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# Measurement of Diffusion and Flow of Gas through a Porous Solid

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Experiments for measuring the flow or diffusion of a gas through a porous solid are described. The experiments allow calculation of an effective diffusion coefficient and the tortuosity factor for a porous sample of undefined pore characteristics.

## 1. Introduction

Transport of gas through a porous solid is of considerable theoretical and practical importance. Accordingly, the subject has received considerable attention in recent years. Some fundamental concepts concerning diffusion and flow of gases through pores have been discussed elsewhere.[1–7]

Diffusion and flow through porous solids involve several uncertainties regarding the pore structure, e.g. roughness, shape and orientation of the pores, their mutual interconnections and lengths. To account for these uncertainties an adjustable empirical constant called the "tortuosity factor" ($\tau$) is generally used. Thus if one is concerned with a mass flux $J$ through a porous sample of overall surface area $A$ and bulk porosity $\epsilon$ then the flux can be considered to be equivalent to one across a pore surface area $A\epsilon/\tau$ if all the pores constitute parallel paths. Here $A\epsilon$ gives the effective pore area on the surface and $\tau$ is incorporated to account for uncertainties in the pore structure. The experiments to be described measure $\epsilon/\tau$ and $\tau$.

### 1.1. Diffusion and flow of gases

Theories on diffusion and flow of gases through porous media are based on relatively well-defined equations where pores are considered analogous to capillaries. When the total pressure on either side of a capillary is the same and gaseous species migrate because of partial pressure gradient, then the mass flux is diffusive in nature. When the capillary radius, $r$, is small compared to the mean free path, $\lambda$ (say $r/\lambda < 0.1$) then the flux is said to involve Knudsen diffusion. Ordinary molecular diffusion takes place when the capillary dimension becomes comparable to the mean free path. When the total pressures on either side of a capillary are unequal, then the gas migration is governed also by the pressure gradient. At low gradients the flow may be simple streamline flow, called Poiseulle's flow. At high gradients with high Reynold's number, however, the flow turns turbulent. In general, in the presence of a pressure gradient both diffusion and flow contribute to the net flux through the capillary.

## 2. Experimental

### 2.1. Experiment 1: flow under pressure gradients

The experimental arrangement for investigating flow under considerable pressure gradients is shown in Figure 1. A porous cylinder is sealed between two glass tubes and the curved surface coated with a sealant as shown. The open flat surfaces are exposed to a vacuum/gas line on one side and a manometer on the other side. The manometer is connected to a large flask which approximates the total volume.

The entire system is first evacuated and checked for leaks. It is then suddenly connected to the gas line to establish immediately a pressure on top surface of the sample. The gas is maintained at one atmosphere pressure by using a simple bubbler arrangement. The gas flows slowly through the sample pores and the manometer reading gradually falls indicating a gradual build-up of pressure. The pressure readings are recorded over an extended period of time. The pressure–time plot allows calculation of $\epsilon/\tau$ as shown subsequently.

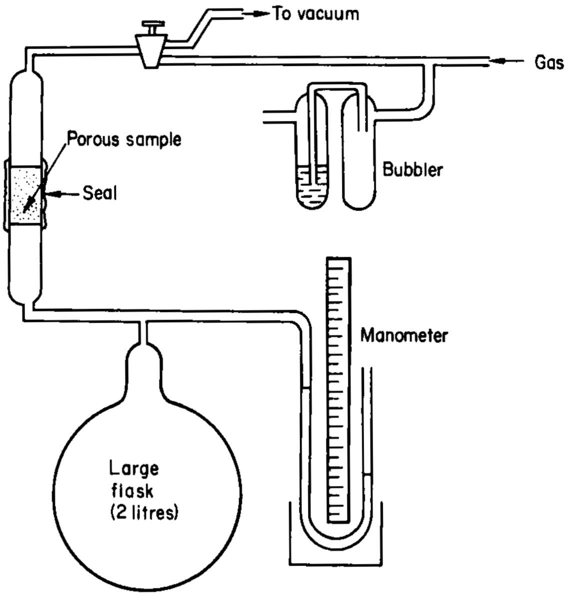

**Figure 1.** Experimental setup for investigating flow under pressure gradients.

## 2.2. Experiment 2: diffusion of gas due to difference in partial pressures

In the diffusion experiments equal pressures are maintained on either side of the porous sample through which hydrogen diffusion takes place unidirectionally. The hydrogen concentration in the gases is measured using a hydrogen concentration cell.

An experimental setup used by Abraham *et al.*[8] is shown in Figure 2. A porous cylindrical sample of nickel is located across two parallel gas streams as shown. Purified argon is passed through $S_1S_7$

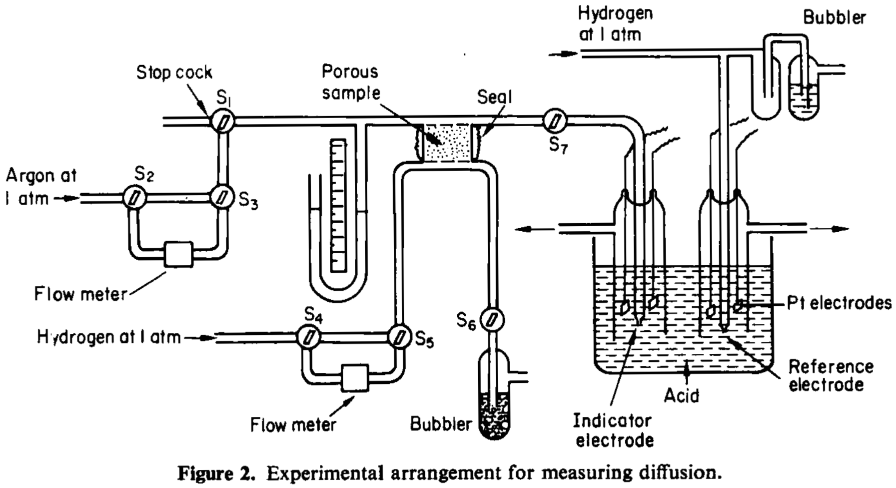

**Figure 2.** Experimental arrangement for measuring diffusion.

while purified hydrogen is passed through $S_5S_6$. This arrangement allows diffusion of hydrogen through the pores against a stream of argon. As a result of the diffusion the argon stream is enriched by hydrogen and vice versa. The hydrogen intake in the argon stream is measured accurately by the concentration cell.

The gas passing out through $S_7$ is made to bubble at a hydrogen indicator electrode of a hydrogen concentration cell. The reference electrode of the cell is constituted by platinum foil at which hydrogen was continuously bubbled at 1 atm pressure. Knowing the flow rate of argon and the e.m.f. of the cell, the concentration of hydrogen in argon stream may be calculated. From this, one can calculate the effective diffusion coefficient of hydrogen in the pores, as well as the tortuosity factor. These values are independent of argon flow rate as will be shown later.

## 3. Theoretical

### 3.1. Theory of experiment 1 involving flow

When a finite pressure gradient exists across a capillary, both diffusion and flow contribute to the net flux. It has been shown[1,7] that, for a uniform capillary, forced flow flux

$$J=-\left(\frac{r^2P}{8\mu}+\frac{4}{3}\frac{rRT}{M\bar{v}}\right)\frac{1}{RT}\frac{\mathrm{d}P}{\mathrm{d}x} \tag{1}$$

where $r$ = radius of capillary, $P$ = pressure at a distance $x$ along the length of a capillary, $\mathrm{d}P/\mathrm{d}x$ = pressure gradient; $T$ = absolute temperature, $M$ = molecular weight of the gas, $\bar{v}$ = mean molecular speed, $R$ = universal gas constant, and $\mu$ = viscosity of the gas.

For the flow equation for the actual sample one has to consider the effective pore area as well as the tortuosity factor. Thus flux through the actual sample is

$$J'=-\left(\frac{r^2P}{8\mu}+\frac{4}{3}\frac{rRT}{M\bar{v}}\right)\frac{1}{RT}\frac{\mathrm{d}P}{\mathrm{d}x}\cdot\frac{\epsilon}{\tau} \tag{2}$$

The second term within the bracket, which accounts for molecular diffusion, is negligible compared to the first, which is the flow term, and may therefore be neglected. This assumption is specially valid when pressure gradients are large. Thus neglecting the flux due to diffusion and remembering that flux also equals the rate of accumulation in the bulb:

$$\begin{aligned}J'&=-\left(\frac{r^2P}{8\mu}\cdot\frac{1}{RT}\frac{\mathrm{d}P}{\mathrm{d}x}\right)\cdot\frac{\epsilon}{\tau}\\&=\frac{1}{A}\cdot\frac{\mathrm{d}}{\mathrm{d}t}(C_tV)\\&=\frac{V}{ART}\cdot\frac{\mathrm{d}P_t}{\mathrm{d}t}\end{aligned} \tag{3}$$

where $V$ = total volume in the manometer side (approximately equal to the volume of the large flask), $P_t$ = gas pressure at time $t$, as shown by the manometer, and $C_t$ = moles per unit volume at time $t$.

Since there is no gas accumulation inside the capillary pores:

$$\frac{\mathrm{d}J'}{\mathrm{d}x}=0 \tag{4}$$

The equation

$$J'=-\frac{r^2P}{8\mu}\cdot\frac{1}{RT}\cdot\frac{\mathrm{d}P}{\mathrm{d}x}\cdot\frac{\epsilon}{\tau}$$

may now be integrated using the boundary conditions:

at $x=0$, $P=P_0$

$x=L$, $P=P_t$ (variable with time)

The result is

$$J' = \frac{r^2}{8\mu RT} \cdot \frac{\epsilon}{2L\tau}(P_0^2 - P_t^2) \tag{5}$$

where $L$ is the thickness of the sample.

Equating equation (5) with the right-hand side of equation (3)

$$\frac{dP_t}{dt} = \frac{ART}{V} \cdot \frac{r^2}{8\mu RT} \cdot \frac{\epsilon}{2L\tau}(P_0^2 - P_t^2) \tag{6}$$

or

$$\frac{dP_t}{(P_0^2 - P_t^2)} = \frac{Ar^2}{16\mu VL} \cdot \frac{\epsilon}{\tau} \cdot dt \tag{7}$$

Integration of the above equation yields

$$\log\left(\frac{P_0 + P_t}{P_0 - P_t}\right) - \log\left(\frac{P_0 + P_t^0}{P_0 - P_t^0}\right) = \left(\frac{Ar^2}{8\mu VL} \cdot \frac{\epsilon}{\tau} \cdot \frac{P_0}{2.303}\right)t \tag{8}$$

where $P_t^0$ denotes the pressure reading of the manometer at zero time. The second term in the left-hand side vanishes if $P_t^0$ is zero, i.e. if manometer readings are recorded right from the beginning. Equation (8) indicates that: (a) a plot of $\log(P_0 + P_t)/(P_0 - P_t)$ against time should be a straight line with slope

$$\frac{1}{2.303} \frac{Ar^2 P_0}{8\mu VL} \cdot \left(\frac{\epsilon}{\tau}\right)$$

(b) the slopes plotted against $1/\mu$ should also give a linear plot with a slope

$$\frac{1}{2.303} \cdot \frac{Ar^2 P_0}{8\mu VL} \cdot \left(\frac{\epsilon}{\tau}\right)$$

From these plots $\epsilon/\tau$ may be found, provided values of $A$, $r$, $P_0$, $\mu$, $V$ and $L$ are all known. Moreover, from statistical considerations $\epsilon$ equals the bulk porosity of the sample.[9] Knowledge of porosity thus yields $\epsilon$.

The derivation of equation (8) is based on a number of assumptions at different steps. The validity of these assumptions taken together may be checked by analysing the equation itself. Thus for three or four different gases, linear plots should be obtained for each gas, each plot having a different slope. These slopes plotted against the reciprocal viscosity should also give linear plots.

It should be remembered, however, that the equations have hitherto considered a single average pore radius $r$. The treatment, therefore, is valid only when the pore size in the sample is reasonably uniform. Various uncertainties may be introduced if there is an appreciable pore size distribution.

### 3.2. Theory of experiment 2 involving diffusion

The e.m.f. of the hydrogen concentration cell is given by

$$E = \frac{1.987T}{2F} \ln\left(\frac{1}{p_{H_2}}\right) \tag{9}$$

where $T$ is the absolute temperature, $F$ the Faraday constant (cal) and $p_{H_2}$ the unknown partial pressure of hydrogen in the argon stream (atm). $E$ is in volts. Measurement of the cell e.m.f., $E$, thus yields $p_{H_2}$.

Again, $p_{H_2}$ may be expressed in terms of molar fluxes:

$$p_{H_2} = \frac{\dot{n}_{H_2}}{\dot{n}_{H_2} + \dot{n}_{Ar}} \tag{10}$$

where $\dot{n}_i$ is the flux of species in the gas (g mol s$^{-1}$). According to Avogadro's law the molar flux terms may be replaced by corresponding volumetric rates at STP.

For "steady-state" flow:

$$\text{rate of hydrogen flow through solid} = \text{rate of hydrogen input in argon stream} \tag{11}$$

Hence,

$$\frac{p_{H_2}.\dot{n}_{Ar}}{(1-p_{H_2})} = \frac{A}{L}(1-p_{H_2}).\frac{D^{eff}}{RT} \tag{12}$$

where $\dot{n}_{Ar}$ is the flowrate of argon, $p_{H_2}$ the steady-state hydrogen partial pressure in argon and $D^{eff}$ is the effective diffusion coefficient given by the equation:

$$D^{eff} = D.\frac{\epsilon}{\tau} \tag{13}$$

where $D$ is the diffusion coefficient.

Equation (12) shows that when $\dot{n}_{Ar}$, $A$, $L$, $R$ and $T$ are known and $p_{H_2}$ is measured by the e.m.f. cell, then the effective diffusion coefficient can be calculated. It is interesting to note that $D^{eff}$ should be independent of different $\dot{n}_{Ar}$ values, each of which would set $p_{H_2}$ at a given value. Equation (12), however, neglects argon flow in counter diffusion. A more general treatment of the diffusion has been made available by Mason and Marrero.[10] The fluxes of the two gases argon and hydrogen are given by the following expressions:

$$J_{H_2} = -(D_{H_2})^{eff}\frac{\partial C_{H_2}}{\partial x} + X_{H_2}\delta_{H_2}J \tag{14}$$

$$J_{Ar} = -(D_{Ar})^{eff}\frac{\partial C_{Ar}}{\partial x} + X_{Ar}.\delta_{Ar}J \tag{15}$$

where $J_i$ stands for flux, $(D_i)^{eff}$ for effective diffusion coefficient, $C_i$ for concentration, and $X_i$ for mole fraction, all for species $i$; $x$ is the distance along the axis of the specimen. $J$ is the total flux given by

$$J = J_{H_2} + J_{Ar}$$

$\delta_{H_2}$ and $\delta_{Ar}$ equal, by definition,

$$\frac{D_{H_2}}{D_{H_2/Ar}} \quad \text{and} \quad \frac{D_{Ar}}{D_{H_2/Ar}},$$

respectively.

The conservation equations of hydrogen and argon are given by the following relationships:

$$\frac{\partial}{\partial x}(r^2 J_{H_2}) = 0 \tag{16}$$

$$\frac{\partial}{\partial x}(r^2 J_{Ar}) = 0 \tag{17}$$

Also at

$$x = 0 \qquad C_{H_2} = C_{H_2}{}^0$$

and at

$$x = L \qquad C_{H_2} = C_{H_2} \tag{18}$$

Equations (14) and (15) after rearrangement can be integrated using relationships (16)–(18). The result is the following:

$$(D_{H_2})^{eff} = \frac{K_2 L J_{H_2}}{\ln(1 - C_{H_2}K_2/1 - C_{H_2}{}^0 K_2)} \tag{19}$$

where

$$K_2 = \frac{\beta_1\delta_2}{C_{H_2}{}^0} \quad \text{and} \quad \beta_1 = 1 - \left(\frac{M_{H_2}}{M_{Ar}}\right)^{1/2} \tag{20}$$

$M_i$ being the molecular weight of gas $i$.

Using equation (13) one obtains from equation (19)

$$\frac{\epsilon}{\tau}=\frac{K_2LJ_{H_2}}{D_{H_2}.\ln(1-C_{H_2}K_2/1-C_{H_2}{}^0K_2)} \tag{21}$$

For equation (21) the value of $C_{H_2}$ is known from a knowledge of $D_{H_2}$, calculated from the measured e.m.f. values. Knowing $p_{H_2}$ and $n_{Ar}$ one can obtain the value of $\dot{n}_{H_2}$ and $J_{H_2}$ using equation (10). The value of $D_{H_2}$ is known from the following relationship:

$$\frac{1}{D_{H_2}}=\frac{1}{D_{H_2}{}^k}+\frac{1}{D_{H_2/Ar}} \tag{22}$$

where $D_{H_2}{}^k$ is the Knudsen diffusion coefficient and $D_{H_2/Ar}$ is the binary diffusion coefficient for the diffusion of hydrogen in argon. This can be calculated using Gilliland's formula.[11] The Knudsen diffusion coefficient $D_{H_2}{}^k$ is given by

$$D_{H_2}{}^k=\frac{2}{3}r_p\left[\frac{8\times8.314\times10^7T}{M_{H_2}}\right]^{1/2} \tag{23}$$

where $r_p$ is the pore radius. The value of $r_p$ is calculated using the following equation

$$r_p=\frac{2V_P}{S} \tag{24}$$

where $V_P$ is the total pore volume and $S$ the total surface area. $V_P$ is obtainable from density measurements and $S$ from porosimetry using nitrogen adsorption.

Thus using sample dimension $L$ and evaluating $C_{H_2}$ it is possible to determine the value of $(\epsilon/\tau)$ using equation (21). One can then also obtain a value for $\tau$.

## 4. Results and discussion

### 4.1. Results of flow experiment

The results of the forced flow experiments are discussed first. Figure 3 shows plots according to

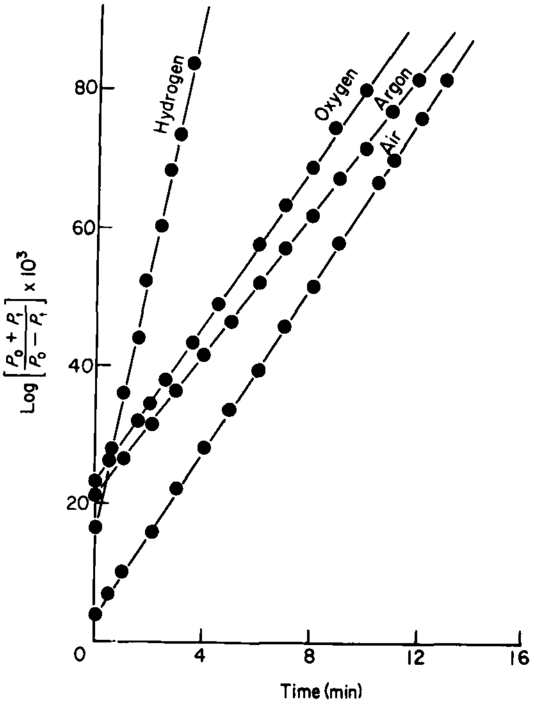

Figure 3. Flow of different gases through porous pellet of reduced hematite. Temperature = 30°C.

equation (8). The plots, which are linear as predicted, were obtained using a porous pellet of reduced hematite. The slopes, plotted against reciprocal viscosity, also yield a linear plot as predicted as shown in Figure 4. The viscosity of air has been obtained as a weighted average of viscosity values for nitrogen and oxygen. The binary gas understandably shows a slight deviation from the line for pure gases.

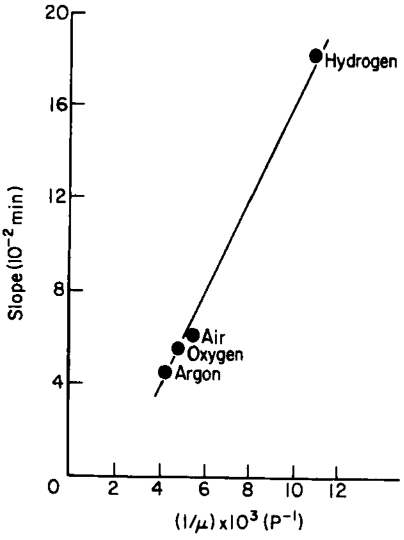

**Figure 4.** Slope *vs* reciprocal viscosity. Temperature = 30°C.

Figure 5 shows the plot according to equation (8) for a porous pellet of reduced cobalt oxide exposed to hydrogen. The experimental parameters are indicated in the figure legend.

The slope of the line is

$$\frac{0.4}{40\times 60}=\frac{1}{2.303}\cdot\frac{Ar^2P_0}{8\mu VL}\left(\frac{\epsilon}{\tau}\right)$$

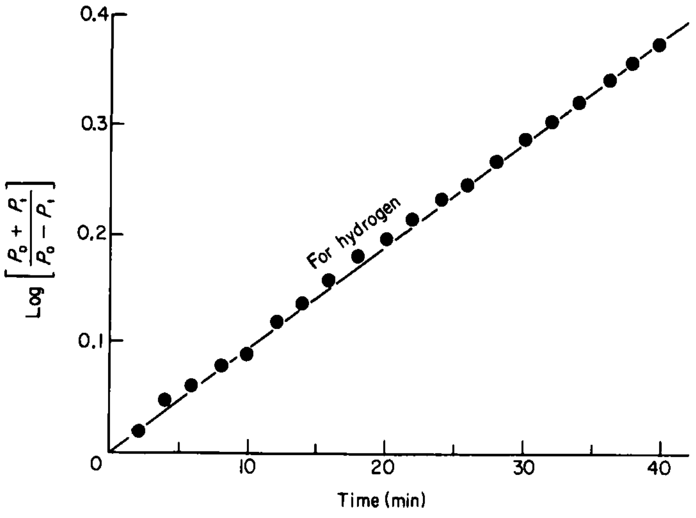

**Figure 5.** Flow of hydrogen through a pellet of reduced cobalt oxide. Temperature = 20°C; pore radius, $r = 10^{-4}$ cm approx.; atmospheric pressure, $P_0 = 74.5$ cmHg; gas viscosity, $\mu = 8.4\times 10^{-5}$ P; system volume, $V = 2$ litres; length of sample, $L = 0.666$ cm; area of sample, $A = 0.576$ cm$^2$; porosity = 65%.

Substituting appropriate values of $A$, $r$, $P_0$, $\mu$, $V$, $L$ and $\epsilon$, $\tau$ is found to be of the order of unity which is reasonable. For gas–solid reactions involving porous oxide pellets $\tau$ is usually assumed to be around 2.[12] In the present case precise calculation of $\tau$ is not possible due to uncertainty of the value of the average pore radius.

### 4.2. Results of the diffusion experiment

The results of the diffusion experiment carried out using hydrogen and argon and a porous nickel pellet are shown in Table 1. The effective diffusion coefficient has been calculated using equation (19). The parameters used for calculation are given in Table 2.

**Table 1.** Calculated values of $D_{H_2}^{eff}$ and $\epsilon/\tau$ at different flowrates

| Argon flowrate (ml/min) | e.m.f. (mV) | $p_{H_2}$ (atm) | $D_{H_2}^{eff}$ (cm²/s) | $\frac{\epsilon}{\tau}$ |
|---|---|---|---|---|
| 71 | 46.0 | 0.0295 | 0.0530 | 0.075 |
| 77 | 47.0 | 0.0273 | 0.0531 | 0.075 |
| 87 | 48.5 | 0.0243 | 0.0532 | 0.075 |
| 99 | 49.2 | 0.0231 | 0.0572 | 0.081 |

**Table 2.** Parameters used for calculation of $D^{eff}$ and $\epsilon/\tau$

| | |
|---|---|
| Length of specimen, $L$ | 0.85 cm |
| Radius of specimen | 0.350 cm |
| Average pore radius (as obtained from porosimetry measurements using nitrogen absorption), $r$ | $0.264 \times 10^{-4}$ cm |
| Temperature, $T$ | 303 K |
| $D_{H_2}$ | 3.13 cm²/s |
| $D_{H_2/Ar}$ | 0.910 cm²/s |
| $D_{H_2}$ | 0.705 cm²/s |

The results show that the effective diffusion coefficient and $\epsilon/\tau$ remain almost unchanged at different flowrates. The directly measured $\epsilon/\tau$ values agree favourably with values obtained indirectly by Deb Roy[13] ($\epsilon/\tau = 0.06$) from kinetic measurements on gas–solid reactions involving single spherical pellet. No explanation is available for the 25% difference.

It may be noted that while the present experiment was used for measuring hydrogen diffusion only, the basic principle may be employed for many other gases provided there is a suitable arrangement for analysis of the argon stream.

## 5. Conclusion

It is concluded that the simple experiments described in the present article may be usefully employed under various situations for direct determination of some important parameters in gas–solid reactions, namely, effective diffusion coefficient and tortuosity factor.

### Acknowledgement

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