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EXPERIMENTAL STUDIES USING A SINGLE PELLET HIGH TEMPERATURE DIFFUSION CELL REACTOR

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ABSTRACT

It is very important to know the effective diffusivities of reactant gases through the porous solid matrices for a diffusion limited reaction. The single pellet high temperature diffusion cell reactor is used to measure the effective diffusivities of argon and nitrogen during the sequence of calcination, sintering, salt addition and sulfation of Greer limestone. This system can be used to study the gas—solid reaction systems where the solid phase undergoes changes between 25 and 1200°C.

INTRODUCTION

The most common method of measuring counter-diffusion of gases in porous solids has been by a steady-state technique first used by Wicke and Kallenbach [1] and modified by Weisz and Schwartz [2] and Wakao and Smith [3]. Two pure gases flow past two sides of a thin pellet of experimental material. The counter-diffusion fluxes of the two gases through the pellet are measured from the composition of the gas exit streams on each side of the diffusion cell. The pressure gradient across the pellet must be maintained at zero. Formerly, experiments were carried out at temperatures as high as 300°C [4].

A new computerized advanced design apparatus has been developed to obtain diffusion data of gases while internal structural changes are taking place within the porous matrix. Changes in gas effective diffusivity due to sintering of the solid matrix including the relative effects of macroporosity and microporosity can be determined. The temperature range over which measurements can be effectively made has been extended to between 1000 and 1200°C. Structural changes occurring during chemical reaction can be followed simultaneously with the extent of reaction. This information is particularly valuable where gaseous reactants are deposited in the porous matrix as a function of reaction extent and result in a change in structure. Macropore vs. micropore effects can be determined by separately measuring the Knudsen and the bulk effective diffusivities, obtained by measuring system parameters at two different pressures.

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EXPERIMENTAL APPARATUS

A diamond coring drill bit is used to make a Greer limestone cylinder which has a diameter of 0.75 in. This cylinder is cut with a carborundum saw to give 0.125 in. thick pellets. The pellet is mounted in the single pellet high temperature diffusion cell (see Fig. 1) with Sauereisen high temperature cement.

The flow chart of the automated experiment is shown in Fig. 2 and the flow sheet of the logical controlled operation in Fig. 3. Different parts of the experiment are shown in Figs. 4—6. The N_2 and Ar are supplied in high pressure cylinders. The pressure regulator, PR 1, reduces the stream pressure to about 45 psig. The other pressure regulator, PR 2, further reduces the N_2 pressure to about 5 psig. During low pressure operations, the pressure in the diffusion cell is determined by PR 2. When high pressure operation is performed, the pneumatic control valve, V1, is opened, thereby bypassing PR 2 and subjecting the diffusion cell to the pressure determined by PR 1. The check valve, S1, permits flow in the forward direction during the low pressure mode but stops N_2 flowing back to PR 2 during the high pressure mode.

The opening of the control valve, V1, is very delicate. Any rapid change in pressure may result in damage to the pellet. The rate of valve opening is an exponential function of time. Therefore, the valve will open slowly at first and then more rapidly. The reverse is true for closure of the valve, i.e. at first rapidly and then more slowly. The differential pressure between both sides of the pellet is controlled during this cycling. If this differential pressure ever exceeds 4 in. of water, the action of the control valve is immediately reduced. This gives time to equilibrate on either side of the pellet.

One of the major requirements for experimental accuracy is having a zero pressure differential between both sides of the pellet. This differential pressure is measured by the d/p cell, PI 5. PI 5 sends a signal to the pneumatic controller, C1, which adjusts the control valve, V2; accordingly, the upstream pressure is regulated by PR 3. This pressure is higher than the operating pressure and so adequate flow through the control valve can be obtained.

The flow rate is determined by using a d/p cell to measure the pressure drop resulting from the flow of the process gas through an orifice. In Fig. 2, PI 1 measures the flow rate of N_2, and PI 4 measures that of Ar. These flow rates are controlled by C2 and C3 pneumatic controllers by making adjustments to control valves V3 and V4. By controlling the pressure before

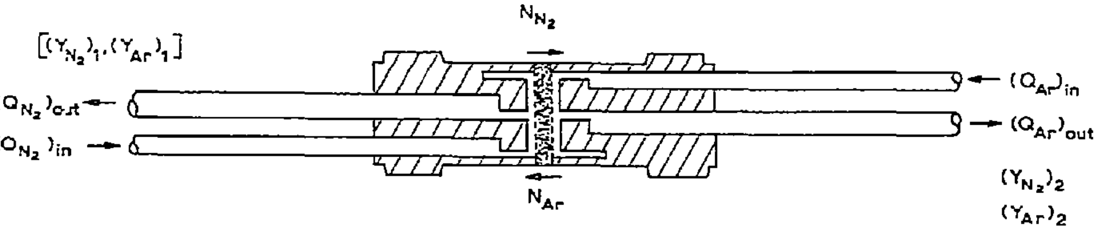


Fig. 1. Single pellet high temperature diffusion cell reactor.

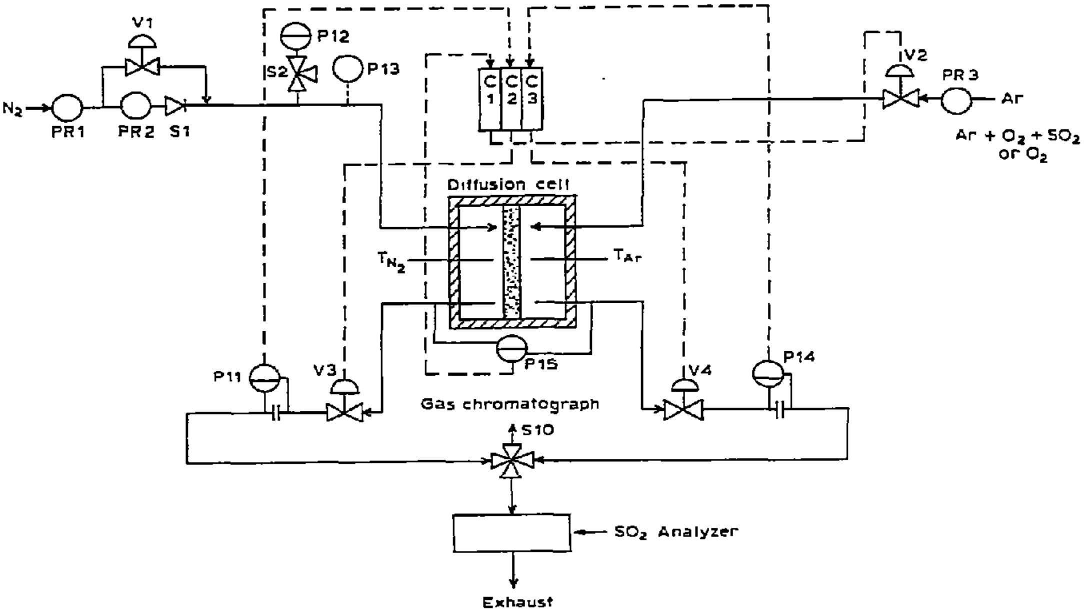


Fig. 2. Flow chart of the automated apparatus.

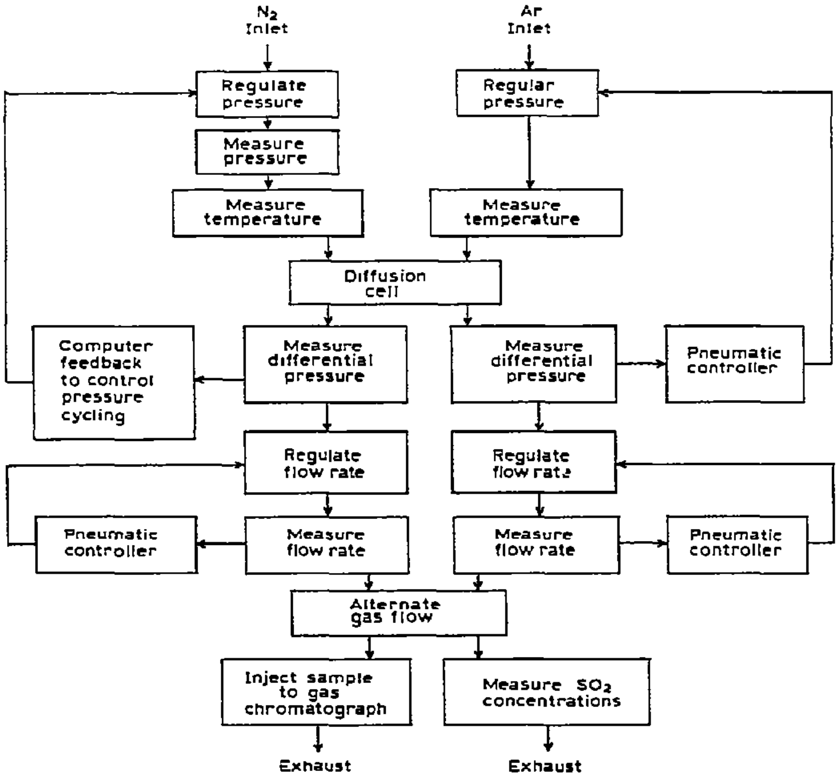


Fig. 3. Flow sheet of the logical controlled operations.

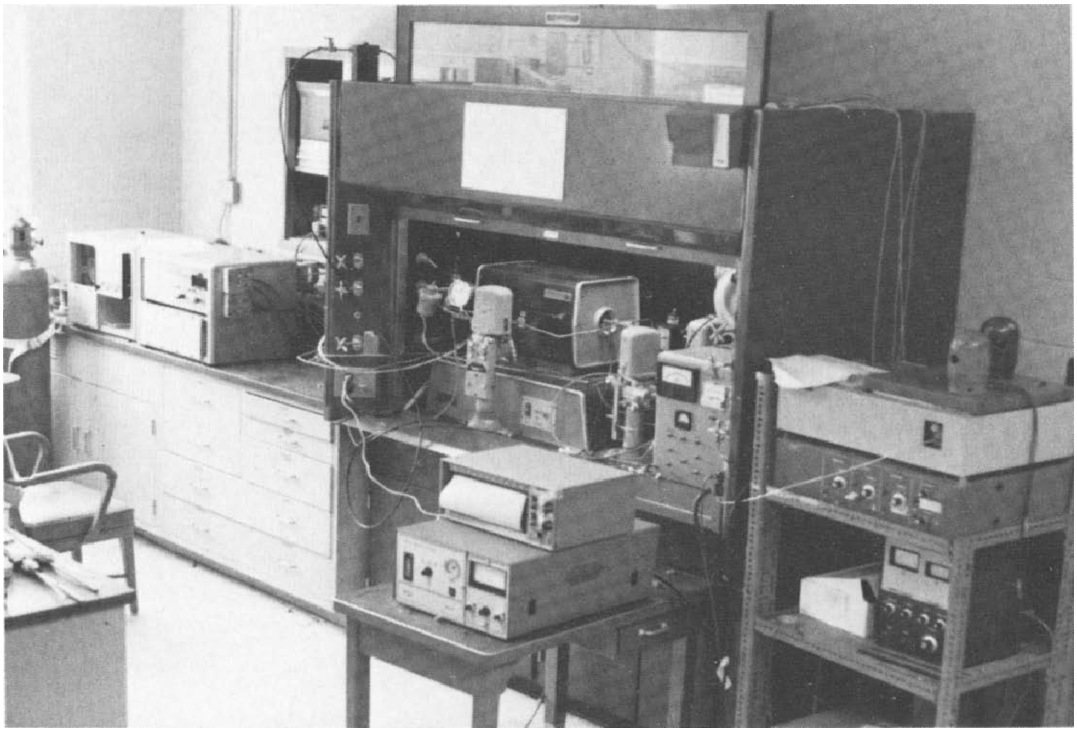


Fig. 4. Overall view of the apparatus.

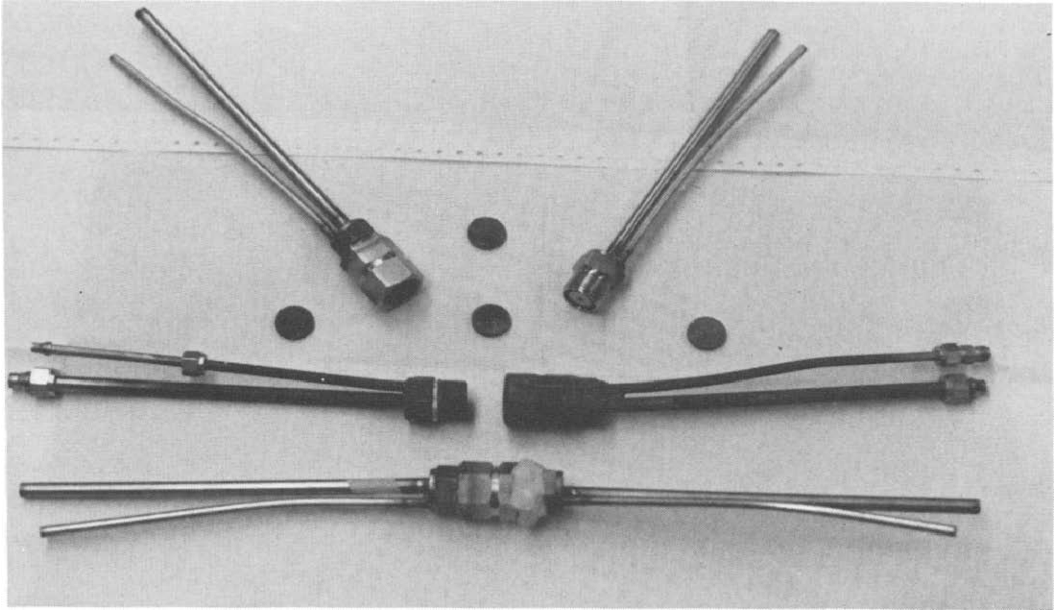


Fig. 5. High temperature diffusion cell reactor.

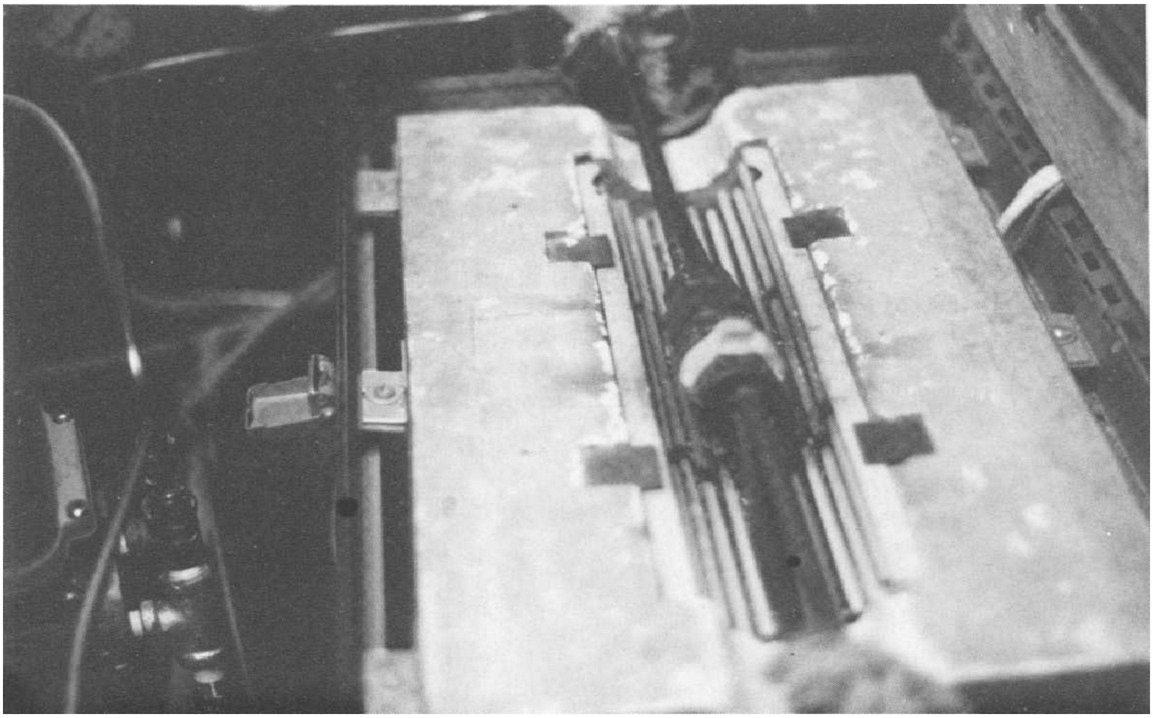


Fig. 6. Open view of the diffusion cell reactor during the experiment.

the diffusion cell and the flow rate after the cell, flow rates and the pressure can be changed independently.

C1, C2 and C3 have proportional and integral action. C1 and C2 should be tuned according to their manual. The Ar control, C3, should be handled in a different way since the Ar pressure is also under pneumatic control. The flow rate and pressure are interacting. If V2 is opened to increase the pressure in the diffusion cell the flow rate increases. This causes the controller, C3, to close V4, thus pressure increases more. The result is that the system tends to oscillate. This can be handled by turning controller C3 loosely.

The accurate measurement of pressure is one of the important factors in obtaining accurate results in this experiment. Two indicators are used to measure the pressure. PI 2 is a d/p cell and measures low pressures up to 200 in. of water. PI 3 is a pneumatic transmitter which measures the pressure up to 75 psig. Both PI 2 and PI 3 measure the pressure in the N_2 stream. The Ar pressure is calculated from the differential pressure measured by PI 5.

The temperature in the cell is measured with chromel—alumel thermocouples on either side of the pellet. These thermocouples were placed 2 mm from the Greer limestone pellet in an old style diffusion cell. They were placed 5 mm from the pellet, in the exit gas stream pipes, in the modified diffusion cell.

The salt is loaded in a handmade stainless steel sieve boat which is attached to the end of an aluminum wire. The salt boat is placed in a dead-end of a T connection located on the Ar inlet stream and outside the oven. When salt addition is desired, the boat is pushed with the wire until the end of the outside pipe is reached, thus having the boat close to the pellet.

The diffusivity calculations require the analysis of the N_2 and argon (or O_2) streams after leaving the diffusion cell. These are obtained by gas chromatography. At the proper time, the computer sends a signal to a four-way switch, S10, to load up the injection coil with the N_2 stream. The N_2 stream is passed through the injection coil, sweeping out any gas remaining from the previous sample. When this is completed, the helium carrier gas is passed through the injection coil, thus injecting the amount of gas contained in the injection coil. A similar procedure is followed for the Ar stream. From the injection system, the helium carrier gas takes the sample directly into the column. The separation of Ar and N_2 (or O_2 and N_2) is achieved by using a 5 Å molecular sieve column. The oven is operated at room temperature to obtain the maximum separation. The column length was 30 ft. It takes approximately, 20 min to process. The areas under the peaks are determined by the PDP8e computer using a variable gain.

Effective diffusivity calculations

Nitrogen and argon enter the cell from opposite ends. Let the flow rates be Q_{N_2} (cm^3 sec^{-1}), and Q_{Ar} (cm^3 sec^{-1}) for nitrogen and argon, respectively. From gas chromatographic results, the volume ratios (or mole ratios) of gases can be calculated at each side of the cell (see Fig. 1).

If the argon side is analyzed by injecting a sample from this side to the gas chromatograph, first the argon peak will be obtained, followed by the nitrogen peak. If the corrected areas are $(A_{Ar})_1$ and $(A_{N_2})_1$, the mole ratio of argon is

$$(y_{Ar})_1 = (A_{Ar})_1/[(A_{Ar})_1 + (A_{N_2})_1] \tag{1}$$

and the mole ratio of nitrogen is

$$(y_{N_2})_1 = (A_{N_2})_1/[(A_{Ar})_1 + (A_{N_2})_1] \tag{2}$$

When a sample from the nitrogen side is injected into the gas chromatograph, $(y_{Ar})_2$ and $(y_{N_2})_2$ can be calculated as on the argon side.

The amount of diffused argon is $(Q_{N_2})_{out} \times (y_{Ar})_2$ (cm^3 sec^{-1}). From a knowledge of the room temperature and pressure, the number of moles of diffused argon can be calculated. Since the diffusion area of the Greer limestone pellet is already known, the number of moles of argon diffused per cm^2 per sec can be calculated.

$$N_{Ar} = -\frac{P}{RT} \cdot D_{eff} \cdot \frac{(y_{Ar})_2 - (y_{Ar})_1}{\Delta r} \tag{3}$$

where Δr is the thickness of the pellet in cm and N_{Ar} is the argon molar flux in g moles cm^{-2} sec^{-1}. The molar flux ratio, N_{N_2}/N_{Ar}, is the same regardless of the extent of the Knudsen and bulk diffusion. Evans et al. [6] have shown this constant to be

$$\frac{N_{N_2}}{N_{Ar}} = \sqrt{\frac{M_{Ar}}{M_{N_2}}} = 1.19 \tag{4}$$

A correction is made to obtain the right experimental results, i.e.

$$\frac{(N_{N_2})_{\text{exp}} + \Delta N}{(N_{\text{Ar}})_{\text{exp}} - \Delta N} = 1.194 \tag{5}$$

$$\Delta N = [1.194 \cdot (N_{\text{Ar}})_{\text{exp}} - (N_{N_2})_{\text{exp}}]/2.194 \tag{6}$$

$$(N_{N_2})_{\text{cor.}} = (N_{N_2})_{\text{exp}} + \Delta N \tag{7}$$

$$(N_{\text{Ar}})_{\text{cor.}} = (N_{\text{Ar}})_{\text{exp}} - \Delta N \tag{8}$$

In the modified diffusion cell for $(y_{\text{Ar}})_1$ and $(y_{\text{Ar}})_2$ the arithmetic mean of the inlet and outlet concentrations is used, i.e.

$$(y_{\text{Ar}})_1 = \frac{0 + (y_{\text{Ar}})_1}{2}, \qquad (y_{\text{Ar}})_2 = \frac{1 + (y_{\text{Ar}})_2}{2} \tag{9}$$

This represents the driving force well.

$(D_e)_{N_2}$ and $(D_e)_{\text{Ar}}$ will be calculated for 1 and 4 atm. The bulk diffusivity is dependent on pressure, whereas the Knudsen diffusivity is not when the mean free path does not change. The Chapman equation is

$$(D_{\text{Ar—N}_2})_{\text{Bulk}} = 0.0018583\,\frac{T^{3/2}(1/M_{\text{Ar}} + 1/M_{N_2})^{1/2}}{P_t \cdot \sigma^2_{\text{Ar—N}_2} \cdot \Omega_{\text{Ar—N}_2}} \tag{10}$$

$$(D_{\text{Ar}})_{\text{Knudsen}} = 9700 \cdot r_e \cdot \sqrt{T/M_{\text{Ar}}} \tag{11}$$

The mean pore radius can be defined as

$$r_e = \frac{2V_g}{S_g} = \frac{2\theta}{S_g \rho_p} \tag{12}$$

where θ is the porosity, S_g is total surface area in $\text{cm}^2\ \text{g}^{-1}$, and ρ_p is the average pellet density in g cm^{-3}. Substituting eqn. (12) in eqn. (11), the Knudsen diffusion coefficient for a porous pellet becomes

$$(D_{\text{Ar}})_{K,e} = \frac{D_K \cdot \theta}{\tau} = 19\,400\,\frac{\epsilon^2}{\tau S_g \rho_p}\sqrt{T/M_{\text{Ar}}} \tag{13}$$

or

$$(D_{\text{Ar}})_{K,e} = \frac{9700 \cdot r_e \cdot \epsilon}{\tau}\sqrt{\frac{T}{M_{\text{Ar}}}} \tag{14}$$

$$(D_e)_{\text{Ar}} = \frac{1}{(1 - y_{\text{Ar}})/(D_{\text{Ar—N}_2})_e + [(1/D_{\text{Ar}})_{K,e}]} \tag{15}$$

where $\alpha = 1 + N_{N_2}/N_{\text{Ar}}$.

Bosanquet [7] showed there is no significant difference between the $(D_e)_{\text{Ar}}$ which were obtained from eqn. (15) and the equation given below.

$$\frac{1}{(D_e)_{\text{Ar}}} = \frac{1 - \alpha y_{\text{Ar}}}{[D_{(\text{Ar—N}_2)}]_e} + \frac{1}{(D_{\text{Ar}})_{K,e}} \tag{16}$$

Let us write eqn. (16) for p_2 atm and p_1 atmosphere absolute pressures

$$\frac{1}{(D_{e,\text{Ar}})_{p_2}} = \frac{1 - \alpha y_{\text{Ar}}}{[D_{(\text{Ar},N_2),e}]_{p_2}} + \frac{1}{[(D_{\text{Ar}})_{K,e}]_{p_2}} \tag{17}$$

$$\frac{1}{(D_{e,Ar})_{p1}} = \frac{1-\alpha y_{Ar}}{[D_{(Ar,N_2)e}]_{p1}} + \frac{1}{[(D_{Ar})_{K,e}]_{p1}} \tag{18}$$

$$\frac{1}{[(D_{Ar})_{K,e}]_{p2}} = \frac{1}{[(D_{Ar})_{K,e}]_{p1}} \tag{19}$$

$$[D_{(Ar,N_2),e}]_{p2} = (p_1/p_2)\,[D_{(Ar-N_2),e}]_{p1} \tag{20}$$

Subtracting eqn. (18) from eqn. (17) and substituting eqns. (19) and (20) gives

$$[D_{(Ar,N_2),e}]_{p1} = (1-y_{Ar})\left(\frac{p_2-p_1}{p_1}\right)\Big/\left[\frac{1}{(D_{e,Ar})_{p2}} - \frac{1}{(D_{e,Ar})_{p1}}\right] \tag{21}$$

$(D_{e,Ar})_{p2}$, and $(D_{e,Ar})_{p1}$ are known. $[(D_{Ar,N_2})_e]_{p1}$, the effective bulk diffusivity of Ar at 1 atm can be calculated from eqn. (21). By substituting this value in eqn. (18), $[(D_{Ar})_{K,e}]_{p1}$ can be found. The temperature and molecular weight of argon are known. If the porosity and tortuosity are known, the average pore radius can be calculated from eqn. (14).

(D_{Ar-N_2}) can be calculated from eqn. (10), and $[(D_{Ar-N_2})_e]_{p1}$ is obtained from the experimental results. From the following equation the tortuosity, τ, will be found

$$[(D_{(Ar-N_2)e}]_{p1} = (D_{Ar-N_2})_{p1} \cdot \frac{\epsilon}{\tau} \tag{22}$$

$$\tau = (D_{Ar-N_2})_{p1} \cdot \epsilon/[(D_{Ar,N_2})_e]_{p1} \tag{23}$$

and the porosity will be found from the amount of evolved CO_2.

When the porosity and tortuosity are known, the mean pore size can be calculated from eqn. (24)

$$r_e = \frac{(D_{Ar})_{K,e} \cdot \tau}{9700 \cdot \epsilon}\sqrt{\frac{M_{Ar}}{T}} \tag{24}$$

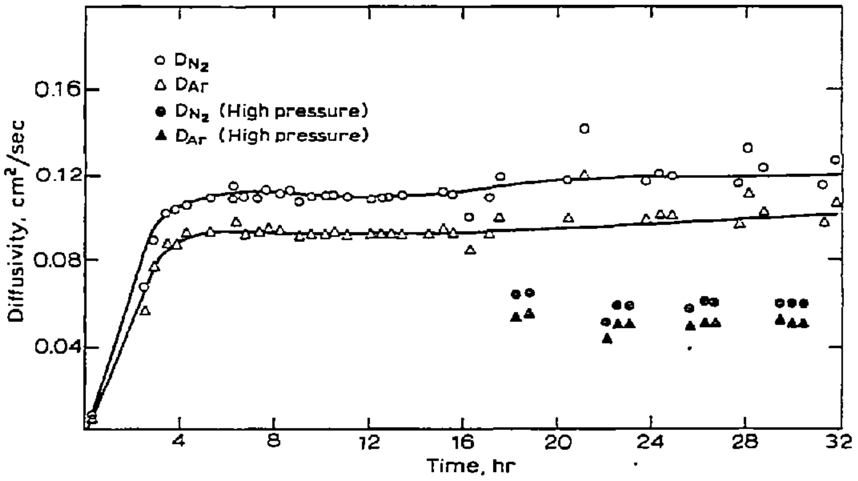
From eqn. (3), the experimental effective diffusivity of argon is

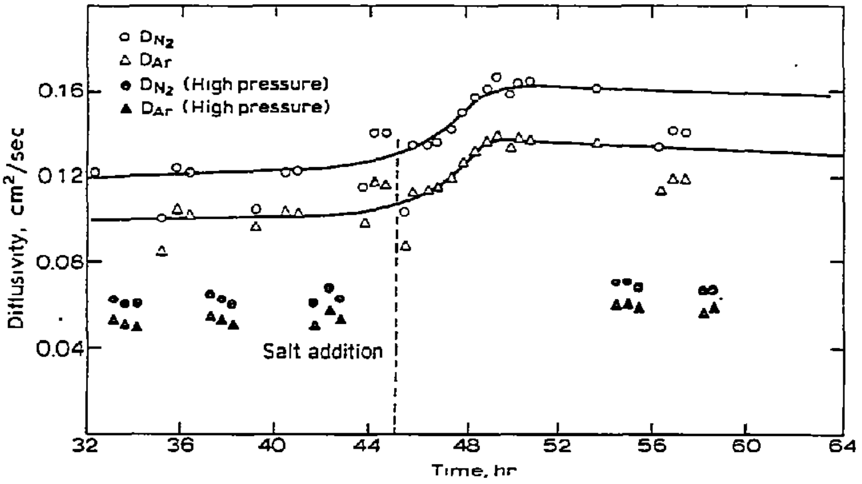
$$(D_{eff})_{Ar} = -(N_{Ar})_{cor.} \cdot RT \cdot \Delta/[p \cdot ((y_{Ar})_2 - (y_{Ar})_1)] \tag{25}$$

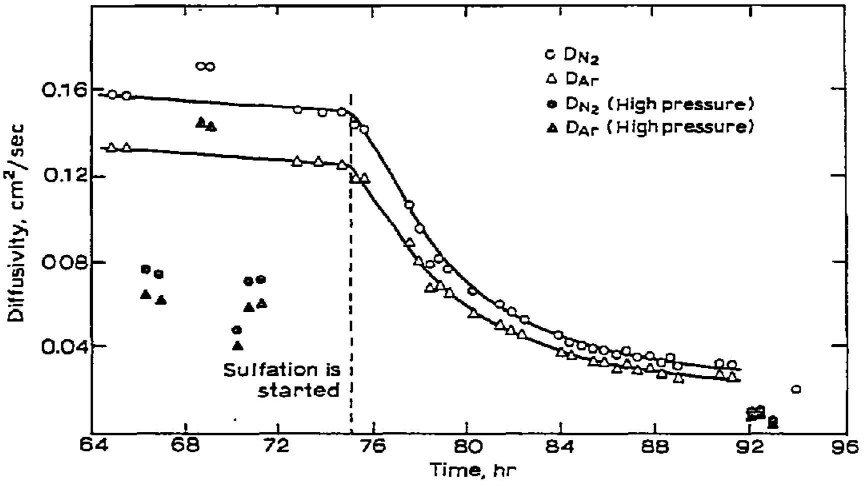
$(D_{eff})_{N_2}$ will be calculated in the same way.

SAMPLE RUN

An experiment at 843°C is carried out for 110 h (see Fig. 7). The diffusivity of argon and nitrogen is increased as a function of calcination time. After 45 h of calcination, a salt boat is pushed close to the pellet. The salt vapor is allowed to open up the pores. The diffusivity of gases is increased. After 74.9 h of calcination, the sulfation is started. Instead of argon, 540 ppm SO_2 and 1.02% O_2 in argon is used. The diffusivity of argon and nitrogen is


○ D_{N_2}
△ D_{Ar}
● D_{N_2} (High pressure)
▲ D_{Ar} (High pressure)
Diffusivity, cm²/sec
0.16
0.12
0.08
0.04
4
8
12
16
20
24
28
32
Time, hr


○ D_{N_2}
△ D_{Ar}
● D_{N_2} (High pressure)
▲ D_{Ar} (High pressure)
Diffusivity, cm²/sec
0.16
0.12
0.08
0.04
Salt addition
32
36
40
44
48
52
56
60
64
Time, hr


○ D_{N_2}
△ D_{Ar}
● D_{N_2} (High pressure)
▲ D_{Ar} (High pressure)
Diffusivity, cm²/sec
0.16
0.12
0.08
0.04
Sulfation is started
64
68
72
76
80
84
88
92
96
Time, hr

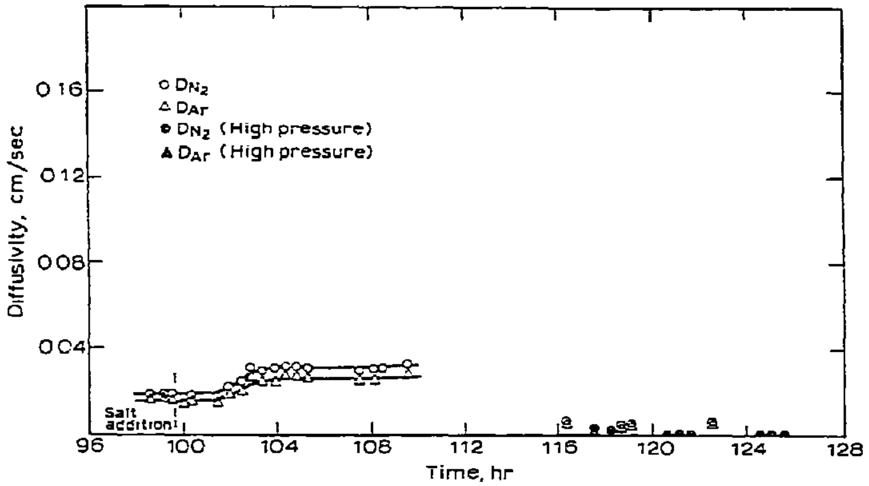


Fig. 7. Diffusivity of argon and nitrogen through calcined Greer limestone during calcination, salt addition and sulfation. Temperature 843.1° C; run no. C6.

decreased as the sulfation reaction takes place. There was no sulfur dioxide on the N_2 steam exit. At 99.8 h salt is added to the system; the diffusivities are increased again during the sulfation.

CONCLUSIONS

The single pellet high temperature diffusion cell reactor can be used to measure the effective diffusivity of gases through the porous pellets at low and high temperatures (20—1200° C). The change in the diffusivity of gases due to the chemical reaction that takes place in the pellet can be determined during the reaction. The effective diffusivity of gases can also be determined at different pressures up to 45 psig. For a diffusion limited reaction, the knowledge of effective diffusivity is one of major concern. The single pellet high temperature diffusion cell can be used as a very important tool in measuring the diffusivities so the reaction can be understood and modeled in a better way.

NOMENCLATURE

A	unit area under the peaks
D_{eff}	effective diffusivity of a gas ($cm^2\ sec^{-1}$)
M	molecular weight (g)
N	rate of diffusion (g mole $cm^{-2}\ sec^{-1}$)
p	the pressure of the gas (atm)
Q	the flow rates (cm^3/sec)
Δr	the thickness of the pellet (cm)
y	the mole ratio of gas

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