$q^* = q(P, T) \quad (5)$$

In a linearized form, it can be written:

$$\Delta q^* = K_p \Delta P - K_T \Delta T \quad (6)$$

The symbol Δ indicates the difference between the quoted parameter and its initial value (q_0 , P_0 and T_0 respectively)

Mass Transfer in the Adsorbent

It is assumed that the mass transfer obeys the Fickian diffusion law inside the particle and that there exists a

transfer resistance at the surface (Kocirik et al., 1990):

$$\begin{aligned} \frac{\partial q}{\partial t} &= \frac{D_c}{r^\sigma} \frac{\partial}{\partial r} \left(r^\sigma \frac{\partial q}{\partial r} \right) - D_c \frac{\partial q}{\partial r} \Big|_{r=R_c} \\ &= k_c (q|_{r=R_c} - q^*) \quad \frac{\partial q}{\partial r} \Big|_{r=0} = 0 \end{aligned} \quad (7-9)$$

where D_c is the diffusion coefficient, and k_c is the surface barrier coefficient.

At the end of the process, when equilibrium is reached, the adsorbed mass q_f is given by the state equation at temperature T_0 and pressure P_f . Let us define the constant K as:

$$K = R_e T K_p \frac{V_s}{V_e} \quad (10)$$

The mass conservation Equation 1 allows the determination of K :

$$K = \frac{\Delta P_M - \Delta P_f}{\Delta P_f} \quad (11)$$

and thus the slope of the isotherm, K_P .

Linear Driving Force Model

Following the work of (Sircar, 1983), we will first analyse the case where the mass transfer is governed by a Linear Driving Force. That come down to neglect the diffusion mass transfer resistance. Thus the concentration is uniform throughout the adsorbent particle. The mass transfer equations is:

$$\frac{dq}{dt} = \frac{(\sigma + 1)k_c}{R_c} (q^* - q) = \frac{q^* - q}{\tau_m} \quad (12)$$

In that case it is possible to solve analytically the equations of the system. The solutions for the pressure and the temperature are given by:

$$\begin{aligned} \frac{\Delta P}{\Delta P_M} &= \frac{1}{1 + K} + \frac{K}{1 + K} \frac{1}{(\tau_1 - \tau_2)} \\ &\times \left[(\tau_1 - \tau_h) e^{-\frac{t}{\tau_1}} + (\tau_h - \tau_2) e^{-\frac{t}{\tau_2}} \right] \end{aligned} \quad (13)$$

and

$$\Delta T = \frac{|\Delta H|}{C_s} K_p \Delta P_M \frac{\tau_h}{(\tau_1 - \tau_2)} \left(e^{-\frac{t}{\tau_1}} - e^{-\frac{t}{\tau_2}} \right) \quad (14)$$

with:

$$\begin{aligned}\frac{1}{\tau_1} &= \frac{B}{2} (1 - \sqrt{1 - 4C/B^2}) \\ \frac{1}{\tau_2} &= \frac{B}{2} (1 + \sqrt{1 - 4C/B^2})\end{aligned}\quad (15-16)$$

$$B = \frac{\tau_m + (1 + K + \gamma)\tau_h}{\tau_m \tau_h} \quad C = \frac{1 + K}{\tau_m \tau_h} \quad (17-18)$$

$$\tau_m = \frac{R_c}{(\sigma + 1)k_c} \quad \tau_h = \frac{R_c C_s}{(\sigma + 1)h} \quad \gamma = \frac{|\Delta H| K_T}{C_s} \quad (19-21)$$

Assuming $\tau_m \ll \tau_h$ a first order development gives the following time constants:

$$\tau_1 = \frac{1 + K + \gamma}{1 + K} \tau_h \left[1 + \frac{\gamma}{(1 + K + \gamma)^2} \frac{\tau_m}{\tau_h} + o\left(\frac{\tau_m}{\tau_h}\right) \right] \quad (22)$$

$$\tau_2 = \frac{1}{1 + K + \gamma} \tau_m \left[1 - \frac{\gamma}{(1 + K + \gamma)^2} \frac{\tau_m}{\tau_h} + o\left(\frac{\tau_m}{\tau_h}\right) \right] \quad (23)$$

Moments

Because the change of the adsorbed mass concentration Δq is proportional to the pressure change, the zero moment of the normalized complementary uptake M_q^0 is the same as the zero moment of the normalized pressure change:

$$M_q^0 = \int_0^\infty \frac{\Delta q_f - \Delta q}{\Delta q_f} dt = \int_0^\infty \frac{\Delta P - \Delta P_f}{\Delta P_M - \Delta P_f} dt \quad (24)$$

M_q^0 can be calculated by Eq. (13) giving the pressure profile:

$$M_q^0 = \frac{1}{1 + K} (\tau_m + \gamma \tau_h) \quad (25)$$

Similarly the two first moments of the temperature profile can be calculated from Eq. (14):

$$\begin{aligned}M_T^0 &= \frac{|\Delta H|}{C_s} K_p \Delta P_f \tau_h; \\ M_T^1 &= \frac{1}{1 + K} M_T^0 [\tau_m + (1 + K + \gamma)\tau_h]\end{aligned} \quad (26-27)$$

Thus the heat transfer characteristic time τ_h can be expressed simply:

$$\tau_h = \frac{M_T^1}{M_T^0} - M_q^0 \quad (28)$$

Let us consider now the temperature profile at large time. Because $\tau_2 < \tau_1$, the second exponential term in Eq. (14) becomes negligible and $\ln(\Delta T)$ is a straight line intersecting the origin at $\ln(Y_0)$ where Y_0 is expressed as follows:

$$Y_0 = \frac{1}{U} \frac{|\Delta H|}{C_s} K_p \Delta P_M \quad (29)$$

with

$$\begin{aligned}U &= \frac{\tau_1 - \tau_2}{\tau_h} \\ &= \left[(1 + K + \gamma)^2 - 2(1 + K - \gamma) \frac{\tau_m}{\tau_h} + \left(\frac{\tau_m}{\tau_h} \right)^2 \right]^{1/2}\end{aligned} \quad (30)$$

Defining the known quantity M as:

$$M = \frac{(1 + K)}{\tau_h} M_q^0 = \gamma + \frac{\tau_m}{\tau_h} \quad (31)$$

Eqs. (30) and (31) allow the calculation of γ :

$$\gamma = \frac{U^2 - (1 + K - M)^2}{4(1 + K)} \quad (32)$$

Parameter Determination

It is now possible to express explicitly all the unknown parameters:

- Eqs. (10) and (11) give the slope of the isotherm, K_p .
- Eq. (28) gives τ_h and Eq. (20) gives the ratio $A = h/C_s$:
- knowing τ_h , Eq. (26) gives the ratio $B = |\Delta H|/C_s$.
- then Eq. (29) gives the parameter U , Eq. (32) gives the parameter γ , and Eq. (21) gives the slope of the isobar, K_T .

Knowing the slopes of the isotherm and of the isobar, the Clausius-Clapeyron equation gives the differential heat of sorption:

$$|\Delta H| = \frac{R_e T_0^2}{P_0} \frac{K_T}{K_p} \quad (33)$$

Then C_s and h are determined by the previously determined ratios $B = |\Delta H|/C_s$ and $A = h/C_s$. Finally the mass transfer characteristic time τ_m is determined by the zero mass moment (Eq. (25)) and Eq. (12) gives the surface barrier coefficient k_c .

One can see that the experimental temperature and pressure profiles are sufficient to determine unambiguously all the physical parameters of the system, thermodynamic as well as kinetic.

Alternative Parameter Determination

It has been shown that the parameters of the system can be determined using the zero moment of the mass and the two first moments of the temperature. However the determination of the temperature moments from experimental data is not accurate, due to the drifts always occurring at large time. To avoid this drawback, the following method is used:

Consider the recordings of the pressure and the temperature after a step. On these records 2 points are selected at times t_1 and t_2 (pressures P_1 and P_2 , temperatures T_1 and T_2) chosen as follows (Fig. 1):

- t_1 is chosen to be an instant at which the energy released towards the walls is small compared to the energy released by the adsorption (for instance the moment where the temperature is close to the maximum).
- t_2 is large, but small enough to avoid the errors due to the drifts.

The masses adsorbed between the instants t_0 and t_1 , and between t_0 and t_2 can be deduced from the pressure. They are:

$$\Delta q_i = q_i - q_0 = \frac{V_e}{V_s R_e T_0} (P_M - P_i) \quad i = 1, 2 \quad (34-35)$$

The heat balance Eq. (4) integrated from t_0 to t_1 and t_2 gives:

$$C_s \Delta T_i + \frac{(\sigma + 1)h}{R_c} I_i = |\Delta H| \Delta q_i \quad i = 1, 2 \quad (36-37)$$

where $I_i = \int_{t_0}^{t_i} \Delta T dt$.

This partial integration method allows to obtain the ratio $A = h/C_s$ (and then the characteristic time τ_h) and the ratio $B = |\Delta H|/C_s$ previously obtained by the

temperature moments:

$$A = \frac{h}{C_s} = \frac{1}{\tau_h} \frac{R_c}{(\sigma + 1)} \quad (38)$$

$$B = \frac{|\Delta H|}{C_s} = \frac{I_1 \Delta T_2 - I_2 \Delta T_1}{I_1 \Delta q_2 - I_2 \Delta q_1} \quad (39)$$

The accuracy on the parameters A and B obtained by this method depends strongly on the characteristics of the adsorbent-adsorbate system as well as on the accuracy of the pressure and temperature sensors and on the stability of the chamber wall temperature. With the LIMSI equipment, an accuracy of a few percent can be obtained with adsorbent-adsorbate systems having a moderate heat of sorption (~ 1 MJ/kg such as NaX-CO₂ system).

Solution in the Fickian Diffusion Case

Most often the dominant mass transfer mode in an adsorbent sample is diffusive, i.e. the mass transfer obeys the Fickian law with eventually an addition of a surface barrier effect.

Using the Laplace Transform and the Van der Laan theorem, it can be shown (Sun, 1988) that the moments can be expressed in a very similar form as in the LDF case, the mass transfer characteristic time, τ_m , being the sum of the diffusive mass transfer characteristic time and the surface barrier characteristic time, i.e.:

$$\tau_m = \tau_D + \tau_s = \frac{R_c^2}{(\sigma + 1)(\sigma + 3)D_c} + \frac{R_c}{(\sigma + 1)k_c} \quad (39)$$

Thus all equations used to determine the system parameters remain valid except Eq. (29): the final slope of the temperature curve is not the same when the mass transfer is diffusive or due to a surface barrier.

In the diffusion case, without surface barrier resistance, the analytical solution has been given by (Kocirik et al., 1984). It involves a transcendental equation and the parameter “ U ” (Eq. (29)) cannot be expressed as a function of the other parameters. Nevertheless, if we assume that the mass transfer kinetics is much faster than the heat transfer kinetics, i.e. that the ratio τ_m/τ_h is a small quantity, it is possible to calculate

a development of “ U ”:

$$U = (1 + K + \gamma) \left[1 - \frac{1 + k - \gamma}{(1 + K + \gamma)^2} \frac{\tau_m}{\tau_h} - \alpha \left(\frac{\tau_m}{\tau_h} \right)^2 \right] \quad (40)$$

with:

$$\alpha = \frac{(1 + K)}{7(1 + K + \gamma)^4} [3(1 + K + \gamma)(1 + K - 2\gamma) - 14\gamma] + o\left(\frac{\tau_m}{\tau_h}\right) \quad (41)$$

the quantity $o(\tau_m/\tau_h)$ tending towards 0 with τ_m/τ_h .

“ U ” is the same as in the LDF case at the first order, as deduced from Eq. (30), but it differs at the second order. Thus, when the mass transfer characteristic time is small enough compared to the heat transfer characteristic time, the parameters can be calculated in the Fickian case in the same way as in the LDF case.

In order to estimate the error occurring when Eq. (32) is applied in the Fickian case, synthetic data files have been calculated running a numerical model with parameters representative of usual experimental conditions ($K = 1$, $\gamma = 0.5$), with various ratios τ_m/τ_h . It has been found that errors on the parameters determination remain less than 3% when $\tau_m/\tau_h < 0.5$. Thus the determination of the thermodynamic parameters in the most general case must be restricted by the condition $\tau_m < 0.5 \tau_h$.

Bidisperse Model

In case of a bidisperse sample such as pellets of zeolite crystals bound with clay, the equations of mass transfer remain the same for the crystals, but a new set of equations must be added to describe the heat and mass transfers at the macropore level. They are:

Overall mass balance:

$$\frac{d}{dt} \left(c_g + \frac{V_s}{V_e} [\bar{\varepsilon} c_p + (1 - \varepsilon) \bar{q}] \right) = 0 \quad (42)$$

Heat balance:

$$C_s \frac{\partial T_s}{\partial t} + (1 - \varepsilon) |\Delta H| \frac{\partial \bar{q}}{\partial t} = \frac{\lambda}{r_p^v} \frac{\partial}{\partial r_p} \left(r_p^v \frac{\partial T_s}{\partial r_p} \right) \quad (43)$$

Mass transfer in the pellet:

$$\frac{\partial c_p}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \frac{\partial \bar{q}}{\partial t} = \frac{D_p}{r_p^v} \frac{\partial}{\partial r_p} \left(r_p^v \frac{\partial c_p}{\partial r_p} \right) \quad (44)$$

where λ is the pellet thermal conductivity, ε the macropore porosity, c_p the gas phase concentration in the macropores and v the geometrical factor for the pellet (0, 1 or 2 for a plane, cylinder or sphere respectively)

The corresponding boundary conditions are:

$$-D_p \frac{\partial c_p}{\partial r_p} \Big|_{r_p=R_p} = k_p (c_p|_{r_p=R_p} - c_g) \quad \frac{\partial c_p}{\partial r_p} \Big|_{r_p=0} = 0 \quad (45-46)$$

$$-\lambda \frac{\partial T}{\partial r_p} \Big|_{r_p=R_p} = h (T|_{r_p=R_p} - T_0) \quad \frac{\partial T}{\partial r_p} \Big|_{r_p=0} = 0 \quad (47-48)$$

The surface resistance could be analogous to the evaporation barrier or due to structural heterogeneities (Kocirik et al., 1990).

The adsorbate concentration at equilibrium must now be defined as a function of the gas phase concentration in the macropores and the crystal temperature:

$$q^* - q_0 = K_c (c_p - c_0) - K_T' (T_s - T_0) \quad (49)$$

A numerical model based on Eqs. (42–49) completed by Eqs. (7–9) for the mass transfer in the crystals (Sun and Meunier, 1987) has been used for the simulation of the adsorbed mass, pressure and temperature responses.

Moments

As for the monodispersed case, the Laplace Transform allows the calculation of the moments of the adsorbed mass and the surface temperature of the pellet. They are:

$$M^0(q) = \frac{1}{1 + K} [\Phi(\tau_{sc} + \tau_{Dc}) + (1 + \beta)(\tau_{sc} + \tau_{Dc}) + \Phi\gamma'(\tau_h + \tau_\lambda)] \quad (50)$$

$$M^0(T) = (1 - \varepsilon) |\Delta H| K_p \Delta P_f \frac{R_p}{(v + 1)h} \quad (51)$$

$$\frac{M^1(T)}{M^0(T)} = \frac{1}{1 + K} [(1 + \kappa)(\tau_{sc} + \tau_{Dc}) + (1 + \beta)(\tau_{sc} + \tau_{Dc}) + (1 + K + \gamma' + \gamma' \kappa)(\tau_h + \tau_\lambda)] \quad (52)$$

The characteristic times are defined as follows:

$$\tau_{D_p} = \frac{R_p^2}{(v+1)(v+3)D_p} \quad \tau_{S_p} = \frac{R_p}{(v+1)k_p} \quad (53-54)$$

$$\tau_{D_c} = \frac{R_c^2}{(\sigma+1)(\sigma+3)D_c} \quad \tau_{S_c} = \frac{R_c}{(\sigma+1)k_c} \quad (55-56)$$

$$\tau_\lambda = \frac{R_p^2 C_s}{(v+1)(v+3)\lambda} \quad \tau_h = \frac{R_p C_s}{(v+1)h} \quad (57-58)$$

The other parameters are:

$$\gamma' = \frac{(1-\varepsilon)|\Delta H|}{C_s} \left(K'_T - \frac{K_p P_e}{T_e} \right) \quad \beta = \frac{1-\varepsilon}{\varepsilon} K_c \quad (59-60)$$

$$\Phi = \frac{\beta}{1+\beta} \quad \kappa = \frac{\varepsilon V_s}{V_e} \quad K = \kappa(1+\beta) \quad (61-63)$$

These expressions can be simplified in practical applications according to the following remarks:

- β is mostly very large excepted for weakly adsorbing species such as argon or oxygen in NaX zeolite (for instance $\beta \sim 1500$ for a NaX-CO₂ system at 30°C and 10 kPa). Thus $1 + \beta \sim \beta$, and $\Phi \sim 1$.

$$K'_T = \left(\frac{\partial q}{\partial T} \right)_c = \left(\frac{\partial q}{\partial T} \right)_p + \frac{K_p P_e}{T_e} \quad (64)$$

Thus the Eqs. (55–59) can be rewritten as follows:

$$\gamma' = \frac{(1-\varepsilon)|\Delta H|K_T}{C_s} \quad \beta = \frac{1-\varepsilon}{\varepsilon} R_e T_0 K_p$$

$$K = \frac{(1-\varepsilon)V_s R_e T_0}{V_e} \quad (65-67)$$

These simplifications come down to neglect the mass of the gas phase inside the macropores which is always very small. The moments are expressed as in the monodispersed case replacing the sample volume V_s by the total volume of the crystals $(1-\varepsilon)V_s$, and replacing the volumic heat capacity C_s by the sum of the heat capacity of a volume unit of crystal, $C_s/(1-\varepsilon)$, and the corresponding heat capacity of the binder. The effective mass transfer characteristic time and the effective

heat transfer characteristic time become respectively:

$$\tau_m = \tau_{D_c} + \tau_{S_c} + (1+\beta)(\tau_{D_p} + \tau_{S_p})$$

$$\tau_{he} = \tau_h + \tau_\lambda \quad (68-69)$$

With these simplifications, the bidisperse case can be treated like the monodispersed one. However a small error arises in the partial integration method because the temperature, measured by infrared detection, is the surface temperature of the pellets which is different from there mean temperature. But the difference is always very small, except at the very beginning of the step.

Identification of the Mass Transfer Parameters

The previous treatment allows the calculation of the overall mass transfer characteristic time τ_m . It is deduced from Eq. (25):

$$\tau_m = (1+K)M_q^0 - \gamma \tau_h \quad (70)$$

Both terms of RHS are often much larger than τ_m . Although the relative error on these terms is generally a few percent, the relative error on τ_m may be much larger (10–30%). The accuracy is improved afterwards by curve fitting.

The previous data analysis does not give any information on the relative contribution of the different mass transfer resistances considered here: diffusion and surface barrier at macropore and micropore levels. Nevertheless, the shape of the pressure and temperature curves at the beginning of the step depends on the dominant types of resistance, and they can be determined by curve fitting (Bülow and Micke, 1995) with a numerical model, as shown below on an experimental example.

Let us remark an interesting possibility of the infrared measurement of the temperature for determining if the mass transfer is micropore or macropore limited. An adsorbent pellet is always strongly emissive in infrared and the measured temperature is the surface temperature. When the mass transfer is limited by the macropores, i.e. the micropore mass transfer is much faster than the macropore one, the temperature of the crystals at the surface of the pellet rises suddenly at the very beginning of the concentration step. Then the heat diffuses in the pellet and the slope of the temperature curve depends on the macropore mass transfer. When the mass transfer is micropore limited, one cannot observe such a change in the slope of the temperature curve (Fig. 3).

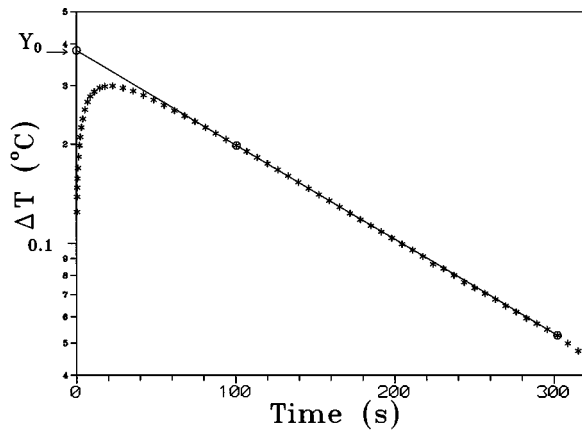


Figure 2. Determination of the parameter Y_0 of the experimental shown in Fig. 1.

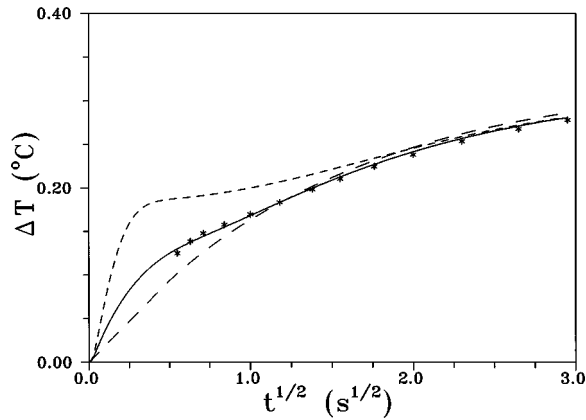


Figure 3. Influence of the pellet conductivity, λ , at the very beginning of the experiment shown on Fig. 1. (*) experimental data. Lines: calculated curves with (—) $\lambda = 0.23 \text{ Wm}^{-1} \text{ K}^{-1}$; (---) $\lambda = 0.10 \text{ Wm}^{-1} \text{ K}^{-1}$; (- - -) $\lambda \gg 1$.

Experimental

As pointed out previously, the apparatus built at L.I.M.S.I. consists of an experimental chamber closed by a bellows which can be rapidly compressed. The sample temperature is measured by infrared detection. The response of the infrared detector is proportionnal to the infrared flux emitted by the sample. Thus it is necessary to convert the flux into temperature by a calibration. This calibration is made using a small black body instead of the sample. However this method does not give the true temperature response of the sample because the sample emissivity, ε_r , is always smaller than unity. Thus the previous treatment of the data is not directly applicable.

Temperature Calibration Effect

Let $\Theta(u)$ be the temperature of the black body giving a detector response “u”. The sample temperature giving the same detector response is $\Theta(u)/\varepsilon_r$. That means that the identified parameters depending explicitly on the temperature (C_s , K_T and h) are expressed in a temperature unit different from 1 Kelvin, in fact $\varepsilon_r \times 1$ Kelvin. Thus the identified values of these parameters are the true values multiplied by $1/\varepsilon_r$. If index ‘e’ denotes the experimental determinations and index ‘v’ the actual values, it can be written:

$$C_{sv} = \varepsilon_r C_{se} \quad h_v = \varepsilon_r h_e \quad k_{Tv} = \varepsilon_r K_{Te} \quad (71-73)$$

For determining the emissivity ε_r , it is necessary to know a priori at least one parameter of the system. Let us assume for instance that the heat of sorption, $|\Delta H|$, is known. It has been shown previously that the experimental data allow the calculation of the following quantities:

$$A = h_e/C_{se} = h_v/C_{sv} \quad B = |\Delta H|/C_{se} \\ \gamma = |\Delta H|K_{Te}/C_{se} = |\Delta H|K_{Tv}/C_{sv} \quad (74-78)$$

The Clausius-Clapeyron equation can be written:

$$|\Delta H| = C K_{Tv} \quad (79)$$

with

$$C = \frac{R_e T_0^2}{P_0 K_P} \quad (80)$$

Thus Eqs. (77) and (79) give ε_r :

$$\varepsilon_r = \frac{B|\Delta H|}{C \gamma} \quad (81)$$

Examples of Parameter Determination

Experiments with NaX- CO_2 will be used to illustrate the possibility of VSTM. The first experiment was performed with anhydrous pellets activated overnight at 400°C under vacuum ($P < 10^{-3} \text{ Pa}$). The second experiment was performed with pellets hydrated, after reactivation, with a small quantity of water. In the first experiment the heat of adsorption is known, allowing the determination of the sample emissivity, ε_r . In the second experiment, the data treatment described above allows the determination of all the parameters, in particular the heat of adsorption.

Table 1. Experimental parameters of both anhydrous and hydrated experiments.

R_c (m)	R_p (m)	V_s (m ³)	V_e (m ³)	ε	T_0 (K)	R_e (J kg ⁻¹ K ⁻¹)	q_0 (k gm ⁻³)
2×10^{-6}	2.0×10^{-3}	7.0×10^{-7}	5.8×10^{-4}	0.4	302	189	105

Table 2. Specific experimental parameters.

Sample	P_0 (Pa)	ΔP_M (Pa)	ΔP_f (Pa)	K	$M^0(q)$ (s)	h/C_s (m s ⁻¹)	$ \Delta H /C_{se}$ (m ³ K kg ⁻¹)	$K_{Tv}/ \Delta H $ (10 ⁻⁶ kg ² J ⁻¹ K ⁻¹ m ⁻³)	Y_0 (K)
Anhydrous	982	87.4	31.5	1.76	40.6	1.83	0.45	2.06	0.392
Hydrated	3210	285.3	177.5	0.62	59.8	1.64	0.39	2.39	0.596

Table 3. Identified parameters.

Sample	K_p (kgm ⁻³ Pa ⁻¹)	ΔH (10 ⁶ J kg ⁻¹)	ε_r	C_{sv} (10 ⁶ J K ⁻¹ m ⁻³)	h_v (wm ⁻² K ⁻¹)	K_{Tv} (kgm ⁻³ K ⁻¹)	D_p (10 ⁻⁶ m ² s ⁻¹)	τ_h (s)	τ_m (s)
Anhydrous	0.0357	0.94	0.93	1.87	3.6	1.93	6.0	109	34
Hydrated	0.0125	0.86	0.93	2.03	3.4	2.05	2.7	122	27

The experimental conditions for both experiments are given in Table 1.

Table 2 gives the experimental conditions for each experiment and the intermediate results of the data analysis obtained by the method described above.

Anhydrous Zeolite Experiment

Figure 1 shows the temperature and pressure records after a step at 1 kPa and 302 K, and Fig. 2 shows the determination of the parameter Y_0 . The value of the heat of sorption has been taken from (Dunne et al., 1996), allowing the determination of the sample emissivity, ε_r .

Table 3 gives the final results introduced in the numerical model and Fig. 1 shows the corresponding temperature and pressure calculated responses. As emphasized previously, the data analysis gives only the overall mass transfer characteristic time. The kinetic parameters have been determined as follows:

- a very steep increase of the temperature can be observed at the very beginning of the step (Fig. 3). This indicates that the process is macropore limited. This is confirmed by the direct measurement of the diffusion kinetics in crystals. The transport diffusivity measured at the same loading by thermal frequency response (Malka-Edery, 1999) is $D_i = 3 \times 10^{-9}$ m² s⁻¹. The self diffusivity measured by P.F.G.–N.M.R. at slightly higher loading

(Kärger et al., 1993) is $D_0 \sim 1.5 \times 10^{-9}$ m² s⁻¹. For 1 μ m radius crystals, the corresponding micropore diffusion characteristic time is completely negligible ($\tau_{Dc} \ll 1$ ms). The amplitude of the temperature jump depends on the thermal conductivity, λ , of the pellet that has been identified by curve fitting ($\lambda = 0.23$ Wm⁻¹ K⁻¹).

- the curve fitting (Fig. 4) shows that no significant surface barrier occurs ($k_p = 0$). Thus the only

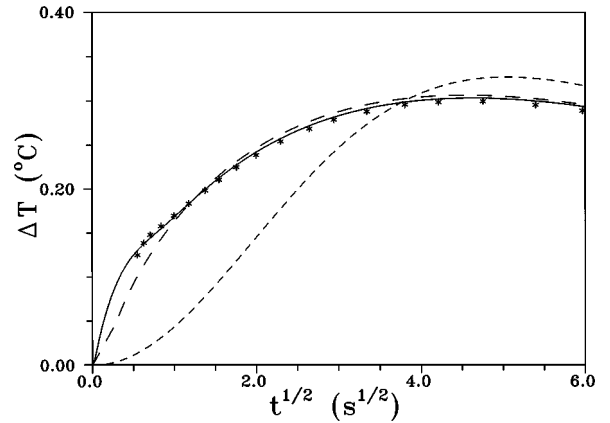


Figure 4. Influence of the dominant mass transfer resistance at the beginning of the experiment shown on Fig. 1 (*) experimental data. Lines: calculated curves with (—) macropore diffusion; (---) surface barrier resistance (at either macropore or micropore level); (-.-) micropore diffusion. All curves were calculated with the same thermodynamic parameters and the same mass transfer characteristic time (34 s).

significant mass transfer parameter is the macropore diffusion coefficient, D_p .

The identified value is $D_p = 6.0 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. The mean macropore diameter is not known exactly but it can be estimated at $\mu \sim 3 \times 10^{-7} \text{ m}$. This is much smaller than the mean free path of carbon dioxide molecules ($\sim 4.2 \times 10^{-6} \text{ m}$ at 1 kPa (Kennard, 1938)). Thus the dominant diffusion is the Knudsen diffusion. The Knudsen diffusivity, D_k , is given by the following expression (Ruthven, 1984):

$$D_k = 48.5\mu(T_0/M)^{1/2} \quad (\text{m}^2 \text{ s}^{-1}) \quad (82)$$

where M is the molecular weight (g/mol) of the diffusing species.

Applying this expression to the related experiment gives: $D_k = 3.8 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. The tortuosity factor is:

$$\tau = D_k/D_p = 6.3 \quad (83)$$

This value is in good agreement with the values (3–6) commonly found in literature (Ruthven, 1984).

Hydrated Zeolite Experiment

After the anhydrous experiment, the sample was reactivated and 2% (by sample mass) of water was introduced in the chamber. For such an amount of water, the equilibrium pressure is less than 0.02 Pa at 30°C. Afterwards, an experiment with carbon dioxide was performed as with the anhydrous sample, at the same carbon dioxide loading. Due to the very low water vapor pressure, it can be shown (Malka-Edery, 1999) that water is not appreciably displaced by carbon dioxide. Thus water in gaseous phase can be neglected and the monocomponent model can be used for treating the experimental data.

The emissivity of the sample, ε_r , being known by the treatment of the anhydrous experiment, the thermodynamic parameters are determined by the method presented previously. The results are given Tables 2 and 3. Figure 5 shows the experimental pressure and temperature responses and the curves calculated with these parameters. One can see that the calculated curves fit well with the experimental data. It can be remarked that the presence of water has a small influence on the heat of sorption. But, surprisingly, one can observe an important slowing down of the macropore diffusion although the gaseous phase is practically the same in the anhy-

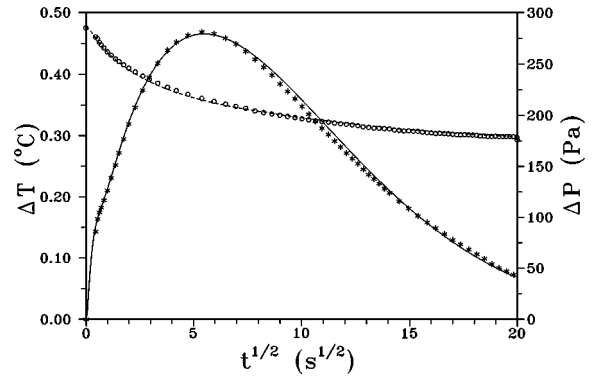


Figure 5. Experiment with NaX zeolite hydrated with 2% water b.w., at 302 K and 105 kg m^{-3} CO_2 loading: (*), (—) temperature experimental and calculated responses respectively; (o), (---) pressure experimental and calculated responses respectively. The calculated curves were obtained with the detector response determined by the anhydrous zeolite experiment.

drous and in the hydrated experiment. This slowing down has not yet found any satisfactory explanation.

Conclusion

The single step method has proved to be a useful tool for the determination of the kinetic and thermodynamic adsorption parameters. It has been shown that the rigorous mathematical treatment allowed by a LDF mass transfer law can be applied in case of Fickian diffusion when the mass transfer characteristic time is much smaller than the heat transfer characteristic time. Although not very accurate for absolute sorption heat measurement, it is very useful to determine the change of that sorption heat under special conditions, such as the presence of a small amount of water in the adsorbent.

Nomenclature

A	Experimental ratio h/C_s (m s^{-1})
B	Experimental ratio $ \Delta H /C_s$ ($\text{m}^3 \text{ K kg}^{-1}$)
C	Ratio $K_T/ \Delta H $ ($\text{kg}^2 \text{ J}^{-1} \text{ K}^{-1} \text{ m}^{-3}$)
c_g	Gas concentration in the chamber (kg m^{-3})
c_p	Gas concentration in the macropores (kg m^{-3})
C_s	Overall heat capacity of the sample ($\text{J m}^{-3} \text{ K}^{-1}$)
D_c	Micropore diffusion coefficient ($\text{m}^2 \text{ s}^{-1}$)
D_p	Macropore diffusion coefficient ($\text{m}^2 \text{ s}^{-1}$)
h	Heat transfer coefficient ($\text{W m}^{-2} \text{ K}^{-1}$)
k	Compression factor
$k_{c,p}$	Mass surface conductance of crystal and pellet respectively (m s^{-1})

K	Adsorption coefficient
K_c	Isotherm derivative versus gaseous adsorbate concentration
K_p	Isotherm derivative versus pressure ($\text{kg m}^{-3} \text{Pa}^{-1}$)
K_T	Isotherm derivative versus temperature ($\text{kg m}^{-3} \text{K}^{-1}$)
L	Linear Driving Force constant (s^{-1})
M_q^0	Zero moment of the complementary adsorbed amount (s)
M_T^0	Zero moment of the temperature (K s)
M_T^1	First order moment of the temperature (K s ²)
P	Pressure (Pa)
P_0	Initial pressure (Pa)
P_M	Maximum pressure (Pa)
q	Adsorbed amount (kg m^{-3})
q_0	Initial adsorbed amount (kg m^{-3})
q^*	Adsorbed amount at current equilibrium (kg m^{-3})
R_e	Specific gas constant ($\text{J kg}^{-1} \text{K}^{-1}$)
$R_{c,p}$	Particle radius (crystal and pellet, respectively) (m)
$r_{c,p}$	Current particle radius (m)
T	Sample temperature (K)
T_0	Equilibrium temperature (K)
V_e	Chamber volume (bellows compressed) (m^3)
V_0	Chamber volume (bellows extended) (m^3)
V_s	Sample volume (m^3)
ΔH	Differential heat of sorption (J kg^{-1})
ΔP	Pressure Change ($P - P_0$) (Pa)
ΔP_M	Maximum pressure change ($P_M - P_0$) (Pa)
ΔP_f	Final pressure change (Pa)
ΔT	Temperature change ($T - T_0$) (K)
ε	Porosity
ε_r	Sample emissivity
γ	Non-isothermality coefficient ($ \Delta H K_T / C_s$)
γ	Gas heat capacities ratio
λ	Pellet conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
σ, ν	Geometrical factor (0, 1 or 2)
τ	Tortuosity factor
τ_h	Heat transfer characteristic time (s)
τ_{Dc}	Micropore diffusion characteristic time (s)
τ_{Dp}	Macropore diffusion characteristic time (s)
τ_m	Overall mass transfer characteristic time (s)
τ_{Sc}	Micropore surface barrier characteristic time (s)
τ_{Sp}	Macropore surface barrier characteristic time (s)
τ_λ	Heat diffusion characteristic time (s)

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Notes

1. In order to fulfill experimentally this assumption, the sample is reduced to a monolayer or a very thin layer of particles situated on a $4 \mu\text{m}$ grid. This avoids "bed effect" and thermal gradient inside the sample.
2. An overpressure (and also a slight overheating of the sample) due to the non-isothermal compression of the gas can be observed at the very beginning of the run. It never lasts more than 1 s and will be neglected.

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