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The Catalytic Effect of Geologic Samples on the Deuterium (Tritium)-Water Exchange Reaction as Studied with a Quadrupole Mass Filter*†

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Evidence of exchange reactions between tritium gas and water has been observed in gas sampled from the vicinity of nuclear detonations. The purpose of this investigation, using deuterium gas as a surrogate for tritium, is to determine the catalytic effects of typical underground materials on the exchange reactions between hydrogenic species and water as a function of temperature. The apparatus constructed for these experiments consists of a constant pressure gas inlet system, a fused quartz tube containing the catalyst to be studied, and a quadrupole mass filter. The temperature range of the experiments was from ambient to 900°C. The two gases, D_2 and H_2O, were mixed in the inlet system and then allowed to pass through the catalyst bed and into the mass filter through a glass leak. The results obtained can be summarized as follows: (1) the reaction is surface catalyzed; (2) equilibration takes place rapidly at room temperature and above, using platinum sponge as a catalyst; (3) for catalytic samples of tuff, alluvium, sandstone, and shale, the onset of observable reaction was between 400 to 500°C with large amounts of products formed at 600°C and above when the temperature was increased from ambient to 900°C over a 6- to 8-hr period; and (4) deuterium and water appear to exchange at 200–300°C in outgassed, partially decomposed limestone, presumably due to the catalytic activity of CaO and MgO.

INTRODUCTION

The Plowshare Program of the United States Atomic Energy Commission has sponsored three nuclear-explosive gas-well stimulation experiments: Gasbuggy in December 1967, Rulison in September 1969, and Rio Blanco in May 1973. The nuclear explosives in these experiments are a source of tritium gas which contaminates the commercially interesting hydrocarbon gases. The exchange reaction

$$HT(g) + H_2O(l) = H_2(g) + HTO(l) \quad (1)$$

has been invoked to explain the observed decrease with time of HT in the gas samples removed from the Gasbuggy well (*1*). The equilibrium indicated in reaction (1) has, in addition, been used to explain the constancy at late times of the HT specific activity of hydrogen in the gas samples taken from the Rulison well (*2*). The catalysis of reaction (1) by chimney rock in Gasbuggy has also been observed at the Nevada Test Site (NTS) in the gas samples taken following tests of other nuclear explosives. The equilibrium constant for reaction (1) is, of course, a

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function of temperature. The temperatures of interest for stimulated gas wells range downward from the condensation temperature of rock (900–1200°C) shortly following detonation to the ambient temperature at detonation depth. The condensation temperature of water is a practical lower limit. Typical chimney gas temperatures encountered upon reentry are of the order of a few hundred degrees Celsius. If the exchange in reaction (1) can be forced to completion under appropriate conditions, it would be a great boon to the nuclear gas well stimulation program, since this process would trap the tritium in the liquid water phase within the chimney.

The equilibrium thermodynamic properties of the gas phase equivalent of reaction (1)

$$HT(g) + H_2O(g) = H_2(g) + HTO(g) \quad (2)$$

have been determined experimentally by Black and Taylor (*3*) in 1943. They found K_2, the equilibrium constant for reaction (2), to be 6.25 at 25°C, indicating that tritium will concentrate in the water species at ambient temperatures. The corrected theoretical values of K_2 as a function of temperature are soon to be published (*4*).

There have been several studies of the kinetics of reaction (2) under various conditions. For example, Hanertz (*5*) studied the mechanism and rate of reaction (2) using platinum as a catalyst and found that the reaction was first order with respect to HT content. Yang and Gevantman (*6*) examined the β-ray induced isotope exchange of tritium with water and found in this special case that the reaction was second order with respect to tritium. Bond (*7*) investigated the catalysis of the reverse of reaction (1) by oxygenated salts which occur naturally in salt formations. He found that at 600°C in experiments where the gas flowed through packed beds of catalyst (in this case, K_2CO_3), the exchange was 80.5% complete. Corresponding values for the other salts were Al_2O_3, 77%; $CaSO_4$, 54%; silica gel, 44%; K_2SO_4, 42.5%; $CaCl_2$, 6.5%; and NaCl, 0.65%. In diffusion controlled conditions where reactant gases were passed over fine powders of $CaSO_4$, the percent exchange was as high as 26% for residence times of 50 s.

The purpose of the present research is to investigate the catalysis by selected natural materials of the hydrogen-water exchange reaction as a function of temperature. We hope to test, insofar as possible in the laboratory, the assertions which were mentioned in the first paragraph. To do this we have selected a surrogate for reaction (2), namely,

$$D_2(g) + H_2O(g) = HD(g) + HDO(g). \quad (3)$$

We selected this particular hydrogen-water exchange reaction because the pure reactants are easily obtained and because it is readily studied using a mass spectrometer. This approach also allows us to avoid exposure to tritium and tritiated water, which are hazardous to work with, especially in the concentrations necessary to do accurate mass spectroscopy, and which require special handling. The substitution of a study of a deuterium exchange reaction for that of a tritium exchange reaction is a valid procedure since the correlation between deuterium and tritium isotope effects in both equilibrium and rate processes has been previously established and corrections to equilibrium and rate constant ratios can be calculated or estimated.‡

The major factor which contributes to the observed hydrogen isotope reactivity sequence (bonds to tritium are less reactive than bonds to deuterium, which in turn are less reactive than bonds to hydrogen) is the difference in zero point energies (*8*). Hence, for analogous exchange reactions, the tritium rate will be

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‡ See J. Bigeleisen, Proceedings of the Symposium on the "Detection and Use of Tritium in the Physical and Biological Sciences," International Atomic Energy Agency and Joint Commission on Applied Radioactivity, Vienna, May 3–10, 1961, pp. 162–168. For the simplest case, where $HX + DY = DX + HY$; K_D and $HX + TY = TX + HY$; K_T, the ratio $\ln K_D/\ln K_T$ lies between the high and low temperature limits of 1.33 and 1.55. Bigeleisen gives formulas for comparing tritium and hydrogen rate constants and equilibrium constants for the general case.

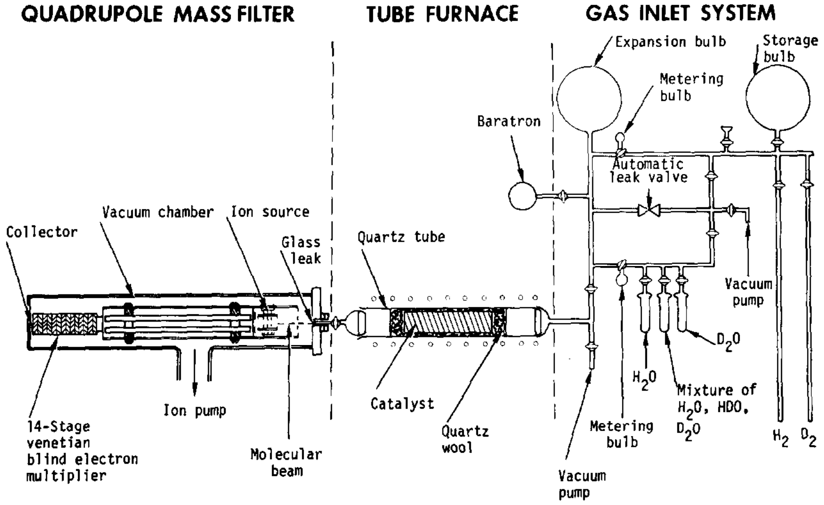

Fig. 1. Experimental apparatus

slower than the deuterium rate. Both deuterium and tritium will concentrate in the water species for the same reason, especially at lower temperatures.

The literature on the exchange reaction

$$HD(g) + H_2O(g) = H_2(g) + HDO(g) \quad (4)$$

which is the deuterium analog of reaction (2), is quite extensive. This reaction is often used to study various catalysts. The most recent theoretical calculation of the equilibrium constant for reaction (4) along with references to early experimental data is given in Ref. (*9*). Recent kinetic studies of the reverse of reaction (4) included the use of platinum on alumina (*10*), ZnO (*11*), and various oxides (*12*) as catalysts.

The present paper describes the apparatus which we designed and built for the exchange reaction studies, as well as the semiquantitative results obtained from a survey of various catalytic systems. Many aspects of the catalytic process such as the effect of the surface area, flow rate, etc. were not examined in this preliminary study. These experiments were intended primarily to map the temperature regimes where reaction occurs. They also serve to show relative catalytic effects on various systems. In future experiments we plan to study details of some of the equilibrium and kinetic processes.

EXPERIMENTAL

Apparatus

The experimental apparatus is shown in Fig. 1. It consists of three sections, a gas-inlet system, a catalyst tube enclosed in a furnace, and a quadrupole mass filter.

The gas inlet system has a Granville-Phillips Automatic Pressure Controller Series 216,** a feature not commonly found in mass spectrometric inlet systems. The controller consists of a power supply and control circuitry plus a servo-driven valve. The leak valve is automatically opened or closed in response to pressure fluctuations and maintains a constant pressure in the expansion bulb and furnace tube. An MKS Baratron Type 90 Pressure Meter is used to monitor the pressure in the low-pressure region of the inlet system and to provide a feedback signal for the pressure controller.

The furnace tube, which has a diameter of 5 cm and a length of 99 cm, is constructed of fused quartz (Corning Vicor) so that the catalyst can be heated to 900°C. The catalyst is packed into a 30-cm region in the center of the tube. The tube

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** Reference to a company or product name does not imply approval or recommendation of the product by the University of California nor the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

furnace is a Lindberg Series 54356. It has three independently controlled temperature zones which can be adjusted and automatically maintained so that the temperature gradient along the inner zone is within ±1°C. The temperature is measured along the tube at five points 14 cm apart by five cromel-alumel thermocouples which are monitored by a Doric Model DS500-13 Thermocouple Indicator, which after calibration is accurate and reproducible to ±1°C.

In order to eliminate the possibility of the hot gases from the furnace reacting with a metal surface, the leak into the mass filter chamber from the furnace tube was constructed from Pyrex. The leak was constructed by gathering the glass on the end of a piece of heavy walled tubing and then drawing the glass down until the hole tapered down to a solid piece. Sections containing leaks of various diameters were cut from this tube and tried in the mass spectrometer until we found one which gave us the desired pressure in the mass-filter vacuum chamber. The thickness of the disc is 0.76 mm and the diameter of the leak is 0.46 mm.

The mass filter was a Spectroscan 750 sold by the Granville-Phillips Co., but manufactured by Finnegan Corporation.

Procedure

The D_2 gas used in this study was supplied by Matheson Gas Products. The H_2O was distilled and was outgassed in the vacuum system by alternating freezing, pumping, and thawing. The sand used in several studies was J. T. Baker "Purified." The sample of platinum metal in the form of "sponge" was supplied by Englehard Industries. The core samples of tuff and alluvium from NTS were used as supplied (usually 1.3 cm in diameter or smaller pieces plus powder, etc.). The limestone from Alaska and sandstone and shale from Rulison were supplied as one piece and required chipping before they could be inserted into the furnace tube. A detailed description of the field samples is given in the Appendix along with chemical analyses.

The furnace tube was loosely packed with the platinum sponge catalyst with a plug of fused quartz wool at each end. Since the coefficient of expansion for sand and the other field samples increases rapidly with temperature whereas the coefficient for vitreous (fused) quartz is nearly constant, it was necessary to line the quartz tube with an outer layer of fused quartz wool before the sample was loaded to prevent breakage of the furnace tube.

Before the experimental runs were begun, it was necessary to outgas the field samples from NTS, Alaska, and Rulison. The amount of water vapor and other volatile species in the samples was so great that the gases would have swamped the quadrupole vacuum system if this procedure had not been followed. During outgassing, the furnace temperature was gradually increased in 100° increments from 200 to 900°C while the furnace tube was being pumped with the sorption pumps. In many cases, it was necessary to pump overnight on the system before the temperature could be increased. Thus it sometimes required as many as five or six working days to completely rid the system of volatile species. In all cases, most of the gases were removed by the time the system reached 800°C.

The outgassed sample was allowed to cool overnight. The next morning, water vapor was allowed to fill the high-pressure region of the inlet system including the storage bulb. The pressure of the water sample was in the range 1.2–2.3 kPa (9–17 Torr), its vapor pressure at room temperature. Then the D_2 gas was added at pressures in the range 2.3–6.4 kPa (17 to 48 Torr). A sample of the mixture was metered into the low-pressure region containing the expansion bulb and furnace tube. The gas was then allowed to enter the mass filter through the glass leak, and the automatic pressure controller was adjusted until the pressure was constant. The constant pressure was maintained throughout the experimental runs and was typically in the range 13.3–40 Pa (0.1–0.3 Torr). At this point, the room-temperature spectrum was recorded from the oscilloscope. The temperature was increased to 200°C, and after 45 min the spectrum was recorded and the temperature increased. The time delay provided the system time to achieve temperature uniformity at the new temperature. This procedure was repeated until the whole temperature range was explored. The voltages applied to the electrodes in the mass filter's electron gun were selected to give the maximum intensity and "best" peak shape. The electron accelerating potential was therefore set to about 40–50 V, which means that the electrons have sufficient energy to create fragment ions, thus increasing the detection sensitivity but complicating the spectrum.

RESULTS AND DISCUSSION

Experiments were performed to estimate the precision of the temperature and peak intensity measurements. Since all of the experiments described in this paper were designed to be qualitative or, at best, semiquantitative, no attempt was made to calibrate either the furnace temperature monitoring system or the thermocouple temperature measuring system. At all temperatures, the two methods agreed with each other to within ±15°C. The experimental results indicate that the temperatures at the ends of the inner furnace zone where the catalyst was placed were within ±15°C of the temperature at the center of the tube. It is possible with sufficient time and care to adjust the furnace at each setting so that the temperature gradients are within ±1°C, but it was deemed unnecessary for these experiments.

All of the mass spectra reported in this work will be shown as bar graphs with the most intense peak in each hydrogen and water spectrum being arbitrarily given a value of one (except in Fig. 3, in which all peaks are compared to mass 3) and all other peaks measured relative to the most intense peak. This procedure minimized errors due to time-dependent decay in the gain of the multiplier. The measurements of the relative peak intensities from the oscilloscope were precise to within 2–20%, depending on the peak height. For the predominant species (>20% relative peak height) it was 10% or less.

The initial phases of the study focused on three questions which have to be answered before the data can be statisfactorily interpreted. These are: (i) does any isotopic fractionation occur in the total experimental system which might obscure the study of the exchange reaction, (ii) does the hot fused quartz tube catalyze the exchange reactions, and (iii) what does the mass spectrum of the fully equilibrated exchange reaction (3) look like at each temperature of interest?

Several experiments were performed to determine whether any isotopic fractionation occurs in the total gas handling and reaction system during the course of a 6- to 8-hr experiment. The two system components of particular concern are the automatic leak valve and the glass leak into the quadrupole chamber. The experiments were performed following the procedure outlined previously described except that no catalyst was present, the furnace was not used, and a mixture of H_2, D_2, H_2O, HDO and D_2O instead of just D_2 and H_2O was observed for an 8-hr period.

A point of concern is that the water species HDO and D_2O will exchange with the adsorbed water in the inlet system, thus masking any fractionation effects which might occur. To minimize this problem, the inlet system was rinsed ten times with the water mixture and then a prepared mixture of H_2, D_2, H_2O, HDO, and D_2O was allowed to sit in the inlet system over a weekend. Three samples of this mixture were analyzed on three succeeding days. It was found that the initial measurement of the day for either the hydrogen or the water species did not agree with the subsequent ones—presumably due to exchange effects in the quadrupole itself. After the initial sample, the change in either the hydrogen or the water species was about 2% on the larger peaks to 6% on the smaller peaks, which is within the stated limits of experimental error. We concluded that isotopic fractionation effects in this experimental system are not significant.

The products in reaction (3) are HD (mass 3) and HDO (mass 19), and it is apparent that the appearance of either of these species in the mass spectrum is a possible indication that reaction (3) has taken place. Self-exchange among the hydrogenic species or decomposition of HDO by the 40 to 50 eV electrons in the ion source can result in the formation of HD^+; HDO, however, can only be formed by an exchange reaction under the conditions of these experiments. Therefore, our discussion of results will focus on the appearance of mass 19 as the indication that exchange is taking place.

Experiments were performed to test the hypothesis that these exchange reactions are surface catalyzed. The initial experiments were performed by increasing the temperature using the experimental procedure described previously, except that the fused-quartz furnace tube was empty. Subsequently, the portion of the tube in the center region of the furnace was packed with fused-quartz wool. The results are shown in Fig. 2. Note that mass 17, which is primarily the OH^+ fragment which is formed by breaking up a water molecule, is an approximately constant fraction of the H_2O^+ peak (mass 18) over the temperature range. Therefore, it is useful to compare the mass 17 and mass 19 peaks to look for signs of exchange. With no catalyst in the tube, there is no indication of exchange until 800°C is reached and no appreciable exchange until we reach 900°C.

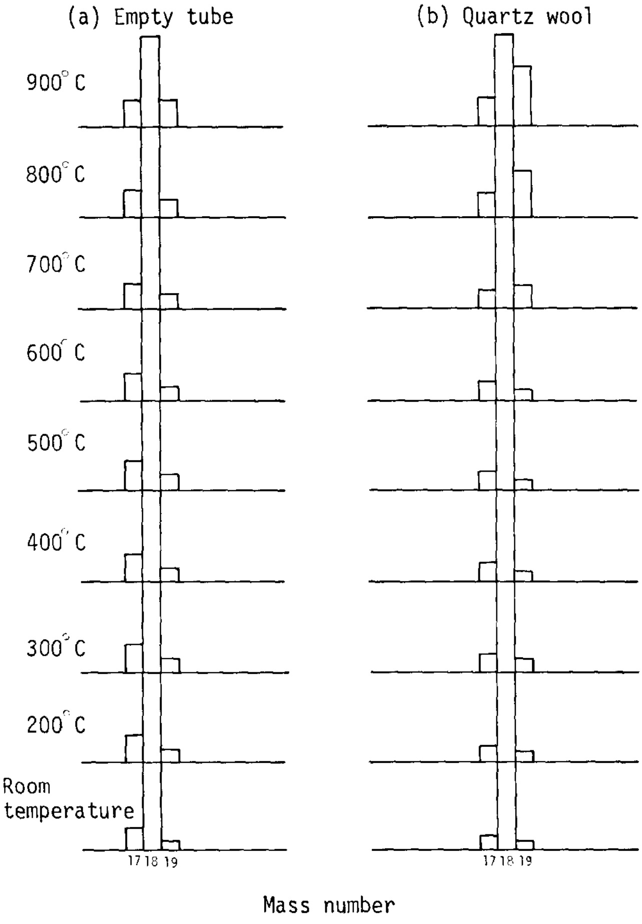

FIG. 2. Mass spectrum of the products under conditions of (a) an empty tube furnace and (b) the presence of quartz wool in the tube furnace.

With the quartz wool in the tube, however, there is evidence of reaction at 700°C and appreciable reaction above that temperature. We therefore conclude that the reaction, as expected, is surface catalyzed, and that the catalysis by the tube itself will not interfere with the subsequent experiments below 900°C. The fused quartz packing will interfere with the interpretation of results at temperatures above 700°C.

In the next experiments, platinum metal sponge was used as the catalyst in the tube in an attempt to check the equilibrium spectra at various temperatures. The results are shown in Fig. 3. The initial mixture contained about twice as much D_2 as H_2O. When the mixture was admitted to the catalyst bed at room temperature (27°C), it appeared to immediately equilibrate. Note that the water species decreased relative to the hydrogenic species. This is believed to be due to preferential adsorption of the water species on the large surface of the catalyst. To support this view, note that at higher temperatures, the relative amounts of the water species increases. This behavior was also observed with the other substances which were used as catalyst in the later experiments. At each temperature, the hydrogen and water species appear to be equilibrated.

Washed and ignited sand was next tried as the furnace tube catalyst. The water results are shown in Fig. 4 and the hydrogen results in Fig. 5. A comparison of the 17 and 19 peak heights in Fig. 4 indicates that the onset of the exchange reaction occurs at approximately 500°C, but as the temperature is increased, the hy-

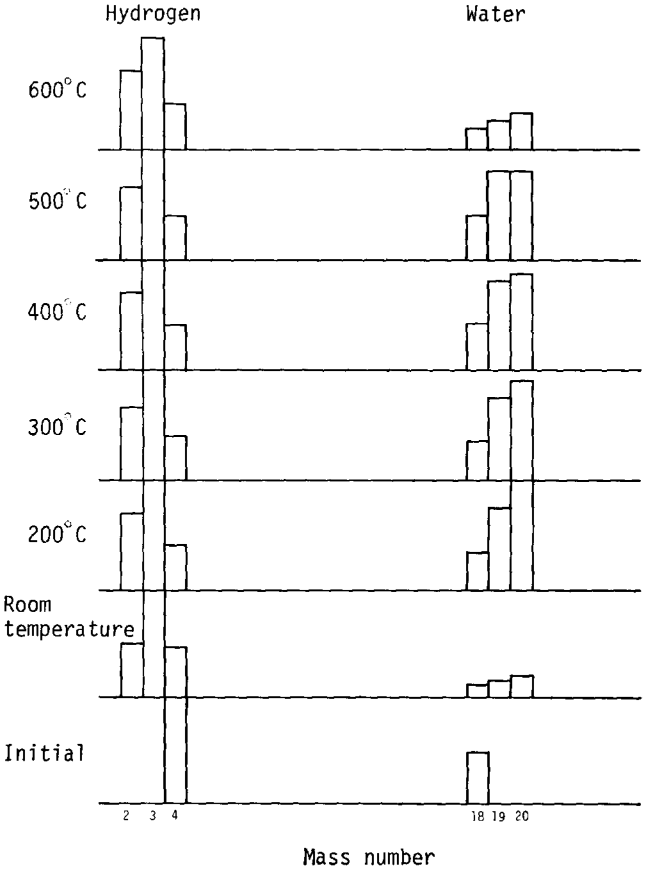

FIG. 3. The mass spectrum of the products of the platinum catalyzed exchange reaction.

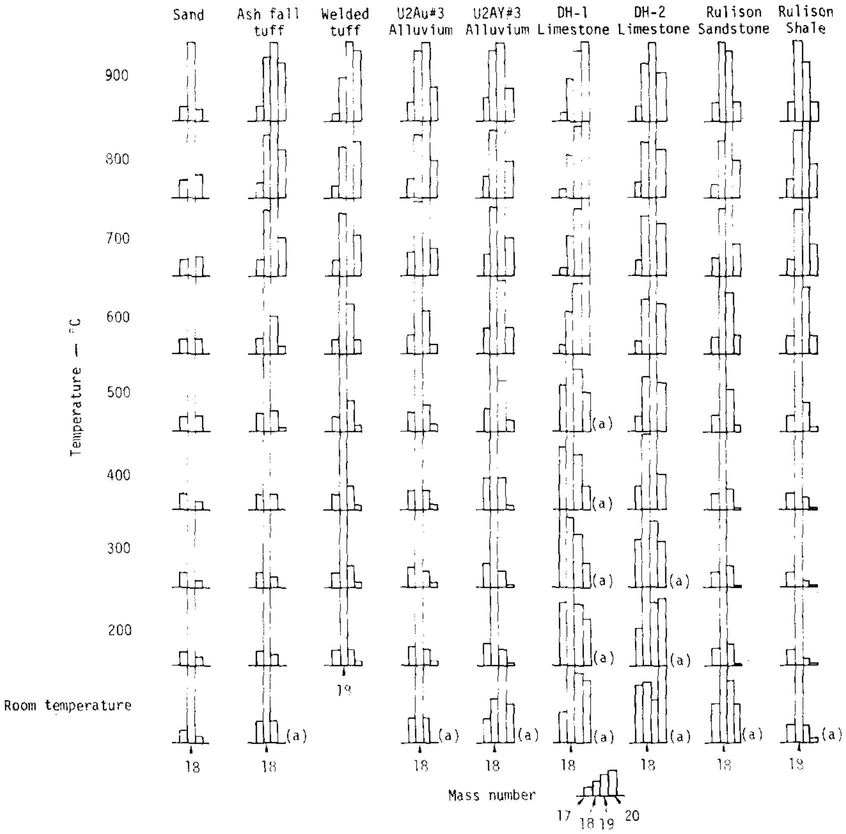

FIG. 4. Mass spectra of the water species. Those spectra labeled (a) show only instrument background.

drogen content of the hydrogenic species increases dramatically without a corresponding increase in the deuterium content in the water species, suggesting a source of hydrogen other than water. In the sand experiments at the higher temperatures, the total pressure of the hydrogenic species was comparable to that of the water species.

Also shown in Figs. 4 and 5 are the results obtained using as the catalyst two different samples each of tuff (NTS), alluvium (NTS), limestone (Alaska), and one each of standstone (Rulison) and shale (Rulison). The results from all of these experiments are similar, except for those involving the limestone, and can be summarized as follows:

From a comparison of the mass 17 and 19 peak heights in Fig. 4, we see that the onset of the exchange reaction occurs between 400 to 500°C (the welded tuff apparently shows onset between 200 and 300°C, although this result is based upon only one experiment and could be erroneous—the duplicate experiment agrees with the rest of the substances).

The exchange reaction increases in rate and extent as the temperature is increased.

The hydrogenic spectra in Fig. 5 tend to confirm first point, but, as previously mentioned, cannot unambiguously confirm the second point.

The exchange reaction characteristics were quite different for the two sets of experiments which used the limestone as the catalyst. Most of the natural substances at room temperature, after having been outgassed at 900°C, adsorbed the water vapor in the sample to the extent

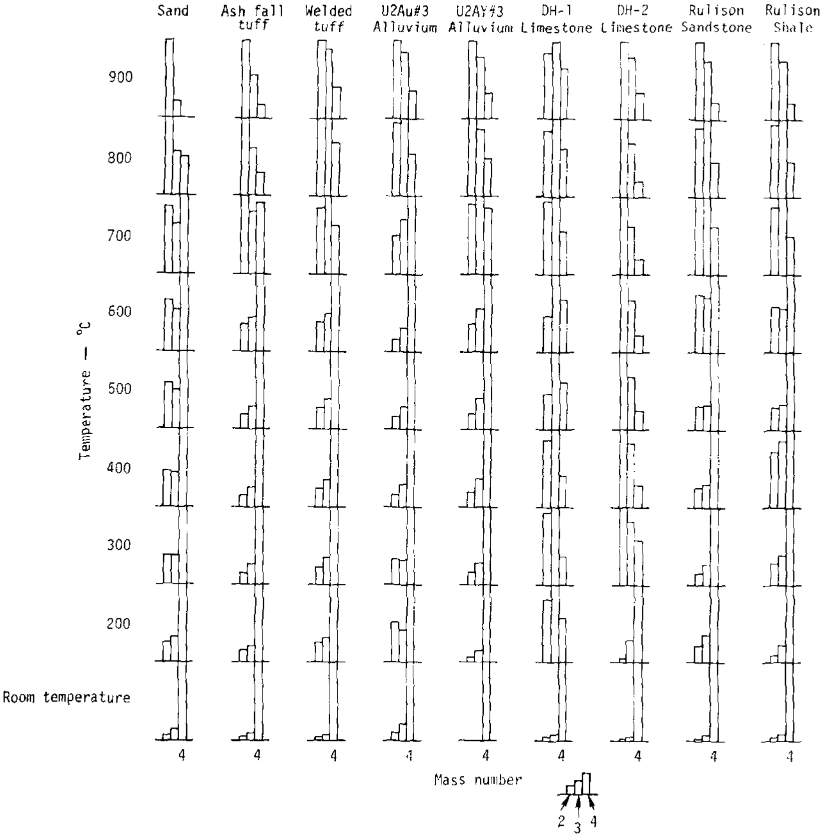

FIG. 5. Mass spectra of the hydrogenic species.

that the water vapor pressure at room temperature was as much as three orders of magnitude lower than the hydrogen pressure. This resulted in only the background water spectrum or no spectrum being recorded (Fig. 4). Inlet gas mixture compositions were reestablished at 200°C. In the case of the limestone samples, however, the water vapor pressure was not comparable to the hydrogen pressure until a temperature of 300°C for DH-2 and 500°C for DH-1 was reached. It should be pointed out that outgassing to 900°C should convert a portion of the $CaCO_3$ to CaO and the $MgCO_3$ to MgO (the appearance of white streaks in the limestone samples after degassing tends to confirm this idea). The water mixture presumably reacts with the oxides to form hydroxides.

It is apparent by the spectra shown in Fig. 4 that the exchange reaction has proceeded apace at lower temperatures than those necessary to drive the water from the catalyst bed. In fact, the hydrogen spectra for the limestone experiments in Fig. 5 are quite different at 200–600°C from what they are for the experiments with other media, indicating that in limestone sample DH-1 at 200°C and in sample DH_2 at 300°C much of the deuterium has undergone exchange. We are therefore attracted to the conclusion that in the limestone, because of the catalytic activity of CaO and perhaps MgO, the deuterium exchange reaction will proceed at a lower temperature than in the other substances examined.

Prior to bakeout at 900°C, each limestone sample was outgassed to 400°C and tried as a catalyst for the exchange reaction as the temperature was incremented to 400°C. There was no evidence of exchange in these preliminary experiments.

In order to complete a temperature rise

of from room temperature to 900°C during the course of a working day, it was necessary to increase the temperature every 45 min to an hour. Typically, the temperature, as measured by a thermocouple at the outer surface of the quartz tube, would rise to the set temperature within one half the allotted time leaving the other half to establish temperature equilibrium. It is of interest to see what the detection threshold might be if the temperature were held at a lower value than the apparent threshold for a longer period time. Accordingly, all-day experiments were run at 200°C, 300°C, 350°C, 400°C, and 500°C using the Rulison sandstone sample. As expected, these results indicate that for all-day experiments, the detection threshold is lower (between 350 and 400°C) than the faster temperature rise experiments (400°C or above). Even lower thresholds might be observed, of course, if an experiment of sufficient duration were run. This result does not negate the general conclusion which will be drawn from the 8-hr temperature rise experiments since, on the one hand, only qualitative observations were sought and, on the other, the only claim is that the thresholds apply to the conditions indicated.

CONCLUSIONS

The tube furnace-quadrupole mass filter system described in this work has proven to be a useful apparatus for studying the catalysis of high-temperature exchange reactions by various geologic samples. The deuterium-water exchange reaction (3) has been shown to be surface catalyzed and to equilibrate rapidly in the presence of platinum sponge even at room temperature. Platinum sponge can be used as a catalyst to determine the equilibrium constant of this reaction at room temperature and above. Isotopic fractionation of the hydrogenic or water species in the experimental apparatus was shown to be within experimental error. For samples of tuff, alluvium, sandstone, and shale in experiments in

TABLE 1

TRACE ANALYSIS OF NTS GEOLOGIC SAMPLES

	Sample description			
Constituent	TPS bedded ash fall tuff (wt%)	TPR welded tuff (wt%)	Alluvium from U2Au No. 3 (wt%)	Alluvium from U2AY No. 3 (wt%)
Si	Major	Major	≧25	≧25
Al	5	5	5.0	5.0
K	2	2	2.0	2.0
Na	2	2	1.5	1.5
Fe	0.6	0.6	1.0	1.0
Ca	0.2	0.2	0.1	2.0
Mg	0.15	0.15	0.5	0.5
Ti	0.03	0.15	0.3	0.3
Mn	0.03	0.03	0.05	0.05
Ba	0.015	0.05	0.05	0.05
Sr	0.004	0.015	0.03	0.03
Zr	0.008	0.008	0.02	0.02
Pb	0.005	0.005	0.025	0.01
Zn	≦0.005	≦0.005	0.005	0.005
B	0.002	0.001	0.003	0.003
Cu	0.0002	<0.0002	<0.001	<0.001
Be	<0.0001	<0.0001	0.0002	0.0002
Ag	<0.0001	<0.0001	0.0002	0.0001
V			0.005	0.005
Cr			0.0025	0.0025
Ni			0.001	0.001

which the temperature was increased from ambient to 900°C over a 6- to 8-hr period, the onset of reaction was observed between 400 to 500°C with large amounts of exchange products at 600°C and above. Deuterium and water [reaction (3)] appear to exchange at 200–300°C in outgassed limestone, presumably due to the catalytic activity of CaO and MgO. These qualitative deuterium results should also generally apply to the analogous tritium reactions. Slightly higher detection threshold temperatures would be expected for the tritium reactions, however, because of the zero-point energy difference.

APPENDIX

Included in the Appendix are the available chemical analyses and geologic descriptions of the samples which were used as catalysts in this work.

Tuff

The two samples of tuff used were from the Nevada Test Site-Paint Brush Formation. They were labeled "TPS Bedded Ash Fall" and "TPR Welded." The TPS and TPR refer to the location in the Test Site. The trace elemental analyses by emission spectroscopy are given in Table 1.

TABLE 2

CHEMICAL AND ELEMENTAL ANALYSIS OF THE LIMESTONE SAMPLES[a]

	LLL DH-1 (wt%)	LLL DH-2 (wt%)
S_iO_2	0.08	37.8
C (total)	12.65	7.45
CO_2 (acid evaluation)	45.34	26.10
H_2	0.060	0.092
Na	0.023	0.042
Mg	5.75	1.40
Al	0.03	0.033
Ca	31.5	21.7
Fe	0.043	0.14
K	0.005	0.106
B	<30 ppm	100 ppm
Li	3 ppm	10 ppm
Y	≦10 ppm	≦10 ppm

[a] The following elements were not detected in either sample: <100 ppm, Ce, Nd, Pr; <30 ppm, Dy, Ge, Sm, Tb; <10 ppm, Er, Eu, Ho, La, Lu, Tm; <1 ppm, Sc, Yb.

Alluvium

The two alluvium samples were taken from device emplacement holes in the Nevada Test Site. The first sample was from Hole U2Au No. 3 at a depth of 1180 ft and the second from Hole U2AY No. 3 at a depth of 1000 ft. The trace elemental analyses by emission spectroscopy are given in Table 1.

Limestone

The limestone sample labeled LLL DH-1 was taken from a drill hole in Confusion Creek, Alaska in 1972 at a depth of 380.9 to 381.25 ft. It was described by the geologist as "Medium brown, coarse-grained, thick-bedded bioclastic limestone. Horizontal Beds. Calcite-filled joints about 1-in. apart dip 60°." The trace elemental

TABLE 3

CHEMICAL AND ELEMENTAL ANALYSES OF RULISON SANDSTONE AND SHALE

	Sandstone (wt%)	Shale (wt%)
Total H_2	0.15	0.37
Total C	1.32	1.82
H_2	1.0	2.5
CO_2 (from carbonates only)	4.31	5.14
H as CH_x	0.04	0.09
Ca	2.59	3.59
Al	3.59	6.96
Fe	1.21	1.41
Mg	0.75	0.91
Na	0.91	0.73
K	0.98	2.04
Si		30.9
Ti		0.47
Mn		320 wt ppm
Li		33 wt ppm
Y		25 wt ppm
Sc		15 wt ppm
Yb		3 wt ppm
Nd		20 wt ppm
Ce		50 wt ppm
Dy		<2 wt ppm
Eu		<1 wt ppm
La		35 wt ppm
B		75 wt ppm

and chemical analyses for this sample are given in Table 2.

The limestone sample labeled LLL D4-2 was also taken from a geologist's drill hole, Confusion Creek, Alaska in 1972, at a depth of 266 ft. It was described as "Dark gray, fine-grained laminated limestone. Apparent dip 10°. Vertical and oblique calcite-filled joints 1- to 2-in. apart." As above, the available analyses are given in Table 2.

Sandstone

The sandstone sample was from the Rulison emplacement hole at a depth of 8403.5 ft—Mesa Verde Formation. The location of the hole is given as "Austral No. 25-95 HAYWARD "A," Section 25, T-7-S, R-29-W, Garfield County, Colorado" (*13*). The chemical and trace elemental analyses compiled by John Hill (*13*) are given in Table 3.

Shale

The shale sample was also from the Rulison emplacement hole at a depth of 8446.5 ft. The chemical and trace elemental analyses from Ref. (*13*) are given in Table 3.

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