diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

# Challenges in Macroscopic Measurement of Diffusion in Zeolites

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## Abstract

The paper presents a brief historical overview of the field of the measurement of diffusion in zeolites. The focus will be on macroscopic measurements, i.e. when diffusion through entire crystals is studied. While this may appear to be a simple task, we will see that there are difficulties in obtaining reliable results. Two case studies, the volumetric/piezometric experiment and the Transient Analysis of Products (TAP) apparatus are discussed and ways to improve either the experiments or the way in which the results are analyzed are presented. The author's perspective into what are the current challenges in the field concludes the paper.

Keywords: diffusion measurements; zeolites; adsorption.

## 1. Introduction

Zeolites are both naturally occurring and synthetic crystals that have very well characterized nanopores [1]. This feature makes these materials extremely useful in several applications in catalysis and adsorption separation processes. These applications are controlled by both adsorption equilibrium and mass transfer kinetics and as a result many different experimental techniques have been developed to measure these quantities.

Measurement of diffusion in zeolites can be divided into two differing approaches: microscopic studies, which typically measure the movement of molecules and relate the root mean square displacement over time to the diffusion coefficient using Einstein's equation, and macroscopic studies, which measure the mass transfer between the gas and the solid adsorbent over the entire crystal and solve Fick's law of diffusion to obtain the diffusional time constant.

The fact that the crystal structure of zeolites is *apparently* well characterized makes them a suitable candidate for the development of theories of diffusion in confined geometries and thus of great importance also for a purely fundamental study.

Figure 1 shows a condensed historical overview of the development of the field. While the specific techniques are very interesting on their own merits, what is important to note is the fact that, apart from the pioneering work of Tiselius [2], who observed by microscopy the adsorption front of water in a very large crystal of natural heulandite, for a considerable period of time uptake rate experiments, introduced originally by Barrer [3], were considered to be the means of carrying out these measurements. To follow the mass of the adsorbent as it changes in time, in the presence of adsorbate molecules, seemed to be the obvious way to measure diffusivities in zeolites. This can be achieved either through a direct measurement of the mass (gravimetric methods) or the measurement of gas pressure in a closed system (volumetric/piezometric methods).

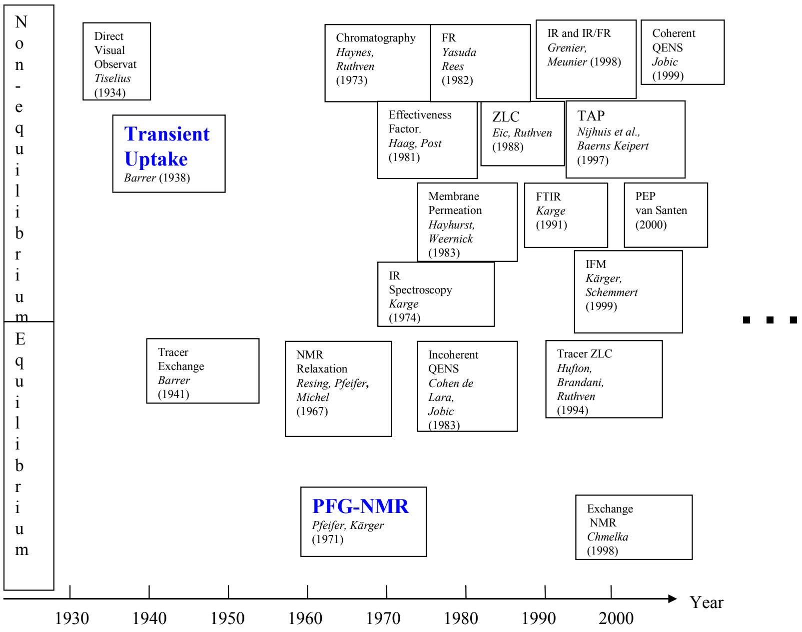

Fig. 1: Development of the measurement of diffusion in zeolites [2-21]. Adapted from [22].

Figure 1 clearly shows a “dramatic event” at the end of the 1960s, early ‘70s, with the introduction of the first NMR measurements [6, 7]. With the advent of the PFG NMR technique, pioneered by Pfeifer and Kärger, a number of inconsistencies in the results reported in the literature came to light. This led to a re-examination of many “fast diffusing” systems for which gravimetric measurements where affected by spurious kinetic resistances. To overcome these limitations many new techniques were proposed. In many cases, the earlier results were shown to be incorrect and by the ’80s and early ‘90s most researchers in the field came to the conclusion that only microscopically determined diffusivities were reliable and that macroscopic methods, when not in agreement with these measurements, reflected the kinetic limitations due to heat transfer, external film, bed effects and surface barriers. For a detailed discussion one should refer to the monograph [23].

The story does not end here. Figure 2 shows results published only in the last 15 years for the system n-hexane/silicalite. These measurements were carried out by groups who knew of the earlier difficulties and ensured that their respective systems were not affected. For particular adsorbents, in this case silicalite, it is apparent that the "measured" diffusivity is dependent on the length-scale and time of the observation. The current general consensus is that all these measurements are in fact correct, within their respective uncertainties, and the results reflect the fact that large silicalite crystals have internal imperfections that dominate the macroscopic measurements. The mass transfer constant measured by macroscopic techniques differs by up to 3 orders of magnitude from what it would be in an ideal crystal, based on the results from neutron scattering and PFG NMR which will be discussed by Hervè Jobic in a separate paper in this book.

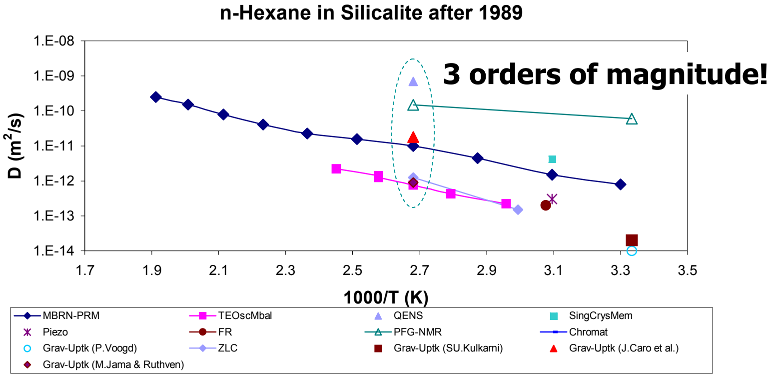

Fig. 2: Recent diffusion in zeolites data reported in the literature [24-32].

The interesting conclusion that can be derived from all this is that, to date, we do not have a valid theory that will be able to predict a-priori the mass transfer kinetics in non-ideal zeolite crystals. As a consequence it will be necessary to carry out macroscopic measurements for the foreseeable future.

This field has relatively few groups who specialize in macroscopic diffusion measurements in nanoporous materials. The majority of the data that is being published is mainly from those who investigate mass transfer kinetics as part of a wider project, who sometimes do not fully understand the underlying difficulties in making such measurements. The problem is also that there are no commercially available instruments designed for this purpose, so researchers often modify or use equipment designed for equilibrium purposes or have to develop their own systems. One of the real challenges is therefore that of providing simple guidelines that can be used to identify when the experiments are likely to be successful. We will discuss this in detail with the aid of two case studies.

## 2. Volumetric/Piezometric method: a closed system.

We begin the discussion with a very simple system, which is shown schematically in Figure 3. This is the volumetric or more accurately the piezometric (pressure is measured) experiment. This system was developed for equilibrium measurements. For this purpose the dosing and uptake (where the zeolite is placed) cells are connected to vacuum and the valve is then closed. The dosing volume is charged to a known pressure, i.e. a finite known amount of gas is introduced into the system. By opening the valve and measuring the final pressure, one can calculate the amount of gas adsorbed. For this measurement one needs only one pressure transducer in the dosing volume.

In principle this system can be used also for kinetic measurements, if the pressure vs time curve is recorded. Consider the following example:

1) Measurements are carried out without the zeolite present to investigate the flow characteristics of the valve.
2) Measurements are carried out with the zeolite present. If a significant difference is observed from the previous experiments, one concludes that mass transfer kinetics is being measured.

An example of this is shown in Figure 4.
Is there something *obviously* wrong with proposition 1 and 2? Not at first sight.

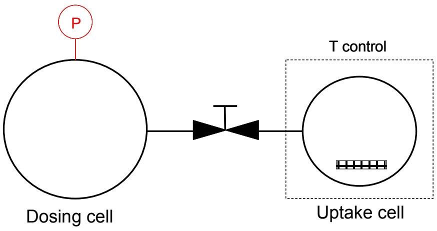

Fig. 3: Volumetric/Piezometric system.

An experimentalist would comment that flow through a valve is non-linear and therefore proposition 1 would establish the characteristics of the valve in a region that is not representative of the adsorption experiments. When adsorption is taking place the gas flowing through the valve can be much larger than that in the non adsorbing case, if fast diffusing and strongly adsorbed components are being investigated. The second issue is that adsorption is a phase change phenomenon and heat is being generated, so one should consider also the effect of heat transfer resistances. If we limit the discussion to single component systems, one has to be careful also with the way the solid is arranged as this will change the heat transfer characteristics. Finally if the pressure step is relatively large, the equilibrium isotherm is not necessarily linear, introducing additional complications in the analysis of the results.

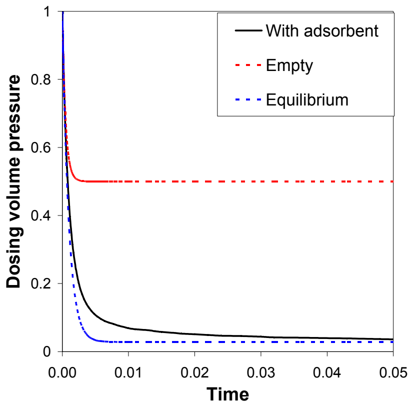

Fig. 4: Qualitative difference between experiments with and without adsorbent present in the uptake cell.

We can conclude that an accurate measurement is more complicated than originally thought. The student with a passion for modeling may suggest to include these effects in the model equations and to determine additional parameters from the experiments. After all, we observe a difference between the adsorbing and non-adsorbing case, so we should be able to measure kinetics.

What we have missed, so far, by focusing on the experimental details is the more general question: can we use the comparison with a non adsorbing system to confirm that mass transfer kinetics is being measured?

The answer to this question is no! This appears to be an obvious conclusion to very few researchers. I will try to justify this answer by looking at Figure 3 and proposing a thought experiment: replace the valve with a very small capillary tube so that the flow between the dosing and uptake volume is slow. The pressure is changing, but the change is so slow that the adsorbed phase equilibrates with the gas immediately. In this case the experiment with and without the adsorbent will be quite different, but the dynamics can be described entirely using only the *equilibrium properties* and the flow characteristics of the capillary. By looking at Figure 3 we can therefore identify two characteristic time constants, one linked to the valve conductance and the other due to the diffusion in the zeolite. It is the ratio of these time constants that dictates in which regime we are and if we can measure diffusion. Figure 4 also shows the limiting case of equilibrium control where the adsorbed phase is always at equilibrium with the gas (see section 4).

Qualitatively the equilibrium control model has a shape that is very similar to that of the full curve, so how can we be sure that we are indeed measuring diffusion? The answer to this question can be the use of accurate models coupled to dynamic sensitivity analysis to distinguish between them, but this solution may lead to cases where one is not *certain* of the result. Is there an unequivocal way to prove directly from the experiments that mass transfer kinetics is being measured? Again look at Figure 3. If we add a second pressure transducer and measure the pressure in the uptake cell we now have unequivocal experimental proof of what we are measuring. This is because, while the pressure in the dosing cell, whichever the controlling mechanism, will be a monotonically decreasing function in time, the pressure in the uptake volume should initially increase, go through a maximum and then decrease to the final equilibrium value if mass transfer or heat transfer limits the dynamics of this system (see Figure 5). The pressure in the uptake cell will be increasing monotonically if the adsorbed phase is always at equilibrium with the gas. Therefore, it is possible to distinguish between these two cases from a direct observation of the shape of the pressure vs time curve of the uptake cell.

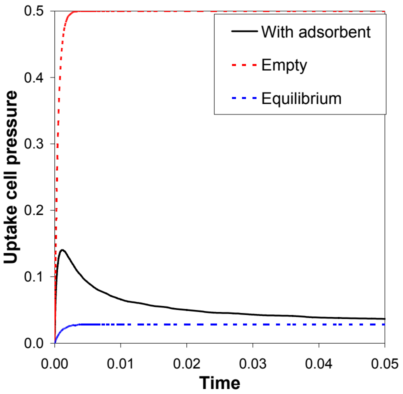

Fig. 5: Pressure transient in the uptake cell.

The second pressure measurement offers an additional advantage. It allows the calculation of the amount of gas present in the adsorbed phase at any time, i.e. the average adsorbed amounts are known. The knowledge of the average solid concentration and the boundary condition on the solid, given by the measured pressure in the uptake cell, allows the interpretation of the uptake data, without the need for an empirical valve model.

Based on this discussion we have shown that it is possible to establish experimentally if diffusion is being measured and that a modification to an equilibrium apparatus can lead to a much improved system as well as ease in the analysis of the results. For a detailed discussion of this system, one should refer to [33], which reports also an analysis of the data for the system benzene-NaX measured using this technique [34]. One still finds in the recent literature data *measured* using a volumetric/piezometric system with very fast diffusion and only the pressure on the dosing cell being recorded [35].

### 3. Transient Analysis of Products (TAP) method: a flow system.

The TAP system is another apparatus that has been used to measure diffusivities. A TAP bed consists of a tube in which the solids are loaded. The column is then exposed to a high vacuum chamber at the outlet. Once the system is equilibrated, a very small pulse of gas is introduced at the inlet of the column. The flux coming out of the adsorbent bed is measured with time and diffusion in the solid is thus calculated. A schematic diagram of a TAP bed is shown in Figure 6.

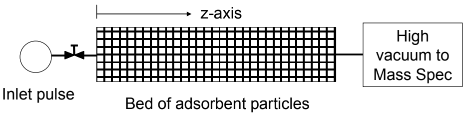

Fig. 6: TAP system.

The fact that the entire system is under vacuum ensures that the experiment is carried out in the region where the adsorption isotherm is linear. The system can be assumed to be isothermal because as the pulse is traveling along the column an approximately equal amount of molecules are being adsorbed and desorbed. One should also consider that there is a very large heat capacity of the bed and metal components in comparison with the heat generated by the relatively small amount of adsorbate molecules. Finally the gas is introduced pure and there are no external mass transfer limitations due to the presence of a second carrier gas, i.e. diffusion through an external film. This seems to be an ideal system to measure the diffusivity at low concentrations. It is not surprising that with this type of system Nijhuis et al. [17] appear to be the only researchers to date who claim to have *measured* macroscopically diffusivities in large silicalite crystals in agreement with PFG-NMR results.

Nijuis adopted the following approach:

1) The column was loaded with silicalite that had the template molecule needed for the sythesis still present. In this case there are no empty nanopores. Experiments were carried out on these crystals, thus showing the response without adsorption.
2) The column was exposed to air at high temperature and the template was burned off, thus opening the nanopores. Experiments were repeated under these conditions and a large difference was observed.

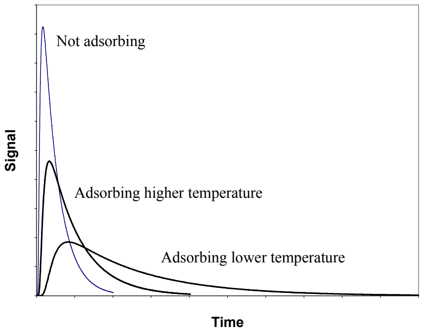

Fig. 7: Qualitative results with/without adsorption.

Nijhuis used a detailed model to interpret his results and claimed that, under the conditions in which he carried out his experiments, statistical analysis of his parameter fitting procedure indicated that he obtained reliable results.

This second example gives the opportunity to explain why I believe that one of the challenges in this field is that of determining directly from the experiments if diffusion is being measured. I will explain this without the use of any mathematical model, but observe that:

1) This system, neglecting any other complicating detail such as premixing and postmixing, has at least two time constants: one linked to diffusion in the zeolites; the second due to Knudsen diffusion in the bed.
2) If we are able to normalize the experimental response using only one time constant, then the system must be controlled by Knudsen transport which is *always* present.

Nijhuis et al. [17] presented complete experimental curves at 527 K and 623 K for the system n-butane/silicalite-1. They reported the signal as measured by the mass spectrometer and the procedure that one should carry out on their data is as follows:

i. Calculate the integral of the signal as a function of time and divide the signal by this amount. An advantage of this is that now the curves do not depend on the actual amount injected into the system.
ii. Divide the time by a characteristic time, such as the time corresponding to the maximum of the curve, or any constant time.
iii. Multiply the signal/integral by this characteristic time, so that the area under the curve is 1 and the plotted curve is dimensionless.

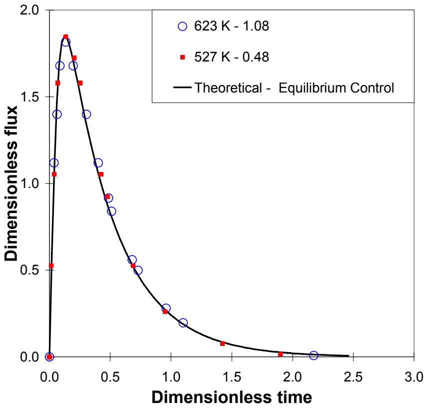

Fig. 8: Normalized plot of experimental data.

If different curves are made dimensionless in both measured quantity and time in this way and it is not possible to distinguish between them, then only one time constant can be extracted from the experiments. This has to be that related to Knudsen flow as explained above. Figure 8 shows the result of the procedure outlined above when applied to the data of Nijhuis et al. [17].

The procedure is extremely simple and can unambiguously prove that the claims of Nijhuis are not correct. Using a very similar apparatus, Keipert and Baerns [36] also studied the same systems, but concluded that they were not able to measure the fast diffusivities. In fact the TAP can be used only in a very small window of conditions, because if the diffusivity in the solid is too low, the adsorbate will exit the column without interacting with the solid, while if the diffusivity is too fast the solid and gas will be at equilibrium.

## 4. Equilibrium control.

What should be apparent by now is that for closed systems there is a need to test the dynamic response of the apparatus in the absence of adsorption, to establish an order of magnitude for its response time. In the case of a flow system, one needs to test the non-adsorbing case to be sure that a significant portion of molecules enters the adsorbent during the experiment. These checks are usually carried out by experimentalists.

For both systems it is also true that there is a second limit that has to be considered but does not appear to be as obvious. We term this limit *equilibrium control*.

To understand what is meant we return to the data of Nijhuis and ask: what did he measure? Nijhuis argues that $D_K / \tau L^2 >> D / R^2$, where $D_K$ is the Knudsen diffusion in the column, $L$ is the length of the column, $\tau$ is the tortuosity in the packed bed (typically 2 to 3), $D$ is the diffusivity in the zeolite and $R$ is the equivalent radius of the crystals. So how can the Knudsen flow be slow compared to the diffusion in the zeolite? The problem in this argument is that we should be comparing the flux in the gas, which is proportional to $D_K / \tau L^2$, with the flux in the zeolite, which is proportional to $HD / R^2$, where $H$ is the equilibrium Henry constant. In zeolites this is often very large.

The best way to explain this is that in the equilibrium control limit the model of the TAP column reduces to Fick's equation. In the TAP bed we can write the mass balance in the gas phase as

$$\frac{\partial c}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial \bar{q}}{\partial t} - \frac{D_K}{\tau} \frac{\partial^2 c}{\partial z^2} = 0 \tag{1}$$

where the three terms in the equation are the accumulation in the fluid, the accumulation in the solid and the dispersion due to diffusion. The mass balance in the solid phase is

$$\frac{\partial q}{\partial t} - D\nabla^2 q = 0 \tag{2}$$

where $\bar{q}$ is the average adsorbed phase concentration. These two equations are coupled with the relevant boundary conditions. If we assume that diffusion in the solid is the controlling mass transfer resistance, then the concentration at the solid surface will be at equilibrium with the gas: $q_S = HC$.

This general model has a limit corresponding to the non adsorbing case if one takes either $D = 0$ or $H = 0$. The second limit is that of equilibrium control, which is obtained when $D = \infty$. In this second limit, there is no internal gradient in the solid particle (otherwise there would be an infinite flux), therefore the average concentration is equal to the concentration at the surface and

$$\frac{\partial c}{\partial t} + \frac{1-\varepsilon}{\varepsilon} H \frac{\partial c}{\partial t} - \frac{D_K}{\tau} \frac{\partial^2 c}{\partial z^2} = 0 \tag{3}$$

This can be rewritten in the form of the diffusion equation

$$\frac{\partial c}{\partial t} - \left( \frac{D_K}{\tau H} \frac{\varepsilon}{1-\varepsilon} \right) \frac{\partial^2 c}{\partial z^2} = 0 \tag{4}$$

Therefore Nijhuis in his experiments measured an effective Knudsen diffusivity (the term in parenthesis), which is only a function of the equilibrium constant!

## 5. Conclusion

I have tried to present very simple examples to show that the macroscopic measurement of diffusion in zeolites is very challenging. I hope that the general approach of comparing kinetic experiments to the equilibrium control limit may be applicable to other fields where diffusion is measured.

In general, as shown in both case studies, it should be possible to devise experiments where one can have direct evidence that the conditions are far from the equilibrium control limit. Since equilibrium can be measured through independent experiments or from the final result in closed systems, even if experimental validation cannot be achieved, one should always compare the dynamic response to that which would be predicted under equilibrium control. Figure 8 includes the curve which corresponds to this limit, showing that the simple model can describe the experimental results. Only if a clear difference in the predicted equilibrium control curve and the measured dynamics can be observed, one can conclude that mass or heat transfer kinetics are quantifiable.

There are no commercially available apparatuses that can be used for the measurement of diffusion in nanoporous materials. Even if these become available, it is unlikely that a single system will be able to provide accurate results for the wide range of time constants that may be encountered in all the materials that need to be tested. This is especially true if one considers also the extension to “formed” materials, such as pellets and monoliths, in which diffusion in the macropores through molecular, Knudsen or viscous flow may be relevant.

In order to have reliable equipment that can be used by the non-expert, the main challenges that will have to be resolved are:

a) The need for experimental protocols that unequivocally confirm the validity of the results.
b) A systematic approach to establish the experimental conditions in which physical parameters may be measured in different apparatuses.
c) The development of automated systems, which are particularly important in industrial applications.
d) The development of software tools that allow the analysis of multiple experiments to extract the diffusion coefficient, combined with dynamic sensitivity analysis.

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