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Determination of diffusion coefficients of hydrogen in fused silica between 296 and 523 K by Raman spectroscopy and application of fused silica capillaries in studying redox reactions

Linbo Shang[a,*], I-Ming Chou[b], Wanjun Lu[c], Robert C. Burruss[d], Youxue Zhang[e]

[a] State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
[b] US Geological Survey, 954 National Center, Reston, VA 20192, USA
[c] State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China
[d] US Geological Survey, 956 National Center, Reston, VA 20192, USA
[e] Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1005, USA

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Abstract

Diffusion coefficients (D) of hydrogen in fused silica capillaries (FSC) were determined between 296 and 523 K by Raman spectroscopy using CO_2 as an internal standard. FSC capsules (3.25×10^{-4} m OD, 9.9×10^{-5} m ID, and ~0.01 m long) containing CO_2 and H_2 were prepared and the initial relative concentrations of hydrogen in these capsules were derived from the Raman peak-height ratios between H_2 (near 587 cm^{-1}) and CO_2 (near 1387 cm^{-1}). The sample capsules were then heated at a fixed temperature (T) at one atmosphere to let H_2 diffuse out of the capsule, and the changes of hydrogen concentration were monitored by Raman spectroscopy after quench. This process was repeated using different heating durations at 296 (room T), 323, 375, 430, 473, and 523 K; the same sample capsule was used repeatedly at each temperature. The values of D (in $m^2\ s^{-1}$) in FSC were obtained by fitting the observed changes of hydrogen concentration in the FSC capsule to an equation based on Fick's law. Our D values are in good agreement with the more recent of the two previously reported experimental data sets, and both can be represented by:

$$\ln D = -(16.471 \pm 0.035) - \frac{44589 \pm 139}{RT} \qquad (R^2 = 0.99991)$$

where R is the gas constant (8.3145 J/mol K), T in Kelvin, and errors at 1σ level. The slope corresponds to an activation energy of 44.59 ± 0.14 kJ/mol.

The D in FSC determined at 296 K is about an order of magnitude higher than that in platinum at 723 K, indicating that FSC is a suitable membrane for hydrogen at temperature between 673 K and room temperature, and has a great potential for studying redox reactions at these temperatures, especially for systems containing organic material and/or sulphur.

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1. INTRODUCTION

The oxygen-buffer technique (Eugster, 1957; Chou, 1987) is routinely used in experimental studies of redox-sensitive geochemical reactions at elevated pressure (P) and temperature (T). In this technique, the hydrogen fugacity (fH_2) in the vapour phase of an H_2O-containing sample system (ss) in a sealed Pt or Ag-Pd capsule at experimental P–T condition is defined by that of the external buffer system (bs) because of high permeability of hydrogen through Pt or Ag-Pd membrane, such that at equilibrium:

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[*] Corresponding author. Fax: +86 851 589 1664.
E-mail address: sss_2000@sina.com (L. Shang).

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$$(fH_2)_{ss} = (fH_2)_{bs} \quad (1)$$

Once the $(fH_2)_{ss}$ is defined at a fixed experimental P–T condition, then, according to the phase rule, all intensive parameters in the vapour phase of the sample system, including $(fO_2)_{ss}$ and $(fH_2O)_{ss}$, are defined. However, two important factors are needed for a proper control of the redox state of the sample system: (a) the actual fH_2 of the buffer needs to be calibrated (Chou, 1978a, 1987), and (b) the container of the sample needs to be a good osmotic membrane for hydrogen (Chou, 1986), such that the condition specified by Eq. (1) can be reached within a reasonable period of experimental duration (e.g., 2 weeks). Consequently, this technique is limited to temperatures above about 673 K because of the low permeability of the sample containers (Pt or Ag-Pd alloys) to hydrogen at lower temperatures (Chou et al., 1978b; Chou, 1986). Preliminary results of Chou et al. (2008a) indicate that the use of fused silica capillary (FSC) containers may extend this technique to lower temperatures because of its high permeability to hydrogen.

Previous experimental data for hydrogen permeation and/or diffusion in various types of silica were collected mostly by heating silica plates in hydrogen at temperatures above 1073 K, and the glasses containing SiOH or SiH were then heat-treated in air to derive the diffusivity (Williams and Ferguson, 1924; Stone et al., 1985; Shelby, 1994; Schmidt et al., 1998; Lou et al., 2003) assuming the hydroxyl or hydride pair formation mechanism (Barrer, 1941; Lee et al., 1962; Kats et al., 1962; Lee, 1963; Lou et al., 2003). Some studies determined molecular deuterium diffusivities in silica (e.g., Lee et al., 1962; Lee, 1963; Shelby, 1977), which were lower than molecular hydrogen diffusivities by about 20% (e.g., Lee, 1963). Only a few of previous studies directly measured the diffusion of molecular hydrogen out of silica tubes at low temperatures (<673 K) (Barrer, 1934, 1941; Lee et al., 1962).

In this study, Raman spectroscopy was used to measure the hydrogen diffusion through the FSC between 296 (room temperature) and 523 K. The temperature-dependent diffusion coefficients of hydrogen (D) were obtained by measuring the time-dependent concentrations of hydrogen in FSC capsules at a specific temperature.

2. EXPERIMENTAL AND ANALYTICAL METHODS

2.1. Experimental methods

FSC capsules, prepared from capillaries purchased from Polymicro Technologies (http://polymicro.com), were used as the diffusion cells in this study. Our experiments involved the following five steps: (1) loading CO_2 in the FSC capsule to provide an internal standard for quantitative Raman spectroscopic measurements of H_2; (2) loading H_2 at elevated pressure and temperature in the FSC capsule, which already contains CO_2, in a sealed Au capsule containing an H_2 buffer; (3) collecting CO_2 and H_2 Raman spectra of the vapour phase in the quenched FSC capsule, which was extracted from the Au capsule, to determine the initial amount of H_2 in the capsule; (4) diffusing H_2 out of the FSC capsule at a fixed temperature under one atmosphere (open air) for a certain period of time; and (5) collecting CO_2 and H_2 Raman spectra of the vapour phase in the quenched FSC capsule to determine the amount of H_2 loss.

In the first step, FSC capsule (3.25×10^{-4} m OD, 9.9×10^{-5} m ID, and ~0.01 m long) was prepared by loading CO_2 cryogenically in a FSC with one end sealed. The open end was sealed with a hydrogen flame under vacuum while the sample end was still frozen in liquid nitrogen, as described by Chou et al. (2008a). In the second step, the capsule was inserted into an open-ended ceramic protection tube and loaded in a gold capsule containing Fe powder and water (Fig. 1). This sample assembly was heated at 573 K under 100 MPa of Ar external pressure (P) in a cold-seal pressure vessel for three days to allow H_2 generated by the Fe–H_2O reaction to diffuse into the FSC capsule. After quench, the gold capsule was opened and the FSC capsule, which serves as our initial sample, was taken out. In the third step, Raman spectra were collected from the vapour phase of the FSC capsule and the peak-height ratios between H_2 (near 587 cm^{-1}) and CO_2 (near 1387 cm^{-1}) were determined. The initial pressures of hydrogen in these tubes were about 10 MPa, which was estimated by comparing their Raman signals with those obtained from pure H_2 samples at various pressures in a high-pressure optical cell constructed by using the FSC of the same dimensions (Chou et al., 2005). In the fourth and fifth steps, the sample capsule was inserted into a preheated cold-seal pressure vessel at one atmosphere, and Raman spectra were collected after quench; the durations required to heat up and quench the sample are less than 2 min. These two steps were repeated with different heating durations at 296, 323, 375, 430, 473, and 523 K (Table 1); the same sample capsule was used repeatedly at each temperature. Reported temperatures are considered to be accurate to ±2 K. The experimental temperatures were relatively low to avoid reactions between H_2 and CO_2 that would consume H_2, and experimental products did not show the appearance of other possible reaction products such as H_2O and CO. As will be discussed later, in order to treat the diffusion problem in a simple fashion, effort is made by preheating the samples such that the H_2 profile in the fused silica reaches a "quasi-steady state" before the actual diffusion experiments start.

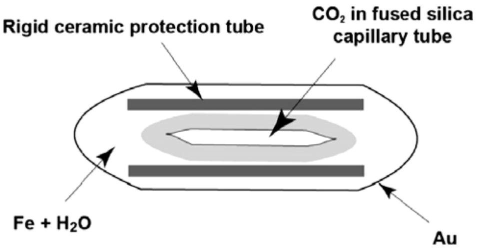


Fig. 1. A schematic diagram, Fig. 14 of Chou et al. (2008a), showing a fused silica capillary capsule containing CO_2, which was enclosed in a gold capsule for loading hydrogen. Hydrogen, produced by the reaction between Fe and water at elevated pressure and temperature, diffused into the FSC capsule, which was later used for hydrogen diffusion experiments. For details, see text.

Table 1
Measured Raman peak-height ratios (HR) between H_2 (587 cm^{-1}) and CO_2 (1387 cm^{-1}) in the FSC capsules as a function of heat-treatment time (in hours, h) at temperatures between 296 and 523 K.

Time (h)	HR (296 K)	Time (h)	HR (323 K)	Time (h)	HR (375 K)	Time (h)	HR (430 K)	Time (h)	HR (473 K)	Time (h)	HR (523 K)
−671.0[a]	6.896[a]	−22.5[a]	0.558[a]	−97.33[a]	1.404[a]	−19.75[a]	2.953[a]	−2.25[a]	2.653[a]	−2.42[a]	6.985[a]
0.0	6.016	0.00	0.546	−48.00[a]	0.979[a]	−15.75[a]	2.711[a]	−1.25[a]	2.574[a]	−0.57[a]	4.752[a]
174.0	5.608	72.00	0.492	0.00	0.707	0.00	1.648	0.00	2.209	0.00	3.895
271.5	5.467	168.00	0.438	43.58	0.525	3.50	1.451	0.80	2.029	0.82	3.252
336.0	5.243	380.25	0.378	86.58	0.403	6.83	1.247	1.60	1.862	1.82	2.564
579.0	5.172	480.00	0.359	133.40	0.292	10.08	0.991	3.07	1.689	2.82	2.068
749.6	4.755	552.85	0.320	183.40	0.212	13.58	0.924	4.07	1.500	3.82	1.509
895.6	4.544	642.68	0.309	210.40	0.171	16.08	0.832	5.57	1.370	4.82	1.229
1111.1	4.631	739.51	0.267	237.85	0.139	19.83	0.776	7.32	1.157	6.27	0.904
1345.1	4.294	837.76	0.239	308.97	0.095	23.58	0.704	8.82	1.034	8.10	0.601
		932.76	0.220	353.55	0.065	27.08	0.564	10.57	0.882	10.35	0.369
		1072.76	0.190	374.88	0.060	30.58	0.518	12.40	0.758		
		1151.76	0.182			34.75	0.420	14.62	0.635		
		1268.76	0.167			40.75	0.384	17.04	0.504		
						43.75	0.335	19.87	0.405		
						47.00	0.313	21.70	0.346		
						50.17	0.265	25.45	0.270		
						53.22	0.232				
						56.20	0.217				
						62.89	0.162				
						65.97	0.147				
						69.72	0.151				
						72.72	0.132				
						76.50	0.113				
						80.25	0.106				

[a] The HR values with negative times were not used in regression for the derivation of *D* (for details, see text).

Spectra were acquired with a JY/Horiba LabRam HR Raman system, using 532.06 nm (frequency doubled Nd:YAG) laser excitation, a 40× Olympus objective with 0.25 numerical aperture, and a 600 grooves/mm grating with a spectral resolution of about 2 cm^{-1}. Approximately 20 mW laser light was focused on a central level of the horizontal tube in order to collecting H_2 and CO_2 Raman signals in the gas phase. Spectra were collected in a single window between 13 and 1700 cm^{-1}, which covers the rotational line of H_2 (near 587 cm^{-1}; Stoicheff, 1957) and the Fermi diad of CO_2 between 1200 and 1400 cm^{-1} (Fig. 2). The peak heights of these H_2 and CO_2 Raman signals were determined by using GRAMS32/AI software.

2.2. Calibration of the Raman system for quantitative analysis

For Raman active species 1 and 2 in a fluid phase, their relative concentrations (*C*) are related to their Raman peak heights (H) by the following formula (Seitz et al., 1996):

$$H_1/H_2 = (G_1/G_2)(C_1/C_2) \tag{2}$$

where G_i's are Raman quantification factors for peak-height relations (Pasteris et al., 1988). Because CO_2 diffusivity at $\leqslant$523 K in silica was negligible in the time scale of our experiments (e.g., CO_2 diffusivity, which is largely composition independent, is only 3×10^{-21} m^2/s at 523 K based on extrapolation from Zhang et al., 2007, resulting in a diffusion distance of only 0.3 μm in a year), CO_2 did not diffuse out of the FSC capsule in our experiments, as also shown by the constant CO_2 density indicated by the constant distance between the Fermi diad peaks of CO_2 (indicated by stars in Fig. 2 at about 1284 and 1387 cm^{-1}; Rosso and Bodnar, 1995), the concentrations of CO_2 in these capsules remained constant and were used as internal standards. Therefore, the peak-height ratios (HR) between H_2 and CO_2 could be used directly as an indicator of the relative concentration of hydrogen in these capsules.

3. ESTIMATION OF *D*

The effective *D* was determined by measuring the decrease in hydrogen concentration in the FSC capsule with Raman spectroscopy. During our diffusion experiments, there was a hydrogen concentration gradient from the inner surface toward the outer surface of the capsule, so that the direction of hydrogen diffusion was from the inner surface ($r = a$) to the outer surface ($r = b$) of the FSC capsule (Fig. 3). For the diffusion of hydrogen in this study, it was assumed that *D* of H_2 is independent of H_2 concentration and the process was treated as occurring through a long circular cylinder by neglecting diffusion at the two ends of the FSC capsule. According to Fick's law, the concentration of hydrogen in the FSC capsule, *C*, is a function of radius *r* and time *t* (Crank, 1975, p. 69):

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial C}{\partial r}\right) \tag{3}$$

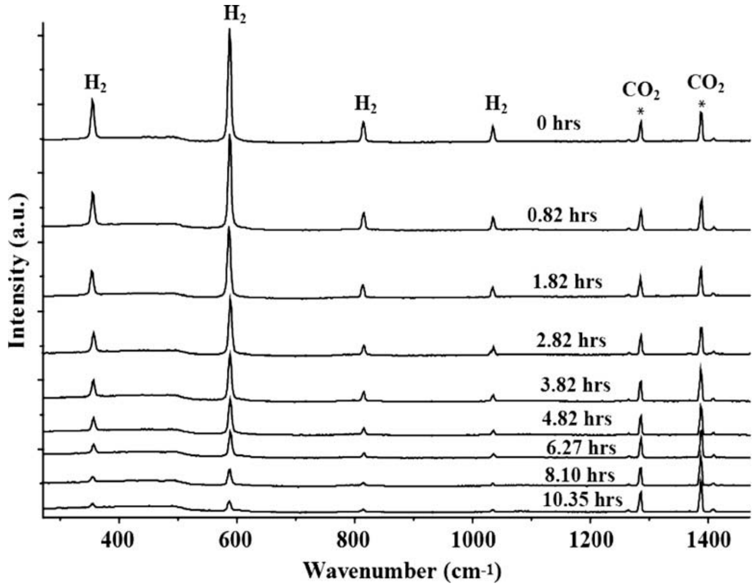


Fig. 2. Raman spectra collected at room temperature (30 s with two accumulations) for the initial sample containing CO_2 and H_2 (top spectrum) and after it was heated at 523 K in open air for various periods of time. The signals marked by stars are the Fermi diad of CO_2, and the rest are from H_2. Spectra were normalized to the CO_2 peak at 1387 cm^{-1}, and the peak height at 587 cm^{-1} was used to calculate the relative concentrations of H_2 before and after each heat treatment.

Because the FSC capsule samples were heated in an open air, and the condition of the outer surface was:

$$C_b = 0, \qquad t \geq 0 \tag{4}$$

where C_b is the concentration of H_2 at the outer surface of FSC.

As the FSC capsules were preheated to reach the "quasi-steady" state in the FSC wall before the start of diffusion experiments at certain temperature, the initial concentration of hydrogen in the wall of capsule right before the diffusion experiment starts was linear to ln$r$, as shown by the dotted curve in Fig. 3 (Crank, 1975, p. 69):

$$C = C_a + \frac{C_b - C_a}{\ln(b/a)} \ln\frac{r}{a} \tag{5}$$

where C_a, the concentration of H_2 at the inner surface of FSC, is related to the concentration of H_2 in the gas phase in the capsule, and can be calculated from the following relation:.

$$\beta = C_a/C_g \tag{6}$$

where β is the dimensionless Ostwald solubility coefficient, which is the equilibrium constant between H_2 concentration at the inner surface of fused silica and H_2 in the gas phase (C_g). The Ostwald solubility coefficients reported by Shackelford et al. (1972) were applied in our calculations.

The concentration of hydrogen in the gas phase inside the FSC capsule is time dependent and can be expressed by:

$$\frac{d(\pi a^2 L C_g)}{dt} = 2\pi a L D \left(\frac{\partial C}{\partial r}\right)_{r=a} \tag{7}$$

where L is the length of the capillary, $\pi a^2 L$ is the inside volume of the capillary, and $2\pi aL$ is the inner surface area of the capillary from which H_2 diffuses out. The above equation can be simplified to:

$$\frac{dC_g}{dt} = \frac{2D}{a}\left(\frac{\partial C}{\partial r}\right)_{r=a} \tag{8}$$

Using Eq. (5) to find the value for $(\partial C/\partial r)_{r=a}$, and the above equation becomes:

$$\frac{dC_g}{dt} = -\frac{2DC_a}{a^2 \ln(b/a)} \tag{9}$$

Combining Eqs. (6) and (9) leads to:

$$\frac{dC_g}{dt} = -\frac{2\beta DC_g}{a^2 \ln(b/a)} = -\frac{C_g}{\tau} \tag{10}$$

where τ is defined as $\tau = a^2 \ln(b/a)/(2\beta D)$ to simplify the above expression. Solving the above equation leads to:

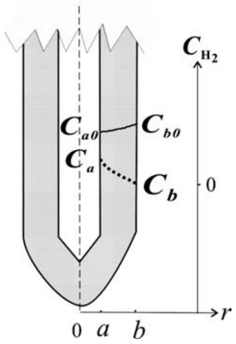


Fig. 3. A schematic diagram showing H_2 concentrations in the wall of FSC capsule, which were saturated with H_2 defined by the Fe–Fe_3O_4–H_2O buffer after loading of H_2 at 573 K for three days at 100 MPa (top solid curve), and reached a quasi-steady state after preheating (dashed curve), assuming they were linear to ln$r$, where r is the radius of the FSC capsule. The diffusion experiment started at $t = 0$ after the quasi-steady state was reached. The internal and external walls of the FSC capsule locate at a and b, respectively.

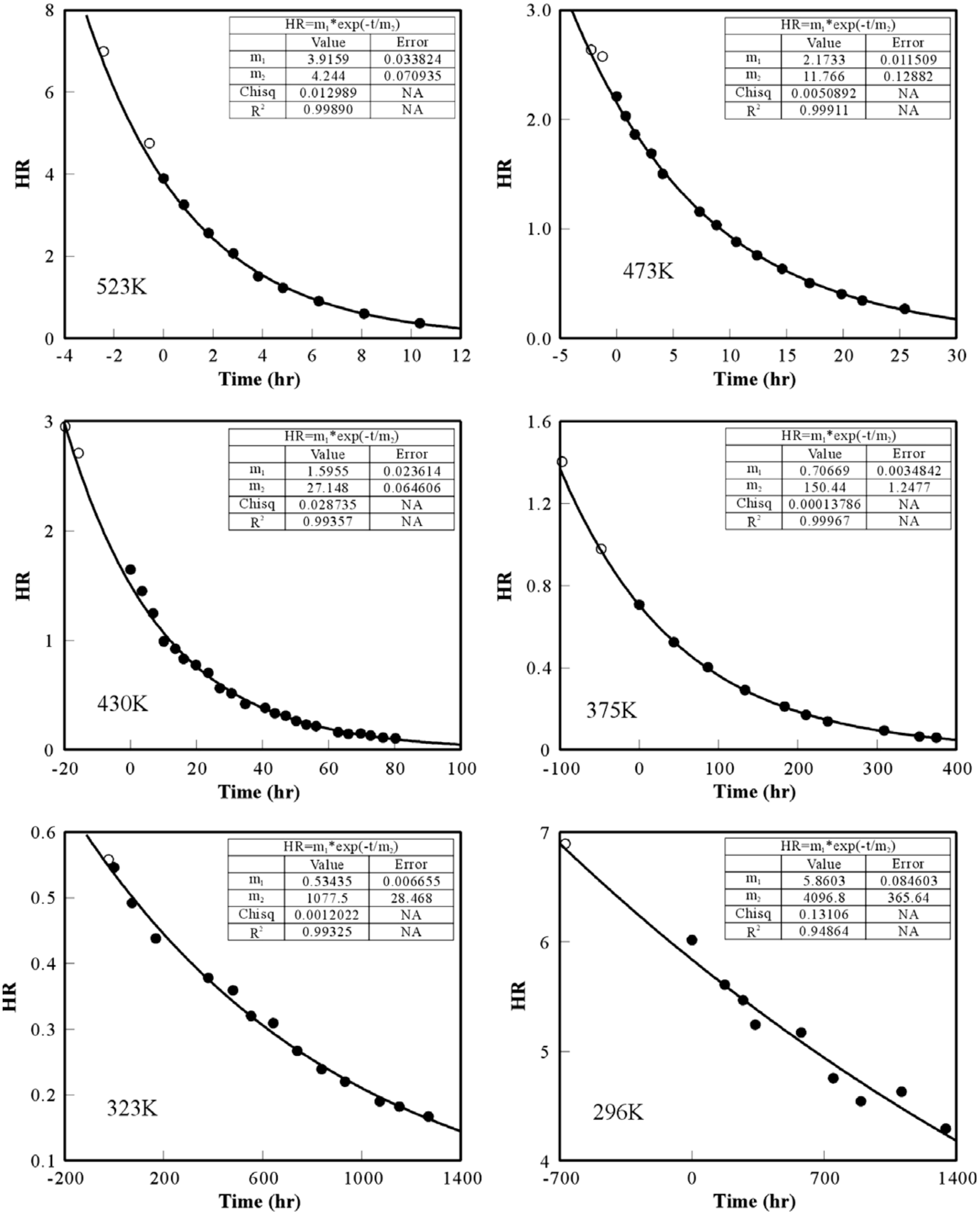
$$C_g = C_{g0} \cdot \exp(-t/\tau) \tag{11}$$

where C_{g0} is the initial hydrogen concentration in the sample fluid. Using relative concentration (peak-height ratio between H_2 and CO_2, HR) to represent concentration, we then have:

$$\mathrm{HR} = \mathrm{HR}_0 \cdot \exp(-t/\tau) \tag{12}$$

By fitting HR as an exponential function of t, the value of τ can be found (Fig. 4), and H_2 diffusivity can be obtained by:

$$D = a^2 \ln(b/a)/(2\beta\tau). \tag{13}$$



523K

$HR=m_1*exp(-t/m_2)$

	Value	Error
m_1	3.9159	0.033824
m_2	4.244	0.070935
Chisq	0.012989	NA
R^2	0.99890	NA

473K

$HR=m_1*exp(-t/m_2)$

	Value	Error
m_1	2.1733	0.011509
m_2	11.766	0.12882
Chisq	0.0050892	NA
R^2	0.99911	NA

430K

$HR=m_1*exp(-t/m_2)$

	Value	Error
m_1	1.5955	0.023614
m_2	27.148	0.064606
Chisq	0.028735	NA
R^2	0.99357	NA

375K

$HR=m_1*exp(-t/m_2)$

	Value	Error
m_1	0.70669	0.0034842
m_2	150.44	1.2477
Chisq	0.00013786	NA
R^2	0.99967	NA

323K

$HR=m_1*exp(-t/m_2)$

	Value	Error
m_1	0.53435	0.006655
m_2	1077.5	28.468
Chisq	0.0012022	NA
R^2	0.99325	NA

296K

$HR=m_1*exp(-t/m_2)$

	Value	Error
m_1	5.8603	0.084603
m_2	4096.8	365.64
Chisq	0.13106	NA
R^2	0.94864	NA

Fig. 4. Raman peak-height ratios between H_2 (587 cm^{-1}) and CO_2 (1387 cm^{-1}) as a function of heat-treatment time at temperatures between 296 and 523 K. The data points are listed in Table 1; the open circles represent the preheating data with negative time, and only those data shown by dots were used for regression. The solid curves are the least-squares fit of the HR data to an exponential function of t (Eq. (12)), and the D values listed in Table 2 were calculated from this relation.

4. RESULTS AND DISCUSSION

Fig. 2 shows the Raman spectra of a quenched sample heated at 523 K for various periods of time. The intensity of the peaks for H_2 decreases with increasing heat-treatment time, indicating the loss of hydrogen through diffusion out of the FSC capsule. Experimental results are listed in Table 1 and plotted in Fig. 4. Fig. 4 shows that HR (relative concentrations of H_2 in the capsules) vs. t can be fit well by exponential function, with the largest scatter at 296 K. In our experiments, the initial samples were prepared by diffusing hydrogen into the FSC capsules, and the direction of hydrogen transfer was opposite to that in the following diffusion experiments. To ensure that the hydrogen concentration gradient in the FSC reached "quasi-steady state" under new conditions, the initial one or two data points (with negative time listed in Table 1; open circles in Fig. 4), corresponding roughly to the time to reach quasi-steady state, were omitted during our estimation of D. Fig. 4 shows that the rate for the decrease of H_2 concentration in the FSC capsules decreases as temperature decreases from 523 to 296 K. The D values (in $m^2 s^{-1}$) calculated by the exponential function at a certain experimental temperature were listed in Table 2. The data were very well fit, resulting in small relative errors of a couple of percent on most D values. On one hand, the small errors demonstrate the high quality of our data as well as the capability of our method. On the other hand, the small errors also mean that uncertainties in extrapolating H_2 solubility from Shackelford et al. (1972) are likely the dominant errors in estimating D. In Fig. 5, our data are compared with literature data. Our D values and data of Lee (1963) (data in Lee et al., 1962 are not used because they were superseded by Lee, 1963) are in excellent agreement. They can be fit together with a least squares routine to the following linear relation ($R^2 = 0.99991$; solid line in Fig. 5):

$$\ln D = -(16.471 \pm 0.035) - \frac{44589 \pm 139}{RT} \tag{14}$$

where R is the gas constant (8.3145 J/mol K), T in Kelvin, and errors at 1σ level. The slope corresponds to an activation energy of 44.59 ± 0.14 kJ/mol, which is similar to 43.5 kJ/mol reported by Lee (1963). However, the pre-1941 data summarized by Barrer (1941) are lower than our data and the data of Lee (1963) by more than one order of magnitude.

The excellent agreement of our data with those of Lee (1963) demonstrates that molecular H_2 diffusivity does not strongly depend on the type of fused silica involved and the history of the individual specimen as long as care is taken to avoid H_2 oxidation, a conclusion also reached by Shelby (1977). This agreement is also a verification of the method used in this study, which is different from the one used by Lee (1963). However, we do not have explanations for the lower D value reported by Barrer (1941) except by noting that the analytical capability in these earlier years was not as good as the later measurements.

Table 2
Diffusion coefficients of hydrogen in fused silica (D) derived from Raman peak-height ratios (HR) between H_2 (587 cm^{-1}) and CO_2 (1387 cm^{-1}) listed in Table 1 at temperatures between 296 and 523 K and Eqs. (12) and (13) for $a = 4.95 \times 10^{-5}$ m and $b = 1.625 \times 10^{-4}$ m.

T (K)	τ (h)	1σ error in τ	Ostwald solubility coefficient (β)	$D \times 10^{14}$ (m^2/s)
523	4.244	0.071	0.0390	244 ± 5
473	11.77	0.13	0.0438	78.5 ± 0.9
430	27.15	0.65	0.0499	29.9 ± 0.8
375	150.4	1.3	0.0626	4.30 ± 0.04
323	1077	28	0.0853	0.44 ± 0.02
296	4097	366	0.1057	0.093 ± 0.010

Note: Reported errors on D are propagated from the fitting errors only and do not include errors on the estimated solubility.

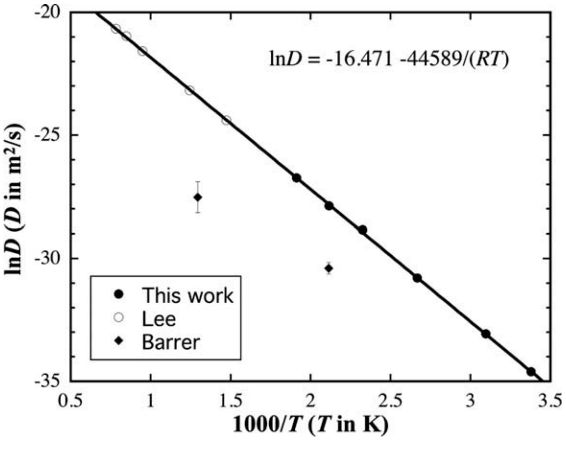


Fig. 5. Comparison of our data for hydrogen diffusion coefficients in fused silica with those of Lee (1963) and Barrer (1941). The solid line is a least-squares fit of both our data and those of Lee (1963). The uncertainties of our data listed in Table 2 are smaller than the size of dots.

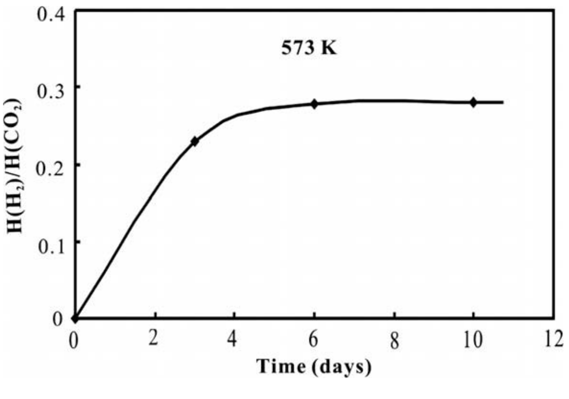


Fig. 6. Relative hydrogen concentrations in FSC capsules, as indicated by the Raman peak-height ratios, equilibrated with the $WO_2 + WO_3 + H_2O$ hydrogen buffer at 573 K and 107 MPa for various experimental durations, showing the system reached equilibrium after about 6 days (for details, see text).

5. APPLICATIONS

Compared with other commonly used hydrogen membranes (e.g., Pt and Ag-Pd alloys), a FSC has much higher diffusion rates for hydrogen. For example, the *D* in FSC determined at 296 K is about an order of magnitude higher than that of Pt at 723 K (Chou et al., 1978b), suggesting that FSC has great potential for studying redox reactions at low temperatures. To test this idea, we conducted reconnaissance experiments using $WO_2 + WO_3 + H_2O$ (WWH) as a hydrogen buffer at 573 K and 107 MPa in place of the $Fe + Fe_3O_4 + H_2O$ hydrogen buffer used in the original diffusion experiments. As shown in Fig. 6, the concentration of hydrogen in the FSC capsule reached equilibrium state (~1.0 MPa) after about 6 days, showing that the FSC can be used as a membrane to effectively control the redox state of the sample within the FSC capsules. However, according to the extrapolated *D* value at 573 K, only about 20 h were needed to reach the equilibrium hydrogen fugacity of the WWH buffer (~1.0 MPa) in the FSC capsule if the equilibrium fH_2 in the buffer system was established at time zero and maintained afterward. This indicates that the generation of hydrogen in the WWH buffer, not the diffusion of hydrogen in FSC, was the rate determining step for this redox-control process.

In another experiment to test redox control in the FSC capsules, we loaded 0.1 m H_2SO_4 into a FSC capsule, which was inserted into an alumina tube, and then sealed together with the WWH buffer in a gold capsule. This sample assembly was loaded in a cold-seal pressure vessel and reacted at 573 K under 107 MPa Ar external pressure for 10 days, which, as described above, were much longer than the 6 days required for the WWH buffer to reach equilibrium. Raman signals of the quenched sample (Fig. 7) show the formation of hydrogen and the transformation of H_2SO_4 to H_2S. In an experiment in which the experimental duration was reduced from 10 to 5 days, SO_2, instead of H_2S, was formed, consistent with previous experiments in which H_2SO_4 was reduced by CH_4 at about 683 K and the in situ Raman measurements indicated the transformation of sulfur from valence 6 to 4 to 0, and finally to −2 (Chou et al., 2008b).

It has been shown (Chou and Burruss, 2007; Chou et al., 2008a) that the diffusion of hydrogen out of FSC capsules promotes the following three reactions at temperatures between 473 and 673 K:

$$\underset{\text{ethane}}{C_2H_6} + H_2O = \underset{\text{ethanol}}{C_2H_5OH} + H_2 \tag{15}$$

$$\underset{\text{ethane}}{C_2H_6} + 2H_2O = \underset{\text{acetic acid}}{CH_3CO_2H} + 3H_2 \tag{16}$$

$$\underset{\text{methane}}{CH_4} + H_2O = \underset{\text{methanol}}{CH_3OH} + H_2 \tag{17}$$

As suggested by Anderson (2008), if these reactions are applied to thermochemical sulphate reduction (TSR) reactions, then we will be able to explain the fact that very light carbon isotopes are not commonly found in Mississippi Valley-type (MVT) deposits. Sulphur is an important element involved in many geological processes, and the formation of many minerals is related to the changes in its valence

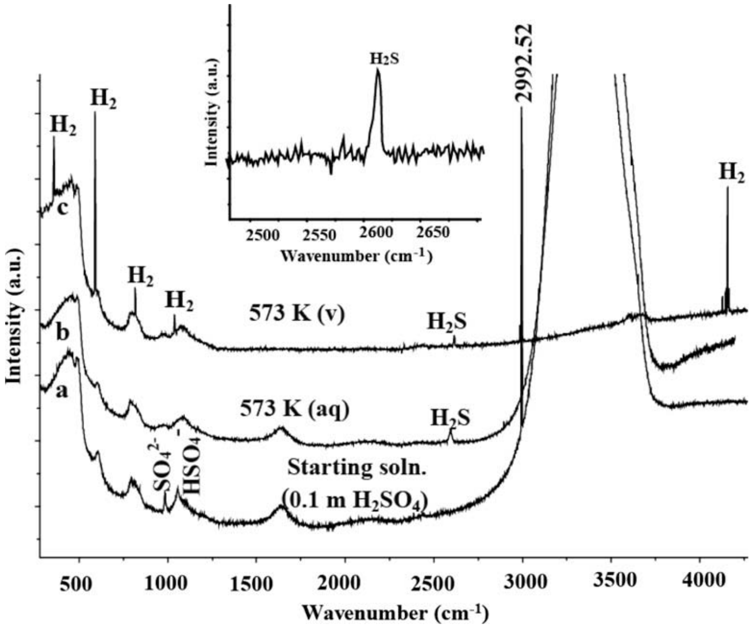


Fig. 7. Raman spectrum collected at room temperature (60 s and two accumulations) for the initial aqueous solution in a FSC capsule containing 0.1 m H_2SO_4, showing the SO_4^{2-} and HSO_4^- signals at 981 and 1052 cm^{-1}, respectively (a). Raman spectrum for the same sample after equilibrated with the WWH hydrogen buffer at 573 K and 107 MPa for 10 days, showing the total conversion of SO_4^{2-} and HSO_4^- to H_2S, as indicated by the signals at 2593 cm^{-1} in the aqueous phase (b) and at 2612 cm^{-1} in the vapour phase (c and the insert). Note that H_2 was also detected in the vapour phase (c). The large signals between 2700 and 3800 cm^{-1} in (a) and (b) are from water, and the signals at 2992.52 cm^{-1} are from He–Ne laser, which was used as an internal standard. For details, see text.

(Worden and Smalley, 1996; Rye 2005; Halevy et al., 2007; Thom and Anderson, 2008; Anderson and Thom, 2008; Anderson, 2008). Our preliminary results indicate the potential of using FSC capsule for redox-sensitive experimental systems at low temperatures, especially for the systems containing organic material and/or sulphur.

6. CONCLUSION

The diffusion coefficients of hydrogen in FSC capsules were determined between 296 and 523 K by measuring the changes in the relative concentrations of hydrogen in the capsules using Raman spectroscopy with CO_2 internal standards. The D values obtained are consistent with the extrapolated values based on previous experiments at higher temperatures. Effective control of redox conditions in the FSC capsules was demonstrated, and the FSC has a great potential for studying redox-sensitive reactions between room temperature and 673 K, especially for systems containing organic material and/or sulphur.

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