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Hydrogen isotope exchange reaction rates: Origin of water in the inner solar system

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Abstract—Rate constants for hydrogen isotope exchange between molecular hydrogen and water ($k(T)_{H_2\text{-}HDO}$) and hydrogen and methane ($k(T)_{H_2\text{-}CH_3D}$) have been determined experimentally. The temperature dependence of the constants can be expressed by:

$$k(T)_{H_2\text{-}CH_3D} = 6.1 \cdot 10^{-25} \exp\left(\frac{4.38 \cdot 10^3}{T}\right) \text{ and } k(T)_{H_2\text{-}HDO} = 2.0 \cdot 10^{-22} \exp\left(\frac{5.17 \cdot 10^3}{T}\right).$$

with $k(T)$ in cm^3/sec. Catalytic effects on charcoal, silica, phyllosilicates, and iron were found to be negligible.

A model describing the evolution (with time) of the hydrogen isotopic composition of water in the solar nebula is proposed: while the temperature is decreasing in the gas, isotope exchange between H_2 and H_2O yields a deuterium enrichment in water.

Using Cameron's numerical models (1972, 1978, 1985) of the solar nebula, we show that the observed difference between the protosolar and the carbonaceous chondrite D/H ratios (i.e., between 30 and 150 10^{-6}, respectively) is well accounted for by our model, provided that (1) water was accreted as ice at a temperature of ≤160 K and (2) the hydrogen pressure was higher than 10^{-5} atm somewhere between 1 and 3 AU. In such conditions, the calculations show that meteoritic phyllosilicates did not form in the gas phase, by reactions between water vapour and silicate grains, but by the subsequent circulation of liquid water, originally condensed as ice. Water on Earth (D/H = $155 \cdot 10^{-6}$) also results from such a cold nebula chemistry.

INTRODUCTION

IN THIS SECTION, we attempt to classify solar system bodies according to their D/H ratio. Such a criterion is clearly related to presolar and (post) accretional histories and, in this respect, should be regarded as a good basis for classification.

The Sun

The D/H ratio is essentially 0: all of the primordial deuterium originally present has been converted into ^{3}He during the first thermonuclear reactions that occurred at the early stage of solar formation (CLAYTON, 1983). Using the ^{3}He/^{4}He ratio in the solar wind, several authors have derived the D/H ratio of the primitive solar nebula (GEISS & REEVES, 1972; BLACK, 1973; GEISS and BOCHSLER, 1985). Recently ANDERS & GREVESSE (1989) reviewed this value and proposed a D/H ratio of 34 ± 10 10^{-6}. In the present paper we use this latest estimate in our calculations.

The Giant Planets

Jupiter and Saturn are believed to have retained primordial nebula gases and thus their atmospheres should have retained the primordial D/H ratio, which should be similar to that which has been derived for the Sun (ANDERS and GREVESSE, 1989). This has been verified by GAUTIER and OWEN (1983, 1989) who quote a mean D/H ratio for the two planets equal

to 20 ± 10 · 10^{-6}. However, these ratios were measured in methane and the corresponding values in molecular hydrogen, which is by far the most abundant species, are recalculated using theoretical isotopic exchange models (BEER and TAYLOR, 1973, 1978; FEGLEY and PRINN, 1988; FEGLEY et al., 1991). In order to test these models, we report laboratory determinations of the rate constant for isotopic exchange between molecular hydrogen and methane. The D/H ratio of Uranus and Neptune has been measured in methane and then recalculated for molecular hydrogen: 6.7 ± 1.0 · 10^{-5} and 11.3 (+11.3, −7.5) 10^{-5}, respectively (FEGLEY et al., 1991; ORTON et al., 1992). Uranus shows a clear enrichment in deuterium relative to the protosolar value. However, it should pointed out that this planet has also a high global water/hydrogen ratio, suggesting in turn, the existence of postaccretional isotopic exchange mechanisms between water and hydrogen (LUTZ et al., 1990). Contrary to the hydrogen-rich giant planets, Titan, a satellite of Saturn, has lost its primordial hydrogen and exhibits a terrestrial like D/H ratio in methane: 1.65 (+66; −3.3) 10^{-4} (DE BERGH et al., 1988). However, such an enrichment may reflect a postaccretional evolution of the atmosphere (OWEN et al., 1986; PINTO et al., 1986; COUSTENIS et al., 1989). Consequently, this planet may very well have exhibited a protosolar ratio at the time of its accretion (ORTON, 1992).

Telluric Planets

The D/H ratio of the atmospheres of Venus (1.8 ± 0.6 · 10^{-2}: BEZARD et al., 1990; DE BERG et al., 1991) and

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Mars ($5.1 \pm 0.2 \cdot 10^{-3}$: OWEN et al., 1988; BJORAKER et al., 1989) are the highest of the solar system. However, such a deuterium enrichment is not a pristine signature but results from atmospheric evolutions: water is photodissociated and atomic hydrogen escapes to space more rapidly than deuterium leading to a marked increase in the D/H ratio of the residual water (HUNTEN and DONAHUE, 1976; YUNG et al., 1988b). However in the case of Venus, such an interpretation has been revisited by GRINSPOON (1993) who proposed that the D/H ratio of the outgassing water mantle was at least ten times that of the Earth.

Organic Matter

Most of the C in chondritic meteorites is in the form of organic macromolecules (ANDERS et al., 1973) having D/H ratios between 350 and $1200 \cdot 10^{-6}$ (ROBERT et al., 1979, 1987; ROBERT and EPSTEIN, 1982; McNAUGHTON et al., 1981; KERRIDGE, 1985; KERRIDGE et al., 1987). The origin of the organic matter, hence the high D/H ratios, remains a topic of debate. The most popular model is that the organic matter originates within the interstellar medium and that its high D/H ratios are the result of ion-molecule reactions (WATSON, 1973, 1976; GEISS and REEVES, 1981; YUNG et al., 1988a). However, it has been pointed out (HALBOUT et al., 1990) that this model does not account for the much larger deuterium enrichment observed in interstellar organic molecules (with D/H up to 10^{-1}) compared to that actually measured in meteoritic macromolecules (D/H $\leq 1200 \cdot 10^{-6}$; ROBERT et al., 1987). Recently EHRENFREUND et al. (1991), have shown that these macromolecules are probably a common product in interstellar space but their D/H ratios remain unknown.

Soluble organic molecules are also enriched in deuterium but to a lesser extent and their link with the organic macromolecules is unclear. For example, hydrothermal processes at the surface of the parent bodies of the meteorites could very well be responsible for the synthesis of these compounds but their direct condensation from the gas cannot be ruled out (BUNCH and CHANG, 1980). An extensive work on this latter point has been reported by BECKER and EPSTEIN (1982), EPSTEIN et al. (1987), SHOCK & SCHULTE (1990a,b), PIZZARELLO et al. (1991) and KRISHNAMURTHY et al. (1992). Among the soluble organic compounds, amino acids exhibit the highest ratios with D/H up to $420 \cdot 10^{-6}$.

Solar System Water

On Earth, the D/H ratio is close to $155 \cdot 10^{-6}$. Such a ratio is comparable to those found in the carbonaceous meteorites where water is under the form of OH groups in phyllosilicates (KOLODNY et al., 1980; ROBERT and EPSTEIN, 1982; KERRIDGE, 1985) or in ordinary chondrites (ROBERT et al., 1979). Comet Halley exhibits also a D/H ratio comparable to that of the Earth: 6 to $48 \cdot 10^{-5}$ (WYCKOFF, 1991). Since H in Halley is mostly under the form of water, its D/H ratio has probably undergone little changes after accretion.

In summary, there is no experimental evidence for primordial D/H ratios in the solar system water much different than those currently observed in carbonaceous meteorites. Contrary to planets, carbonaceous meteorites have not been affected by post accretional isotopic fractionation and in addition, their D/H ratios are known accurately. Consequently, in the present paper, we will use the carbonaceous meteorite D/H ratio as a face value for the protosolar system water: it varies from 130 up to $280 \cdot 10^{-6}$ with a mean value of 140. In this respect, the protosolar system water is enriched in deuterium relative to H by a factor of ca. 5 ($150 \cdot 10^{-6}$/ $30 \cdot 10^{-6}$).

In order to account for the meteoritic (and terrestrial) D/H ratios of water, GEISS and REEVES (1972) proposed that isotope exchange, between protosolar H_2 and H_2O, occurred at 200 K in the solar nebula. As stated above, the presence of deuterium-rich organic compounds in meteorites has opened the possibility that interstellar products were incorporated during the formation of the solar system. As a consequence, the protosolar model of GEISS and REEVES (1972) was reexamined by GEISS and REEVES (1981). It was argued that, at low temperatures (200 K), the rate of isotope exchange would have been too slow and meteoritic (or terrestrial) D/H ratios could not have been attained within the lifetime of the solar nebula (GRINSPOON and LEWIS, 1987).

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EXPERIMENTAL

Principles

D_2O-H_2 and CD_4-H_2 mixtures were processed at various temperatures and pressures. The rate of isotope exchange between D_2O (or CD_4) and H_2 was observed by monitoring the formation of HD. This isotope exchange reaction was stopped by quenching the sample at liquid N temperature. This was followed by a cryogenic separation of H_2 from D_2O (or CD_4). The HD/H_2 ratio was then analyzed mass spectrometrically. The duration of the isotope exchange, the D/H ratio before and after exchange, the pressures and the temperature at which exchange took place, were all measured precisely. These parameters allowed the determination of the isotopic exchange rate constants.

Gas Mixing Apparatus and Reaction Tubes

The gas mixing glass line and an example of a reaction tube are depicted in Fig. 1. In the line, gas pressures were recorded qualitatively by measurement of the thermal conductivity of gases (see the two gauge heads in Fig. 1) and quantitatively by a mercury manometer. The temperature of the charcoal U-trap (1 mg C: < 100 mesh) located in the center of the apparatus, can be adjusted between the temperature of liquid N and $+100°C$ with a precision of $\pm 2°C$. The principal parts of the line were heated at $80°C$ to prevent condensation of water vapour. The gases were mixed in section 'A' of the line (Fig. 1). Isotope exchange experiments were performed in Pyrex reaction tubes heated to temperatures of 100-$500°C$. In the experimental Tables, the reaction temperature refers to the temperature measured inside the furnace. The temperature gradient in the furnace has been measured: $\Delta T/T < 5\%$. All the volume ratios of the line and of the
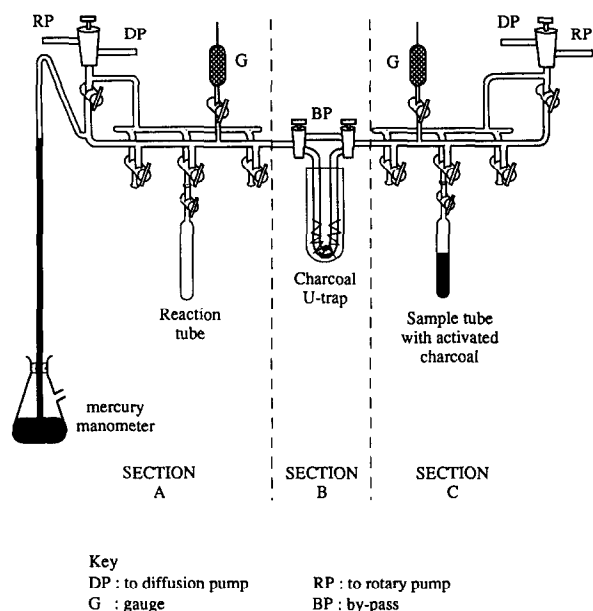
FIG. 1. Glass line used to mix and separate D_2O, CD_4 and H_2. CD_4 is separated from H_2 on the U-trap at $-169°C$. Purified H_2 is trapped at liquid N_2 temperature on charcoal for mass spectrometric analyses. See Experimental section.

different volumes used in gas transfers were calibrated by measuring the pressure variations during gas expansions. These calibrations allowed the calculation of the different pressures in volumes where the gases (H_2, D_2O, or CD_4) were condensed.

Industrial CD_4 (from the French Atomic Commission; CEA, Saclay) was purified because it was found to contain trace amounts of HD ($1.25 \ 10^{-4}$ per vol.). The separation of this HD from CD_4 was achieved by transferring CD_4, at liquid He temperature, to a $250 \ cm^3$ glass volume containing copper oxide. In the presence of CuO at $450°C$, CD_4 remains stable but HD (and D_2) is oxidized to water. The water was then removed from CD_4 at liquid N temperature.

CD_4/H_2 mixtures were prepared in a $250 \ cm^3$ glass vessel. Purified CD_4 was transferred to this volume and added to H_2 by trapping the two gases at liquid He temperature. The CD_4/H_2 ratio was adjusted to be close to 1 in order to have a maximum rate of exchange (ROBERT, 1989). Aliquots, representing about 1% of such a mixture, were transferred to reaction tubes. The pressure of these aliquots in the sample tubes and in the line was determined manometrically. After condensation in the reaction tube, the pressure was determined using the appropriate volume ratio.

In the case of D_2O/H_2, the mixing of the two species was performed in the reaction tubes themselves. D_2O was expanded at saturated vapour pressure (which gave typically 8 μmoles of water in the 7.5 cm^3 reaction tube) and frozen at liquid N temperature in the reaction tube. Hydrogen was then expanded in the reaction tube and its pressure measured manometrically.

After reaction, CD_4 or D_2O were separated from H_2 by expanding the mixtures from the reaction tubes to sections 'B' and 'C' of the line (see Fig. 1). CD_4-H_2 mixtures were expanded on the charcoal U-trap (section 'B') where methane was condensed ($-191°C$). The remaining H_2 was trapped, in section 'C' of the line, on a sample tube containing 3 g of activated charcoal at liquid nitrogen temperature ($-196°C$). Contrary to CD_4, it has been found by using pure H_2, that H_2 does not remain trapped at liquid N temperature on the charcoal U-trap (probably because of the small amount of charcoal in the U-trap; 0.5 mg). This situation improves greatly the cryogenic purification of H_2 from CH_4.

In the case of D_2O-H_2 mixtures, D_2O was condensed at liquid N temperature in the reaction tube itself. H_2 was then expanded from the reaction tube into the section 'A' through the by-pass (see Fig. 1) and trapped in the charcoal sample tube at $-196°C$. All the reaction

tubes and charcoal sample tubes were outgassed at 300°C prior to reaction. The charcoal U-trap was outgassed at 100°C before each CD_4-H_2 separation.

Efficiency of Hydrogen Purification

In order to check upon the efficiency of the gas separations, several experimental tests were performed. For example, before mixing, the absolute amounts of CD_4 and H_2 were determined with a Toepler pump (typical sample size ranging between 100-200 μmoles). Homogenization of the two gases was achieved by recycling with the Toepler pump. The efficiency of this experimental protocol was verified by measuring the CD_4/H_2 ratio with a 24 collector Cameca mass spectrometer used to analyze the chemical compositions of volcanic gases (JAVOY et al., 1986). CD_4/H_2 ratio were determined on numerous aliquots of the same mixture. All these determinations are reproducible within ±1% and, therefore, it was concluded that a CD_4-H_2 mixture was internally well mixed. The internal mixing of a CD_4-H_2 prepared by simple condensation at liquid He temperature (as described in the previous section) was also verified by the same procedure (i.e., using the Cameca mass spectrometer). No noticeable difference was found between the two methods of sample preparation and thus all the results reported here have been obtained on CD_4-H_2 mixtures prepared by simple condensation at liquid He temperature.

The removal of CD_4 from H_2 on the charcoal U-trap at $-191°C$ (see Fig. 1 and the previous section) was also checked by analyzing H_2 with the Cameca mass spectrometer. The calibration of the mass spectrometer was performed with different CD_4-H_2 mixtures whose CD_4/H_2 ratios were determined with the Toepler pump. Using this calibration, H_2 was found to contain always less than 0.5 vol% CD_4 after purification. The H_2 remaining on the charcoal U-trap, together with trapped CD_4, was in all cases below 3% of the total H_2. Pure H_2 was also introduced to the charcoal U-trap in order to verify that negligible amounts of H were trapped, and thus lost, on charcoal at $-191°C$. Note that, although the temperature of $-191°C$ is reproducible within ± 2°C, the exact charcoal temperature is unknown, since an important temperature gradient should exist between the thermocouple and the charcoal itself. For D_2O-H_2, the complete removal of D_2O from H_2 at liquid N temperature was checked mass spectrometrically: no traces of D_2O or D_2 were detected in the mass spectrum.

Isotopic Analyses of the Reacting Gases

In this section, the variations in the D/H ratio are reported in δD units:

$$\delta D(‰) = \left(\frac{R_t}{R_0} - 1 \right) 1000, \tag{1}$$

with R the D/H ratio of H_2 and with the subscripts 0 and t standing for the isotopic composition before and after exchange, respectively. R_t and R_0 were measured mass spectrometrically. We used an initial H_2 having a δD value of $-405‰$ relatively to Standard Mean Oceanic Water (SMOW), that is $R_0 = 92.2 \ 10^{-6}$. In the following, this H will be considered as a standard for our measurements. The relative precision (expressed by the ratio ± $\delta D/\delta D$) lies in the range 0.5-2% for δD values ranging from 0 to $+3000‰$, respectively. For higher δD values, this relative precision is not better than 10% because the m/z 3 current (HD^+) for R_t and R_0 was not recorded on the mass spectrometer with the same amplification gain.

In the mass spectrum of CD_4, the peak corresponding to the CD_3H species was lower than 1% relative to the major peak. However, CD_4 was shown to contain traces of D_2 and HD. After its purification from HD (on CuO at 450°C), the mass spectrum of CD_4 still revealed trace amounts of HD. The precise contribution of deuterated molecular H from CD_4 in the CD_4-H_2 mixtures was determined as follows: H_2 separated from CD_4 immediately after mixing, exhibited a mean δD value of $+90‰ \pm 40‰$. Such an isotopic enrichment was ascribed to the contribution of HD from CD_4 and corresponds to a HD/CD_4 ratio of $7 \pm 3 \ 10^{-6}$ in pure CD_4. A similar experiment was performed with the D_2O-H_2 mixtures. The H_2 isotopic composition

was determined immediately after its separation from D_2O and yielded a mean δD value of $+130 \pm 45\%$. According to these results, we decided that $+130\%$ and $+90\%$ for H_2 in the D_2O-H_2 and CD_4-H_2 experiments, respectively, were minimum values (i.e., did not result from an exchange of isotopes).

Memory effects in the mass spectrometer were insignificant for water experiments. Indeed, after several isotopic determinations of deuterium-rich H_2 (D/H ratio up to 1%), pure H_2 was introduced into the mass spectrometer. The δD values of this pure H_2 were $\sim +100\%$. The memory effect of the mass spectrometer as a whole was considered to be negligible.

The situation is clearly different for the reaction tubes, especially after heating. When pure H_2 was expanded in reaction tubes which had been previously in contact with D_2O and had been heated from 200–450°C for durations comparable with those chosen for exchange reactions, δD values were in the range $+300$ to $+2000\%$. These values demonstrate that trace amounts of D_2O are still present in the reaction tubes, probably under the form of deuterated hydroxyl groups. In some cases it was impossible to eliminate these deuterium traces. Because these memory effects were largely irreproducible, no corrections were made on the data. However, some clearly irreproducible experiments were ignored and repeated with uncontaminated sample tubes. As we will see later, memory effects can probably explain a few unexpected results of the D_2O-H_2 exchange experiment. No memory effects were detected when CD_4 was used in place of D_2O.

Isotopic fractionation of H_2 on charcoal traps was determined to be negligible (i.e., $\delta D \leq 10\%$).

Catalyzed Reactions

Four catalysts were studied: organic polymer (activated charcoal), silica (quartz powder and quartz wool), clays (montmorillonite), and iron (industrial fibers). These catalysts have been chosen for their similarities with compounds present in the solar nebula and thus may have some relevance for the formation of the solar system.

Catalysts were sealed in reaction tubes similar to those used when exchange reactions were performed without catalysts (volume ~ 7.5 cm^3). For each catalyst, three different sample tubes were sealed with three different weights. The specific surface of powdered activated charcoal was 2000 m^2/g. In the case of montmorillonite ([Si_4O_{10} $(OH)_2$] Al_2 4 H_2O), the specific surface area was 700 $m^2 \cdot g^{-1}$ (NADEAU, 1985). For quartz powder, the specific surface was calculated using the granulometry of the powder: 100 cm^2/g. For iron and quartz wool, the specific area was calculated by measuring the size of the wires under the microscope: 1.0 and 0.13 m^2/g, respectively.

Hydrogen concentrations in activated charcoal outgassed at 500°C were determined by pyrolysis at 1100°C: $H_2 = 1000 \,\mu$mole per gram of C. This chemically adsorbed hydrogen is not outgassed during isotope exchange experiments for which the temperature was never higher than 500°C. On the contrary, it was tested experimentally that this concentration could be readily re-established when water vapour is in contact at 200°C with a charcoal previously outgassed at 1100°C. The concentration was not re-established when H_2 was used in place of water, suggesting that this H is chemically adsorbed under the form of C-OH. This observation is important because it will be shown later that an isotope exchange between a deuterated activated charcoal and H_2 did occur at any temperature.

Montmorillonite was outgassed at 150°C. At this temperature the labile water is outgassed and hydroxyl-groups remains in the crystalline structure (H_2O^+ = 7.8 wt% and H_2O^- = 11.6 wt%). Thus all experiments were performed below 150°C. Several experiments were also performed in order to rehydrate an outgassed montmorillonite with heavy water. As for the charcoal, it will be shown later that an isotope exchange between deuterated montmorillonite and H_2 did occur at all temperatures.

THEORETICAL ASPECT

As an example, the isotope exchange between heavy water and H is described hereafter

$$D_2O + H_2 \rightarrow HDO + HD. \qquad (2)$$
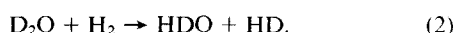
The rate of appearance of HD is

$$\frac{d[HD]}{dt} = k(T)[D_2O]^a[H_2]^b. \qquad (3)$$

$k(T)$ is the rate constant which is known to vary with temperature according to the usual Arrhenius relation. [D_2O] and [H_2] are the number densities (or partial pressures in the present experimental conditions) of heavy water and molecular H, respectively, with t standing for time. In the following, we consider for simplicity that the two constants a and b are equal to 1 (such an approximation is discussed quantitatively in the Result section). One can write the conservation of water as

$$[D_2O]_0 = [D_2O]_t + [HDO]_t. \qquad (4)$$

with [D_2O]$_0$ and [D_2O]$_t$ the initial and final pressures and [HDO]$_t$ the partial pressure of the new species produced via reaction 2. The [HDO]$_t$ and [HD]$_t$ partial pressures being strictly equal,

$$[D_2O]_0 = [D_2O]_t + [HD]_t.$$

Similarly for [H_2],

$$[H_2]_0 = [H_2]_t + [HD]_t. \qquad (5)$$

Equation 3 can be rewritten under the form

$$\frac{d[HD]}{dt} = k(T)([D_2O]_0 - [HD])([H_2]_0 - [HD]). \qquad (6)$$

When [H_2]$_t \gg$ [HD], [HD]^2 can be neglected in Eqn. 6. For small degree of conversion of H_2 into HD, [H_2]$_0$ = [H_2]$_t$ and Eqn. 6 can be integrated

$$\frac{[HD]}{[H_2]_0} = \exp\{-k(T)t([D_2O]_0 + [H_2]_0)\}A + x_{D_2O}. \qquad (7)$$

with:

$$A = \frac{[HD]_0}{[H_2]_0} - x_{D_2O} \qquad (8)$$

$$x_{D_2O} = \frac{[D_2O]_0}{[D_2O]_0 + [H_2]_0}. \qquad (9)$$

Equation 7 can also be written

$$2(D/H)_t = [2(D/H)_0 - x_{D_2O}]\exp\{-k(T)tP\} + x_{D_2O}. \qquad (10)$$

with $(D/H)_0$ equal to $92.2 \cdot 10^{-6}$ (i.e., the isotopic composition of H_2 before isotopic exchange). In the present experiments $(D/H)_t$ in H_2 was measured mass spectrometrically while x_{D_2O}, the molar fraction of D_2O and P, the total pressure were both measured manometrically. The validity of Eqn. 10 was verified by computing rigorously Eqn. 3; i.e., with no ap-

proximations and by taking into account the reverse reaction 2. In our experimental conditions for which $(D/H)_0$ is close to 10^{-5}, the departure between the true $(D/H)_t$ and that calculated via Eqn. 10 does not exceed 5% for $(D/H)_0 \leq 5 \cdot 10^{-2}$. Because in our experiments the $(D/H)_t$ in H_2 is always $< 5 \cdot 10^{-2}$, Eqn. 10 was inverted to provide the experimental values of $k(T)$ reported here. It will be shown in the Results section that no marked departure from the linear Arrhenius equation was observed on $k(T)$ values calculated by this method. A similar reasoning can be extended to the CD_4-H_2 exchange experiments.

It should be noted that the $k(T)$ values for the reactions with D_2O and CD_4 involve two and four atoms of D, respectively. In natural conditions where $H \gg D$, the only contributing reactions are

$$HDO + H_2 \rightarrow H_2O + HD \qquad (11)$$

and

$$CH_3D + H_2 \rightarrow CH_4 + HD. \qquad (12)$$
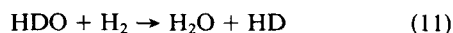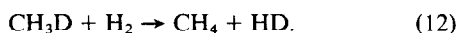
In order to be applicable for the exchange of 1 atom H with 1 atom D, the rate constants obtained with D_2O and CD_4 were divided by 2 and 4, respectively (HENCHMAN et al., 1981). Owing to the reproducibility on $k(T)$ values, mass and symmetry effects can be entirely neglected.

RESULTS

Rate constants calculated for the HDO-H_2 and CH_3D-H_2 reactions are reported in Tables 1 and 6, respectively. Reactions in the presence of catalysts are given in Tables 2-5 for HDO-H_2 and in Tables 7-8 for CH_3D-H_2. Partial pressures are reported at room temperature and expressed in mm Hg, time in seconds, temperature in K and isotopic compositions in ratios (not in δ units). $k(T)$ is expressed in 1/atm.sec. In order to eliminate the pressure dependency (which depends on temperature), $k(T)$ is usually expressed in cm^3/sec (last column in the tables)

$$k(T)_1 = k(T)_2 \times \frac{T}{(298 \times 2.687 \cdot 10^{19})}, \qquad (13)$$

with $k(T)_1$ and $k(T)_2$ expressed in cm^3/sec and 1/atm.sec, respectively.

For catalytic reactions the mass of the catalyst and the global C/H, Si/H, and Fe/H, ratios are also listed. The logarithm of the rate constant values have been averaged at each temperature and the mean values are reported as a function of the inverse of temperature for the water-hydrogen (HDO-H_2) and the methane-hydrogen (CH_3D-H_2) exchanges (see Figs. 2 and 3). When no exchange was detected, rate constants are not reported in the tables but were taken into account in the mean values plotted in Figs. 2 and 3. In such diagrams, linear correlations are expected. The physical significance of these correlations is discussed in the next two sections.

Catalytic Reactions

The results for homogeneous reactions are compared with those obtained for catalytic reactions in the diagrams Log(k)

vs. T^{-1} (see Figs. 2 and 3). Error bars represent 2 standard deviations calculated on the mean value corresponding to a given temperature. It should be noted that the error bars do not always overlap the regression line for all the catalytic and homogeneous reactions. No simple experimental parameters have been found to explain this discrepancy.

For HDO-H_2 (Fig. 2), experiments were performed with the four catalysts: activated charcoal, montmorillonite, iron metal, and quartz. The rate of the isotopic exchange with activated charcoal appears to be systematically faster (with the exception of the low temperature experiments: $10^3 \cdot T^{-1}$ = 3.36). However, if we ascribe conservatively an uncertainty on the $k(T)$ values of one order of magnitude (that is the 2 sigma envelope of the linear correlation), catalytic, and homogeneous reactions are indistinguishable.

Experiments with quartz powder exclude catalytic effects on reaction tube glass-walls during homogeneous reactions. Indeed, these powders represent an increase in glass surface of 36%, 94%, and 150% for the three reaction tubes. No noticeable increase in the exchange rate is associated with these increases in surface. Additional tests were made with 0.4 g. of quartz wool, corresponding to an increase in the glass surface $\geq 10^3$ relative to the sample tube. Once again no noticeable catalytic effects were detected (see Table 4).

For the CH_3D-H_2 system (Fig. 3), measurements were restricted to two catalysts: activated charcoal and montmorillonite. As for the HDO-H_2 system, rate constant values obtained when reactions were performed with catalysts, were not markedly different than those obtained for homogeneous reactions.

pH2 (mm Hg)	pD2O (mm Hg)	T (K)	Time (sec)	$[D/H]_{H2,t}$	k(T) (1/atm.sec)	k(T) (cm³/sec)
27.0	20.0	298	8.64E+4	1.66E-4	1.62E-08	6.02E-28
22.0	18.5	298	2.56E+5	9.10E-4	6.57E-08	2.44E-27
20.0	20.0	298	2.59E+5	2.89E-4	1.45E-08	5.39E-28
26.5	20.5	298	3.46E+5	1.23E-4	1.64E-09	6.09E-29
20.0	20.0	298	3.46E+5	1.92E-4	5.50E-09	2.05E-28
31.5	19.0	298	4.32E+5	1.15E-4	1.05E-09	3.92E-29
26.5	20.5	298	4.32E+5	1.17E-4	1.07E-09	3.99E-29
20.0	20.0	298	4.32E+5	1.67E-4	3.30E-09	1.23E-28
32.0	19.5	298	5.18E+5	1.30E-4	1.42E-09	5.28E-29
33.0	19.5	298	6.05E+5	1.31E-4	1.23E-09	4.60E-29
18.0	20.0	298	6.05E+5	1.35E-4	1.33E-09	4.95E-29
33.0	16.5	338	3.46E+5	4.64E-4	2.18E-08	9.21E-28
38.0	17.5	338	4.32E+5	1.30E-4	1.68E-09	7.08E-29
16.0	21.0	373	6.05E+5	1.21E-4	6.77E-10	3.15E-29
18.0	21.0	373	6.05E+5	1.62E-4	1.66E-09	7.72E-29
52.0	19.0	373	8.64E+5	1.11E-4	3.49E-10	1.63E-29
53.5	19.0	373	1.37E+6	2.06E-4	1.33E-09	6.18E-29
27.0	21.0	373	2.33E+6	1.42E-4	3.07E-10	1.43E-29
20.0	20.0	473	2.59E+5	2.13E-4	5.58E-09	3.30E-28
22.0	16.0	473	2.59E+5	2.43E-4	8.74E-09	5.16E-28
20.5	20.5	473	3.46E+5	4.82E-4	1.32E-08	7.78E-28
22.0	20.0	473	5.18E+5	1.34E-4	9.71E-10	5.73E-29
43.0	21.0	473	5.18E+5	1.86E-4	2.07E-09	1.22E-28
30.5	18.0	473	5.18E+5	3.54E-4	6.73E-09	3.98E-28
33.5	20.0	473	6.05E+5	1.68E-4	1.50E-09	8.84E-29
25.0	25.0	473	6.05E+5	9.44E-4	1.35E-08	7.98E-28
40.5	20.5	473	7.78E+5	1.89E-4	1.46E-09	8.61E-29
26.0	19.0	573	1.55E+5	1.41E-3	8.84E-08	6.33E-27
23.5	20.0	573	4.10E+5	2.43E-2	6.00E-07	4.30E-26
31.0	19.0	573	4.99E+5	6.72E-3	1.39E-07	9.98E-27
19.5	21.5	673	1.55E+5	2.47E-2	1.27E-06	1.07E-25
52.0	16.5	673	1.60E+5	9.58E-2	7.77E-06	6.53E-25
25.5	21.0	673	4.08E+5	7.14E-3	1.40E-07	1.17E-26
23.5	21.0	673	4.12E+5	6.92E-2	1.45E-06	1.22E-25
62.0	19.0	707	5.08E+5	3.61E-2	6.49E-07	5.73E-26

Table 1 : Rate constants for HDO-H2 isotopic exchange. Partial pressures of H_2 and D_2O (in mm Hg at room temperature), time (in second), D/H ratio measured in H_2 at time t and k(T) values in 1/atm.sec and in cm³/sec. Only detectable exchanges are reported.

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weight (g)	pH2 (mm Hg)	pD2O (mm Hg)	T (K)	Time (sec)	$[D/H]_{H2,t}$	C/H ratio	k(T) (1/atm.sec)	k(T) (cm3/sec)
0.12696	63.0	23.0	373	3.17E+05	3.88E-04	190.6	1.23E-08	5.75E-28
0.03259	66.5	23.0	373	3.17E+05	1.30E-04	46.4	1.58E-09	7.30E-29
0.44936	62.0	22.0	373	3.17E+05	2.00E-03	685.6	8.36E-08	3.88E-27
0.12696	89.5	19.5	423	2.25E+06	2.85E-03	121.9	1.70E-08	8.98E-28
0.03254	85.5	19.5	423	2.25E+06	9.03E-04	36.0	4.95E-09	2.62E-28
0.03259	40.0	74.6	423	5.76E+04	6.73E-04	77.1	3.62E-08	1.91E-27*
0.12696	40.0	290.9	423	5.76E+04	2.62E-03	300.3	4.04E-08	2.15E-27*
0.44936	40.0	1029.7	423	5.76E+04	1.28E-02	1062.7	5.80E-08	3.06E-27*
0.03259	94.0	22.5	473	4.07E+05	7.61E-03	35.8	2.01E-07	1.18E-26
0.03259	41.0	74.6	573	7.20E+04	3.61E-02	75.2	1.36E-06	6.84E-26*
0.12696	41.0	290.9	573	7.20E+04	6.82E-02	292.9	6.69E-07	4.79E-26*
0.44936	39.0	1029.7	573	7.20E+04	1.31E-01	1090.0	3.75E-07	2.69E-26*
0.03259	36.0	74.6	673	1.35E+04	4.24E-02	85.6	7.30E-06	6.13E-25*
0.12696	36.0	290.9	673	1.35E+04	9.80E-02	333.6	4.44E-06	3.73E-25*
0.44936	35.0	1029.7	673	1.35E+04	1.08E-01	1214.6	1.39E-06	1.16E-25*

Table 2 : Rate constants for HDO-H2 isotopic exchange with activated charcoal. (see Table 1 for units). Charcoal weights are in grams and C/H ratio expressed in atoms. Rate constants with (*) designate experiments for which the deuterium is exchanged between a deuterated charcoal and H2. These rate constants are calculated taking into account the amount of adsorbed deuterated OH on charcoal . Other values were calculated using the partial pressure of D2O (see discussion in IV.1.) mixed with H2 in presence of 'light' charcoal.

weight (g)	pH2 (mm Hg)	pD2O (mm Hg)	T (K)	Time (sec)	$[D/H]_{H2,t}$	Si/H ratio	k(T) (1/atm.sec)	k(T) (cm3/sec)
0.63307	62.0	22.0	373	3.17E+05	1.65E-04	99.9	1.25E-09	1.47E-28
0.13167	39.5	503.3	373	7.29E+04	1.21E-04	32.6	2.36E-10	1.10E-29*
0.63307	39.5	2420.1	373	7.29E+04	1.87E-04	156.7	1.63E-10	7.60E-30*
0.97276	38.5	3718.7	373	7.29E+04	7.75E-04	247.1	7.65E-10	3.56E-29*
0.13167	85.0	23.0	423	3.99E+06	1.38E-03	15.1	3.77E-09	1.99E-28
0.19288	87.0	18.5	423	7.78E+05	1.95E-03	21.7	3.47E-08	1.84E-27
0.82034	82.0	17.0	423	1.21E+06	1.64E-03	97.8	2.02E-08	1.07E-27
0.13167	26.5	503.3	423	6.66E+04	1.50E-03	48.6	1.13E-08	5.95E-28*
0.63307	26.5	2420.1	423	6.66E+04	3.32E-03	233.6	5.36E-09	2.83E-28*
0.97276	25.5	3718.7	423	6.66E+04	8.73E-03	373.1	9.38E-09	4.95E-28*
0.63307	45.0	19.0	573	1.80E+04	4.93E-03	137.6	2.82E-06	2.02E-25
0.63307	38.0	18.0	573	5.40E+03	1.43E-04	162.9	1.04E-07	7.47E-27
0.13167	40.0	19.0	573	5.40E+03	1.29E-03	32.2	2.30E-06	1.65E-25

Table 3 : Rate constants for HDO-H2 isotopic exchange with montmorillonite. (see Table 1 and 2 captions for units and comments).

weight (g)	pH2 (mm Hg)	pD2O (mm Hg)	T (K)	Time (sec)	$[D/H]_{H2,t}$	Si/H ratio	k(T) (1/atm.sec)	k(T) (cm3/sec)
0.19288	52.0	20.0	373	1.96E+06	1.44E-04	70.1	3.99E-10	1.86E-29
0.43035	53.0	21.0	373	1.96E+06	1.99E-04	153.5	7.87E-10	3.66E-29
0.82034	53.0	21.0	373	1.96E+06	2.06E-04	292.6	8.37E-10	3.90E-29
0.19288	61.0	40.0	473	1.03E+06	5.40E-03	59.8	3.11E-08	1.83E-27
0.43035	92.0	32.0	473	1.03E+06	1.21E-02	88.4	8.91E-08	5.25E-27
0.82034	95.0	32.0	473	1.03E+06	4.62E-03	163.2	3.32E-08	1.96E-27
0.19288	50.5	18.5	573	5.18E+05	1.39E-02	72.2	2.93E-07	2.10E-26
0.43035	49.5	18.5	573	5.18E+05	6.55E-03	164.3	1.35E-07	9.64E-27
0.82034	49.0	18.0	573	5.18E+05	4.16E-02	316.4	9.60E-07	6.84E-26
0.42(*)	35.0	19.0	573	5.18E+05	9.14E-04	104.2	1.65E-08	1.12E-27
0.42(*)	33.5	20.0	573	6.05E+05	2.40E-03	242.8	3.79E-08	1.37E-27
0.42(*)	32.0	20.0	573	6.05E+05	2.03E-03	484.5	3.16E-08	2.27E-27

Table 4 : Rate constants for HDO-H2 isotopic exchange with quartz powder and quartz whool (*). See Table 1 and 2 captions for units and comments.

weight (g)	pH2 (mm Hg)	pD2O (mm Hg)	T (K)	Time (sec)	$[D/H]_{H2,t}$	Fe/H ratio	k(T) (1/atm.sec)	k(T) (cm3/sec)
0.023630	32.0	21.0	373	2.30E+05	1.10E-04	15.29	1.09E-09	5.10E-29
0.057070	34.0	32.0	373	2.30E+05	1.15E-04	34.02	1.30E-09	6.05E-29
0.094954	35.0	32.0	373	2.30E+05	1.05E-04	54.99	7.56E-10	3.52E-29
0.023630	57.0	33.0	473	1.58E+05	1.43E-04	8.40	2.34E-09	1.38E-28
0.057070	82.0	24.0	473	1.58E+05	1.51E-03	14.11	9.02E-08	5.31E-27
0.094954	68.0	23.0	473	1.58E+05	7.21E-04	28.30	4.15E-08	2.45E-27
0.023630	33.0	20.0	573	9.94E+04	3.92E-03	14.51	3.83E-07	2.74E-26

Table 5 : Rate constants for HDO-H2 isotopic exchange with iron. (see Table 1 and 2 captions for units and comments).

pH₂ (mm Hg)	pCD₄ (mm Hg)	T (K)	Time (sec)	[D/H]$_{H_2,t}$	k(T) (1/atm.sec)	k(T) (cm3/sec)
377.9	504.9	298	3.55E+05	1.17E-04	2.64E-11	9.83E-31
167.7	216.5	298	1.40E+07	1.37E-04	2.82E-12	1.05E-31
19.9	26.6	373	6.05E+05	1.22E-04	2.80E-10	1.30E-29
24.4	62.6	473	1.44E+05	1.14E-04	2.88E-10	1.70E-29
27.8	37.2	473	3.55E+05	3.86E-04	2.66E-09	1.57E-28
24.0	32.0	473	3.55E+05	2.91E-04	2.10E-09	1.24E-28
30.8	41.2	473	5.18E+05	1.25E-02	7.05E-08	4.16E-27
105.2	135.9	473	6.05E+05	1.11E-04	2.68E-11	1.58E-30
18.6	24.9	473	6.05E+05	4.04E-04	2.48E-09	1.47E-28
23.3	31.2	473	6.91E+05	3.86E-04	1.63E-09	9.64E-29
97.8	126.3	473	9.50E+05	1.13E-04	2.03E-11	1.20E-30
34.6	21.4	473	9.50E+05	2.55E-04	9.60E-10	5.67E-29
35.5	22.0	473	1.38E+06	1.34E-04	1.64E-10	9.71E-30
26.1	34.9	573	5.76E+04	7.08E-04	3.03E-08	2.17E-27
33.4	44.6	573	6.12E+04	2.45E-04	5.54E-09	3.96E-28
31.3	17.2	573	6.84E+04	1.25E-03	9.76E-08	6.98E-27
35.3	17.7	573	1.49E+05	2.98E-04	7.70E-09	5.51E-28
32.6	15.4	573	1.66E+05	1.36E-04	1.68E-09	1.21E-28
35.3	17.7	573	2.39E+05	1.16E-03	2.50E-08	1.79E-27
36.5	17.7	573	5.08E+05	1.14E-03	1.16E-08	8.27E-28
34.1	19.4	573	9.50E+05	1.01E-03	4.90E-09	3.51E-28
32.8	19.2	573	1.21E+06	1.18E-04	1.11E-10	7.96E-30
94.2	121.7	573	2.68E+06	3.29E-04	7.18E-11	5.14E-30
35.6	18.9	673	6.12E+04	2.08E-03	1.45E-07	1.22E-26
35.8	19.2	673	6.12E+04	5.27E-04	3.12E-08	2.62E-27
32.8	17.2	673	6.84E+04	3.08E-03	2.15E-07	1.80E-26
35.0	18.0	673	1.49E+05	2.67E-03	8.12E-08	6.83E-27
32.3	17.7	673	1.55E+05	4.41E-03	1.33E-07	1.12E-26
33.0	16.0	673	1.55E+05	3.08E-03	1.02E-07	8.56E-27
49.0	95.5	673	3.55E+05	2.21E-02	5.56E-08	4.68E-27
29.8	16.7	673	5.18E+05	7.38E-02	8.02E-07	6.74E-26
31.7	42.3	673	6.05E+05	3.07E-02	1.04E-07	8.71E-27
22.1	29.4	673	6.05E+05	1.22E-04	1.40E-10	1.18E-29
21.8	29.2	673	7.78E+05	1.66E-02	6.21E-08	5.22E-27
34.8	17.2	673	9.50E+05	4.76E-02	2.64E-07	2.22E-26
37.0	20.0	673	1.04E+06	9.29E-04	3.39E-09	2.85E-28

Table 6 : Rate constants for CH₃D-H₂ isotopic exchange. (see Table 1 captions for units and comments).

An interesting observation has been made for the reactions involving montmorillonite or charcoal: some experiments were performed with pure H_2 (i.e., without D_2O in the gas phase) but with catalysts enriched in deuterium prior to experiments. Such enrichments were performed as follows: charcoal was placed in contact with D_2O vapour (at a saturated vapour pressure corresponding to 25°C) and heated to 300°C for one day. A similar protocol was set up for montmorillonite but heated to 150°C. The two catalysts were then outgassed under vacuum at 300 and 150°C, respectively. Thus, no H_2O was added to the catalysts and it can be assumed that these experiments resulted only in a replacement of H atoms (bounded to the catalysts) by D atoms. When these deuterium-rich catalysts were in contact with H_2 an isotopic enrichment took place: see the results reported in

Tables 2 and 3 designated by (*). This observation demonstrates that the isotopic composition of the catalyst plays a role in the exchange rate. For similar durations and temperatures, the D/H ratio of H varies drastically and is obviously correlated with the weight of the deuterated charcoal or montmorillonite in contact with H_2 (see Table 2). Therefore, the rate constants were calculated on the basis that the deuterated H of the catalysts was present in the form of D_2 in the gas phase. The rate constants calculated by this method are fairly reproducible (see k(T) in Tables 2 and 3) and do not show any dependence on the weight of the catalyst. As a consequence, variations of the D/H ratio depend only on the total amount of D introduced by the charcoal and not on the available surface of the charcoal: the catalytic reaction per se plays a negligible role.

It is worth noting that the k values obtained with deuterated and normal charcoal are indistinguishable in the diagram $Log(k) = f(T^{-1})$ (see Fig. 4). In such a diagram the activation energy of the reaction can be calculated from the slope of the correlation which is equal to $\Delta E/R$. For the reactions with deuterated charcoal, $\Delta E = 11.3$ kcal/mole and 11.1 kcal/mole with normal charcoal. This remarkable agreement confirms our previous conclusion that no noticeable catalytic effects can be measured. A similar statement can be made for reactions performed with deuterated montmorillonite.

Gas Phase Reaction

Since no marked and systematic enhancement in k(T) values can be detected in catalytic reactions, all the rate constants reported in Figs. 2, 3, and 4 have been averaged. Note that, while in some experiments no isotope exchange was observed, their corresponding maximum k(T) values were nevertheless taken into account in the mean values reported in the figures. The two isotopic systems CDH₃-H₂ and HDO-H₂ are compared in Fig. 5. The correlations with temperature are quite satisfactory. A linear relation can be drawn through the data that gives an activation energy for the isotope exchange of 10.27 ± 0.28 kcal/mol for HDO-H₂ and 8.70 ± 0.22 kcal/mol for CH₃D-H₂ (calculated from the statistical treatment developed by MINSTER et al., 1979). The 2 sigma envelope of the linear relations reported in Figs. 2, 3, and 4 corresponds to a precision on individual k(T) values no better than one order of magnitude. For example, $k(298) = 4 \pm 65 \; 10^{-28}$. The corresponding precision on the parameters a and b (see

weight (g)	pH₂ (mm Hg)	pCD₄ (mm Hg)	Time (sec)	T (K)	[D/H]$_{H_2,t}$	C/H ratio	k(T) (1/atm.sec)	k(T) (cm3/sec)
0.03259	34.8	21.2	7.38E+04	373	9.90E-05	88.59	6.62E-10	3.09E-29
0.12696	39.4	20.6	7.38E+04	373	9.83E-05	304.83	6.07E-10	2.83E-29
0.44936	36.6	18.9	7.38E+04	373	9.97E-05	1161.40	8.18E-10	3.82E-29
0.12696	37.8	21.2	1.48E+05	473	1.06E-04	317.74	5.45E-10	3.21E-29
0.03259	37.1	19.4	1.48E+05	473	1.49E-04	83.10	2.39E-09	1.41E-28
0.44936	34.4	16.6	1.48E+05	473	1.15E-04	1200.83	1.09E-09	6.43E-29
0.03259	39.1	18.9	2.32E+05	573	3.02E-04	358.52	4.73E-09	3.39E-28
0.12696	37.7	18.3	2.32E+05	573	5.73E-04	318.58	1.12E-08	8.01E-28
0.44936	35.4	16.6	2.32E+05	573	1.76E-03	1200.83	4.29E-08	3.07E-27
0.12696	33.5	14.0	5.76E+04	673	7.60E-03	358.52	7.94E-07	6.67E-26
0.03259	34.3	13.7	5.94E+04	673	6.62E-04	89.88	5.90E-08	4.95E-27
0.12696	33.0	12.0	5.94E+04	673	1.10E-03	363.95	1.19E-07	1.00E-26
0.44936	31.6	11.4	5.94E+04	673	1.62E-03	1345.24	1.91E-07	1.60E-26

Table 7 : Rate constants for CH₃D-H₂ isotopic exchange with charcoal. (see Table 1 and 2 captions for units and comments).

weight (g)	pH₂ (mm Hg)	pCD₄ (mm Hg)	Time (sec)	T (K)	[D/H]$_{H_2,t}$	Si/H ratio	k(T) (1/atm.sec)	k(T) (cm3/sec)
0.13167	36.2	18.3	1.46E+05	373	1.12E-04	35.59	1.11E-09	5.16E-29
0.63307	37.1	18.9	1.46E+05	373	1.24E-24	166.95	1.78E-09	8.29E-29
0.13167	35.6	17.4	1.46E+05	373	2.94E-04	36.19	1.20E-08	5.61E-28

Table 8 : Rate constants for CH₃D-H₂ isotopic exchange with montmorillonite. (see Table 1 and 2 captions for units and comments).

Eqn. 3) has been calculated by a numerical propagation of the precision on $k(T)$ values: if $a = b$, $a = 1 \pm 0.35$ or if $a = 1 \pm 0$, $b = 1 \pm 0.7$. In the calculations of $k(T)$ values, we have assumed that $a = b = 1$ (see Eqn. 11). The present uncertainties on the linear correlation in the Arrhenius plots of Figs. 2, 3, and 4 show that the theoretical assumption $a = b = 1$, is correct within 35%.

The rate constant for water-hydrogen exchange is systematically higher than for methane-hydrogen exchange indicating that the isotope exchange rate is faster with water than with methane. However, the activation energy is higher for water-hydrogen (ΔE_{H_2O}) compare to methane-hydrogen (ΔE_{CH_4}). This would be clearly incorrect if isotope exchange occurred in a single stage process for both reactions because the chemical bond for C-D (in CD₄) is more energetic than for O-D (in D₂O). In fact, it is likely that the deuterium transfer is not restricted to a single reaction but represents the contribution of several individual steps. This situation is often encountered in Arrhenius diagrams (MELANDER, 1960). As mentioned earlier, memory effects in reaction tubes could also play a role in this apparent difference between ΔE_{H_2O} and ΔE_{CH_4}.

The variations of the rate constants with the temperature can be expressed as: $k(T) = A \exp(-E/RT)$. From the data reported in Fig. 5, we have for HDO-H₂:

$$A = 2.0(+6.4, -1.5)10^{-22} \text{ cm}^3 \cdot \text{sec}^{-1} \qquad (14)$$

$$E/R = 5.168 \ 10^3 \pm 140 \text{ K}, \qquad (15)$$

and for CH₃D-H₂:

$$A = 6.8(+2.0, -5.1)10^{-25} \text{ cm}^3 \cdot \text{sec}^{-1} \qquad (16)$$

$$E/R = 4.378 \ 10^3 \pm 150 \text{ K}. \qquad (17)$$

Error bars represent 2 standard deviations of the mean values. The predicted theoretical relation between the pre-exponential factor 'A' and the temperature (GREENE and KUPPER-MANN, 1968) could not be observed here and, thus, can be supposed to be restricted within the experimental precision on A.

DISCUSSION

Theoretical Approach

We first derive a general equation for isotopic exchange reaction rates that can be applied to the solar nebula. In such conditions, the reverse reaction 2 should be taken in account:

$$\text{HD} + a\text{H} \quad \overset{-\frac{1}{2}k^+(T)\rightarrow}{\underset{\leftarrow k^-(T)-}{}} \quad \text{H}_2 + a\text{D}. \qquad (18)$$
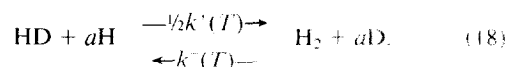
with 'a' designating OH or CH₃ (that is 'a' standing for water and/or methane). The two rate constants $k^+(T)$ and $k^-(T)$ stand for the exchange of one atom H with one atom D. The factor 1/2 is introduced in Eqn. 18 because, in the forward direction, only half of the reactions leads to the observable product H₂ while the other half lead to HD during the unobservable exchange between H and H (HENCHMAN et al., 1981). The rare deuterated species (i.e., CD₂H₂, CD₃H, CD₄ etc.) can be neglected owing to the low natural abundances of D (D/H ~ 10^{-4}). The rate constant $k^-(T)$ for the reverse reaction Eqn. 18 is related to $k^+(T)$ by:

$$\frac{k^+(T)}{k^-(T)} = \alpha(T) = \frac{(D/H)_{aH}}{(D/H)_{H_2}}, \qquad (19)$$

with $\alpha(T)$ the isotopic fractionation factor between H₂ and aH under thermodynamical equilibrium conditions. $k^-(T)$
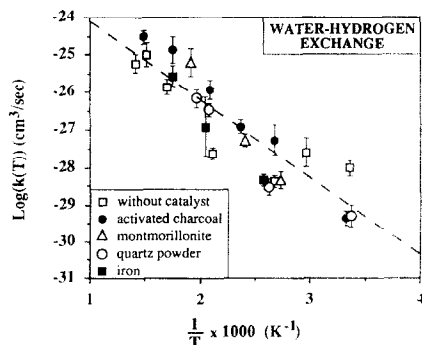

FIG. 2. Logarithm of the rate constant $k(T)$ vs. $1/T$ for hydrogen isotopic exchange between water and H. Squares, circles, and triangles stand for the type of catalyst used in experiments. $k(T)$ values obtained with and without catalyst cannot be distinguished. The slope of the linear correlation (dashed line) corresponds to $\Delta E = 10.27 \pm 0.28$ kcal/mole. Error bars represent 2 standard deviations.
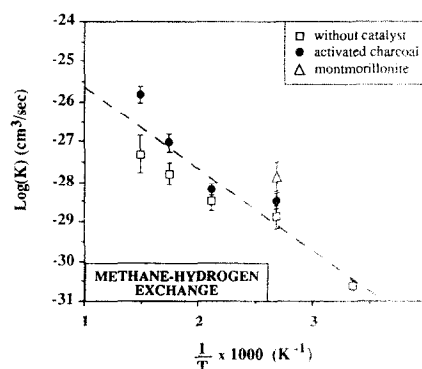

FIG. 3. Logarithm of the rate constant $k(T)$ vs. $1/T$ for hydrogen isotopic exchange between methane and hydrogen. $\Delta E = 8.70 \pm 0.22$ kcal/mole (see Fig. 2 for comments).
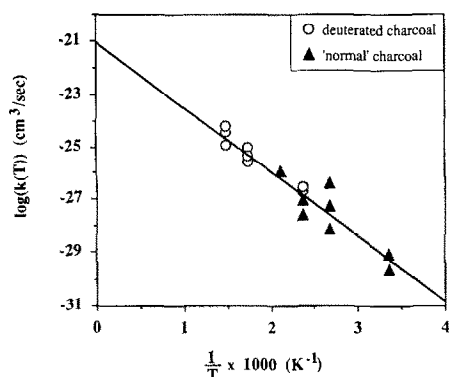
FIG. 4. Comparison of the rate constants $k(T)$ for two types of isotopic exchange: (1) D_2O-H_2 in presence of industrial charcoal and (2) H_2 in presence of deuterated charcoal. The data represent individual determinations (not mean values as in previous figures). No catalytic effect is detectable in this diagram (see discussion in IV.I.).

is the rate constant measured in the present paper. The rate of appearance of (aD) in Eqn. 18 is

$$\frac{d[aD]}{dt} = [HD][aH]^{1/2}k^+(T) - [aD][H_2]k^-(T). \quad (20)$$

In the solar nebula $[H2] \gg [aH]$. Thus, $[HD]/[H_2]$ can be considered to be constant. In addition, because $H \gg D$, $[aH]$ is also constant. Equation 20 can be written

$$\frac{d[aD]}{dt} = \frac{[HD]}{[H_2]}[H_2][aH]^{1/2}k^+(T) - [aD][H_2]k^-(T), \quad (21)$$

$$\frac{d[aD]}{[aH]}\frac{1}{dt} = \left(\frac{D}{H}\right)_{H_2}[H_2]k^+(T) - \frac{[aD]}{[aH]}[H_2]k^-(T). \quad (22)$$

That is also

$$\frac{d(D/H)aH}{dt} = [H_2]k^-(T)\left(\alpha(T)\left(\frac{D}{H}\right)_{H_2} - \left(\frac{D}{H}\right)_{aH}\right). \quad (23)$$

All the parameters of this last equation are known: $(D/H)_{H_2}$ is the D/H ratio of the protosolar H, $[H_2]$ is the total pressure (since H_2 is by far the dominant species), $k^-(T)$ has been determined in the present work, and $\alpha(T)$ has been calculated previously (RICHET et al., 1977). In dynamical models of the solar nebula, the pressure and temperature (P-T) vary with time. In that case a numerical computation of Eqn. 23 has been performed. If the pressure and temperature of the gas are constant all along the course of the isotopic exchange, the integration of Eqn. 22 gives the usual result (McKAY, 1938; BANK et al., 1960),

$$\frac{(D/H)_{aH,t} - \alpha(T)(D/H)_{H_2}}{(D/H)_{aH,0} - \alpha(T)(D/H)_{H_2}} = \exp - ([H_2]tk^-(T)), \quad (24)$$

where $(D/H)_{aH,x}$ are the isotopic compositions at $t = 0$ and at time t (subscripts 0 and t, respectively). The term $\alpha(T)$

$(D/H)_{H_2}$ represents the isotopic composition of aH if thermodynamical equilibrium was to be attained between aH and H_2.

Numerical Results

The variations of $k^-(T)$ with temperature are described by Eqns. 14 and 15.

The P-T variations in the solar nebula has been modelled by Cameron (CAMERON, 1972, 1978, 1985; CAMERON and PINE, 1972; LIN and PAPALOIZOU, 1985; BOSS, 1987; BOSS and TSCHARNUTER, 1989). P-T varies with time and with the distance from the Sun. These variations were introduced into Eqn. 23 by empirical numerical relations derived from the figures published by Cameron. The aim of these calculations was to establish whether terrestrial and/or meteoritical deuterium enrichments could be reached in the water present within the nebula.

An example of these calculations is given in Fig. 6. The variations of the D/H ratio in water vapour in contact with molecular hydrogen are drawn as a function of time and/or temperature (LÉCLUSE and ROBERT, 1992). An initial D/H ratio of $34 \pm 10 \ 10^{-6}$ for molecular H was used in these calculations. Such a value is derived from the $^3He/H$ ratio of the Sun, recently revisited by ANDERS and GREVESSE (1989), and is somewhat larger than the previous value of 20 10^{-6} proposed by GEISS and BOCHSLER (1985) (see the discussion in ANDERS and GREVESSE, 1989). Two durations for the life time of the nebula are considered: $2 \ 10^5$ and $2 \ 10^6$ years. Such durations seem reasonable in view of the numerous models developed in the literature (CASSEN and BOSS, 1988; WOOD and MORFILL, 1988). The temperature in the collapsing nebula shows a maximum at 367 K and then decreases while the pressure varies from $3.4 \ 10^{-4}$ atm at 367 K down to $5.6 \ 10^{-5}$ atm at 140 K, but no minimum temperature is assigned to the nebula in Cameron's models. The D/H ratio of water is assumed to be equal to that of the solar nebula H_2 before the collapse of the nebula (at $t = 0$ in Fig. 6b and 6c). It increases during the collapse and reaches a plateau corresponding to the temperature for which the exchange reaction is inhibited by slow kinetics. Note that, for a lifetime of 2 My (Fig. 6c), the intermediate D/H plateau
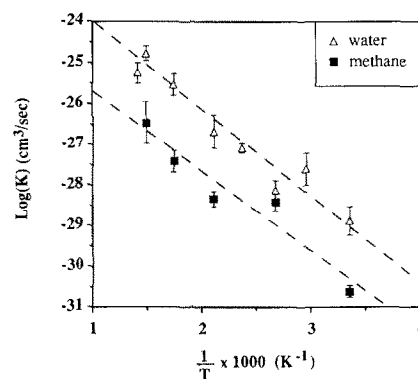

FIG. 5. Comparison of the rate constants $k(T)$ for the hydrogen isotopic exchange between D_2O and H_2 and between CD_4 and H_2. All the $k(T)$ values obtained via catalytic and noncatalytic reactions have been averaged. Error bars represents 2 standard deviations.
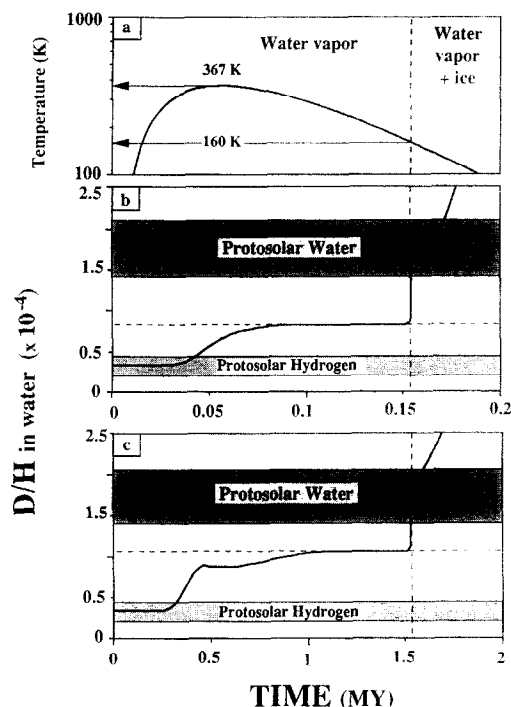
FIG. 6. Evolution of the water D/H ratio as a function of duration for two lifetimes of the protosolar nebula: $2 \cdot 10^5$ y. (Fig. 6b) and $2 \cdot 10^6$ y. (Fig. 6c). The calculation is performed at 3 Astronomical Units for which the temperature and the pressure in the solar nebula reach maximum values of 367 K (Fig. 6a) and $3.4 \cdot 10^{-4}$ atm. respectively (CAMERON & PINE, 1972, 1978, 1985; LIN & PAPALOIZOU, 1985). Water condenses at 160 K. In that case the isotopic fractionation between ice and vapor causes a marked increase in the D/H ratio of ice, which ranges in the protosolar water domain defined by Earth and meteorites.

corresponds to isotopic equilibrium between water and hydrogen. For a shorter lifetime (Fig. 6b) such an equilibrium cannot be attained.

An additional isotopic fractionation must be taken into account if the condensation temperature of water was attained in the nebula. Under these circumstances, water ice would

have appeared in the gas and would have been incorporated into the planetesimals (see the model developed by LUNINE et al., 1991). The variations of the ice-vapour isotopic fractionation factor as a function of the temperature has been established experimentally (MERLIVAT and NIEF, 1965) and has been introduced in our calculations. The temperature of water condensation was calculated by assuming that the solar O/H ratio corresponds to the molar fraction of water in H (within a factor of 2). This condensation temperature lies between 170 and 160 K (MORFILL, 1985; MORFILL et al., 1985; PRINN and FEGLEY, 1989) but does not depend upon the distance from the Sun in the adiabatic model of Cameron. In Fig. 6 the isotopic composition of ice is reported along with that of water vapour below this condensation temperature (160 K). The ice-vapour isotopic fractionation causes a marked departure from the water vapour D/H plateau (see Fig. 6). In our model the vapour is considered as an infinite reservoir, i.e., only a minute fraction of the available water condensed as ice.

All the calculations reported in Fig. 6 are performed for a distance from the Sun of 3 AU (1 Astronomical Unit is the distance between the Sun and the Earth). It seems likely that 3 AU corresponds to the location of the formation of the water-rich carbonaceous chondrites. Nevertheless, according to the present calculations, no marked isotopic gradient should have existed in the nebula for distances corresponding to terrestrial planets (see the calculations reported in Table 9). In Table 9, the D/H ratios in the protosolar water vapour are restricted to values between 83 and $106 \cdot 10^{-6}$ corresponding to quenching temperatures for the isotopic exchange from 558 K to 438 K, respectively.

The terrestrial and meteorite domain drawn in Fig. 6 (indicated as protosolar water), has been defined from measured D/H ratios in meteorite phyllosilicates (KOLODNY et al., 1980; ROBERT and EPSTEIN, 1982; KERRIDGE, 1985), and range from $130-280 \cdot 10^{-6}$. The D/H ratio of terrestrial oceanic water with $155 \cdot 10^{-6}$ lies within this range. Although much higher D/H ratios have been measured in LL3 meteorites (ROBERT et al., 1979, 1987; MCNAUGHTON et al., 1981), there is no clear indication that phyllosilicates act as sink for deuterium-rich hydrogen. On the contrary, it has been clearly

Distance from the Sun (A.U.)		Lifetime of the nebula (years)	Temp. T(K)	D/H in water vapour	D/H in water ice
Earth	1 A.U.	2E+05	160	83 E-06	143 E-06
			170	83 E-06	133 E-06
		2E+06	160	101 E-06	174 E-06
			170	101 E-06	162 E-06
Asteroid belt	3.5 A.U.	2E+05	160	83 E-06	144 E-06
			170	83 E-06	134 E-06
		2E+06	160	106 E-06	182 E-06
			170	106 E-06	169 E-06

Table 9 : D/H ratio in water during the cooling of the nebula. The calculations were performed for 2 condensation temperatures (170 and 160 K), 2 life-times for the nebula (2.10^5 and 2.10^6 years) and two distances from the Sun corresponding to the Earth (1 A.U.) and to the asteroid belt (3 A.U.). The D/H ratio in vapour was obtained by computation of equation (23) and in ice from the experimental isotopic fractionation factor between ice and vapor (MERLIVAT & NIEF, 1965). These calculations demonstrate that the terrestrial and meteorite D/H ratios (lying between 130 and 280.10^{-6}) can be reached by thermal processes in the solar nebula.

shown that a major fraction, if not all, of this heavy H is bound to C in the form of insoluble organic macromolecules (YANG and EPSTEIN, 1983; ERHENFREUND et al., 1991). The origin of this deuterium enrichment is usually ascribed to interstellar chemistry occurring while the solar gas was in the form of a dense cloud (DULEY and WILLIAMS, 1984; HAL-BOUT et al., 1990). Therefore, these high LL3 D/H ratios are not included in the present estimate of the D/H range of protosolar *water*. On the contrary we assume that the process that gave rise to the isotopic composition of the organic macromolecules was unrelated to that governing the water D/H ratio.

Consequences for Origin of Water in the Solar System

According to the present experimental results, the protosolar water D/H ratio can be reached if the H_2 pressure is close to 10^{-5} atm. somewhere between 1 and 3 AU. In view of the protosolar nebula models, pressures much higher than 10^{-5} seem unreasonable and are not considered in the present paper. In addition, even for pressures around 10^{-5} atm, the protosolar water value is reached only if ice appeared in the solar nebula, ice being enriched in deuterium by a factor of ca. 1.7 relative to its vapour. The error bars on $k(T)$ values (see Eqns. 14 and 15) have been numerically propagated on the maximum D/H ratio that can be reached by water vapour. According to these calculations, a variation of $k(T)$ within two standard deviations is equivalent to a factor of 3 on the hydrogen pressure. In such conditions, as the pressure in the nebula is still a subject of controversy (within several orders of magnitude; see WOOD and MORFILL, 1988), the present experimental precision on the $k(T)$ value has a negligible effect on the final precision of the calculated D/H ratio.

In our calculations, water vapour was assumed to be an infinite reservoir relative to that condensed as ice. This is quite reasonable in view of the large amount of water in the solar nebula compared to the presently observable water in terrestrial planets. For example, between 0 and 3 AU, the water mass ($O/H = 10^{-3}$) in the nebula should exceed 10^{-5} times the solar mass. This would correspond to three times the Earth mass which obviously exceeds by far the total amount of water now present on the terrestrial planets and meteorites. Therefore, a mechanism must have prevented the condensation of water. For example, it is possible that the gas was blown out by the T Tauri solar phase before the total condensation of water vapour. It is also possible that a large super-saturation of water was reached in the nebula because of the lack of nucleating solids.

According to Table 9, no marked isotopic gradient should have been present in the solar nebula. Consequently, our calculations are in agreement with the observation that water on Earth and in meteorites have similar D/H ratios and thus, a similar origin.

The present model shows that phyllosilicates should be considered as secondary products formed by hydrothermal alteration on the surface of meteorite parent bodies (BUNCH and CHANG, 1980). Indeed, if the alteration of silicates had occurred in the gas via the water vapour, the D/H ratio of the water ($D/H = 110 \cdot 10^{-6}$) would represent a maximum value for OH bearing minerals, i.e., a D/H ratio in phyllo-

silicates $\leq 110 \cdot 10^{-6}$. On the contrary, in carbonaceous meteorites, phyllosilicates have a D/H ratio $\geq 120 \; 10^{-6}$. As a consequence, the nebula water vapour cannot be the source of silicate hydration.

Using the present isotope exchange rate, it can be shown that the CH_4 in the nebula never reach D/H ratios much higher than $90 \; 10^{-6}$, while organic molecules in carbonaceous meteorites exhibits currently D/H ratios up to $500 \; 10^{-6}$. It is thus quite clear that organic macromolecules observed in meteorites do not result from the polymerization of CH_4. This conclusion is also in agreement with the fact that the formation of CH_4 in the nebula is kinetically inhibited at temperature ≤ 300 K (FEGLEY and PRINN, 1988). Interstellar chemistry remains the more plausible mechanism to account for these high deuterium enrichments in organic macromolecules.

Finally, it is interesting to note that during the evolution of the solar nebula, the D/H ratio of any pre-existing water (of interstellar origin?) may have been reset to solar system values. This is due to the fact that water in the inner solar system, once in the form of vapour, is in isotopic equilibrium with hydrogen down to 370 K. This is illustrated in Fig. 6c where the intermediate D/H plateau corresponds to the D/H ratio of water in equilibrium with H_2 at 370 K. Thus, the isotopic composition of molecular hydrogen buffers that of water. Of course this is not so in the case of the outer part of the solar system where temperatures are not high enough to vaporize any hypothetical pre-solar water ice, enriched in deuterium before the formation of the solar nebula. According to OWEN et al. (1986), D/H variations in the outer Solar System suggest that presolar (interstellar) deuterium-rich water could be the endmember of a two component mixing model. In order for such a water to preserve its high D/H ratio, the present data show that its vapour should have remained in contact with molecular hydrogen during a short period of time ($\leq 10^4$ years) at temperatures not exceeding 220 K. A quantitative treatment of this aspect will be presented elsewhere.

In conclusion, we repeat the point we wish to emphasize: the D/H ratio of the solar system water may result from isotope exchange between water and H in the primordial nebula. If so, then water in carbonaceous chondrites and in terrestrial planets would have been accreted as ice.

REFERENCES

ANDERS E. and GREVESSE N. (1989) Abundance of the elements: meteoritic and solar. *Geochim. Cosmochim. Acta* **53**, 197–214.

ANDERS E., HAYATSU R., and STUDIER M. H. (1973) Organic compounds in meteorites. *Science* **182**, 781–790.

BANK C. A., VERDURMEN E. A. T., DE VRIE A. E., and MONTERIE F. L. (1960) Oxygen isotope exchange between CO and O_2. *J. Inorg. Nucl. Chem.* **17**, 295–301.

BECKER R. H. and EPSTEIN S. (1982) Carbon, hydrogen, and nitrogen isotopes in solvent-extractable organic matter from carbonaceous chondrites. *Geochim. Cosmochim. Acta* **46**, 97–103.

BEER R. and TAYLOR F. W. (1973) The abundance of CH_3D and the D/H ratio in Jupiter. *Astrophys. J.* **179**, 309–327.

BEER R. and TAYLOR F. W. (1978) The D/H and C/H ratios in Jupiter from CH_3D phase. *Astrophys. J.* **219**, 763–767.

BEZARD B., DE BERGH C., CRISP D., and MAILLARD J. P. (1990) The deep atmosphere of Venus revealed by high-resolution night-side spectra. *Nature* **345**, 508–511.

BJORAKER G. L., MUMMA M. J., and LARSON H. P. (1989) Isotopic abundance ratios for hydrogen and oxygen in Martian atmosphere. *Bull. Amer. Soc.* **21**, 991.

BLACK D. C. (1973) Deuterium in the Early Solar System. *Icarus* **19**, 154–159.

BOSS A. P. (1987) Theory of collapse and protostar formation. In *Interstellar Processes* (ed. D. J. HOLLENBACH and H. A. THRONSON). pp. 321–348. Reide D.

BOSS A. B., MORFILL G. E., and TSCHARNUTER W. M. (1989) Models of the formation and evolution of the Solar Nebula. In *Origin and Evolution of Planetary and Satellite Atmospheres* (ed. S. K. ATREYA, et al.), pp. 35–77. Univ. Arizona Press.

BUNCH T. E. and CHANG S. (1980) Carbonaceous chondrites: II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543–1577.

CAMERON A. G. W. (1972) Accumulation Processes in the Primitive Solar Nebula. *Icarus* **18**, 407–450.

CAMERON A. G. W. (1978) Physics of the primitive solar accretion disk. *Moon Planets* **18**, 5–40.

CAMERON A. G. W. (1985) Formation and evolution of the primitive solar nebula. In *Protostars and Planets II* (ed. D. C. BLACK and M. S. MATTHEWS), pp. 1073–1099. Univ. Arizona Press.

CAMERON A. G. W. and PINE M. R. (1972) Numerical Models of the Primitive Solar Nebula. *Icarus* **18**, 377–406.

CASSEN P. and BOSS A. P. (1988) Protostellar collapse dust grains and solar system formation. In *Origin and Evolution of Planetary and Satellite Atmospheres* (ed. S. K. ATREYA, et al.), pp. 304–328. The University Arizona Press.

CLAYTON D. D. (1983) *Principle of Stellar Evolution and Nuclosynthesis.* Univ. Chicago Press.

COUSTENIS A., BÉZARD B., and GAUTIER D. (1989) Titan's atmosphere from Voyager infrared observations II. The CH_3D abundance and D/H ratio from the 900–1200 cm^{-1} spectral region. *Icarus* **82**, 67–80.

DE BERG C., LUTZ B. L., OWEN T., and CHANVILLE J. (1988) Monodeuterated methane in the outer solar system III. Its abundance on Titan. *Astrophys. J.* **329**, 951–955.

DE BERG C., BEZARD B., OWEN T., CRISP D., MAILLARD J. P., and LUTZ B. L. (1991) Deuterium on Venus: Observations From Earth. *Nature* **251**, 547–549.

DULEY W. W. and WILLIAMS D. A. (1984) *Interstellar Chemistry.* Acad. Press.

EHRENFREUND P., ROBERT F., and BEHAR F. (1991) Comparison of interstellar and meteoritic matter at 3.4 μm. *Astron. Astrophys.* **252**, 712–717.

EPSTEIN S., KRISHNAMURTHY R. V., CRONIN J. R., PIZZARELLO S., and YUEN G. U. (1987) Unusual stable isotope ratios in amino acids and carboxylic acid extracts from the Murchison meteorite. *Nature* **93**, 477–479.

FEGLEY B., JR. and PRINN R. G. (1988) The predicted abundances of deuterium-bearing gases in the atmospheres of Jupiter and Saturn. *Astrophys. J.* **326**, 490–508.

FEGLEY B., JR., GAUTIER D., OWEN T., and PRINN R. G. (1991) Spectroscopy and chemistry of Uranus. In *Uranus* (ed. J. T. BERSTRALH, et al.), pp. 147–203. Univ. Arizona Press.

GAUTIER D. and OWEN T. (1983) Cosmological implication of helium and deuterium abundances of Jupiter and Saturn. *Nature* **302**, 215–218.

GAUTIER D. and OWEN T. (1989) The composition of outer planet

atmospheres. In *Origin and Evolution of Planetary and Satellite Atmospheres* (ed. S. K. ATREYA, et al.), pp. 487–512. Univ. Arizona Press.

GEISS J. and REEVES H. (1972) Cosmic and solar system abundances of deuterium and helium-3. *Astron. Astrophys.* **18**, 126–132.

GEISS J. and REEVES H. (1981) Deuterium in the early solar system. *Astron. Astrophys.* **93**, 189–199.

GEISS J. and BOCHSLER P. (1985) Ion composition in the solar wind in relation to solar abundances. In *Rapport isotopiques dans le système solaire* (ed. CNRS), pp. 213–218. Cepadues Eds.

GREENE E. F. and KUPPERMANN A. (1968) Chemical Reaction Cross Sections and Rate Constants. *J. Chem. Ed.* **45**, 361–369.

GRINSPOON D. G. (1993) Implications of the high D/H ratio for the sources of water in Venus' atmosphere. *Nature* **363**, 428–431.

GRINSPOON D. H. and LEWIS J. S. (1987) Deuterium fractionation in the presolar nebula: Kinetics limitation on surface catalysis. *Icarus* **72**, 430–436.

HALBOUT J., ROBERT F., and JAVOY M. (1990) Hydrogen and oxygen isotope compositions in kerogens from the Orgueil meteorite: Clues to solar origin. *Geochim. Cosmochim. Acta* **54**, 1453–1462.

HENCHMAN M. J., ADAMS N. G., and SMITH D. (1981) The isotope exchange reactions $H^+ + D_2 \leftrightarrow HD + D^+$ and $D^+ + H_2 \leftrightarrow HD + H^+$ in the temperature range 200–300K. *J. Chem. Phys.* **75**, 1201–1206.

HUNTEN D. M. and DONAHUE T. M. (1976) Hydrogen loss from the terrestrial planets. *Ann. Rev. Earth Planet. Sci.* **4**, 265–292.

JAVOY M., PINEAU F., and DELORME H. (1986) Carbon and nitrogen in the mantle. *Chem. Geol.* **57**, 41–62.

KERRIDGE J. F. (1985) Carbon, hydrogen and nitrogen in carbonaceous meteorites: Abundances and isotopic compositions in bulk samples. *Geochim. Cosmochim. Acta* **49**, 1707–1714.

KERRIDGE J. F., CHANG S., and SHIPP R. (1987) Isotopic characterization of kerogen-like material in Murchison carbonaceous chondrite. *Geochim. Cosmochim. Acta* **51**, 2527–2540.

KOLODNY Y., KERRIDGE J. F., and KAPLAN I. R. (1980) Deuterium in carbonaceous chondrites. *Earth Planet. Sci. Lett.* **46**, 149–158.

KRISHNAMURTHY R. V., EPSTEIN S., CRONIN J. R., PIZZARELLO S., and YUEN G. U. (1992) Isotopic and molecular analyses of hydrocarbons and monocarboxylic acids of the Murchison meteorite. *Geochim. Cosmochim. Acta* **56**, 4045–4058.

LECLUSE C. and ROBERT F. (1992) Origin of the deuterium enrichment in the solar system. *55th Ann. Meet. Meteor. Soc. Copenhagen.* **27**, 248.

LIN D. N. C. and PAPALOIZOU J. (1985) On the dynamical origin of the solar system. In *Protostars and Planets II* (ed. D. C. BLACK and M. S. MATTHEWS), pp. 981–1072. Univ. Arizona Press.

LUNINE J. I., ENGEL S., RIZK B., and HORANY H. (1991) Sublimation and Reformation of Icy Grains in the Primitive Solar Nebula. *Icarus* **94**, 333–344.

LUTZ B. L., OWEN T., and DE BERGH C. (1990) Deuterium Enrichment in the Primitive Ices of the Protosolar Nebula. *Icarus* **86**, 329–335.

McKAY H. A. C. (1938) Kinetics of exchange reactions. *Nature* **142**, 997–998.

McNAUGHTON N. J., BORTHWICKS S., FALLICK A. K., and PILLINGER C. T. (1981) D/H ratio in unequilibrated ordinary chondrites. *Nature* **294**, 639–641.

MELANDER L. (1960) *Isotope Effects on Reactions Rates.* Ronald.

MERLIVAT L. and NIEF G. (1965) Fractionnement isotopique lors des changements d'état solide-vapeur et liquide-vapeur de l'eau à des températures inférieures à 0°C. *Tellus* **19**, 122–127.

MINSTER J. F., RICARD L. P., and ALLEGRE C. J. (1979) ^{87}Rb-^{87}Sr chronology of enstatite meteorites. *Earth Planet. Sci. Lett.* **44**, 420–440.

MORFILL G. E. (1985) Physics and chemistry in the primitive solar nebula. In *Birth and Infancy of Stars* (ed. R. LUCAS and A. OMONT), pp. 693–794. North Holland.

MORFILL G. E., TSCHARNUTER W., and VÖLK H. J. (1985) Dynamical and chemical evolution of the protoplanetary nebula. In *Protostars & Planets II* (ed. D. C. BLACK and M. S. MATTHEWS). pp. 493–533. Univ. Arizona Press.

NADEAU P. H. (1985) The physical dimensions of fundamental clay particles. *Clay Miner.* **20**, 499–514.

ORTON G. S. (1992) Ground-based observations of Titan's Thermal Spectrum. In *Proc. Symposium Titan;* ESA Publ. Div., pp. 91–95.

ORTON G. S., LACY J. H., ACHTERMAN J. M., PARMAR P., and BLASS W. E. (1992) Thermal Spectroscopy of Neptune: The Stratospheric Temperature, Hydrocarbon Abundances and Isotopic Ratios. *Icarus* **100**, 541–555.

OWEN T., LUTZ B. L., and DE BERGH C. (1986) Deuterium in the Solar System: Evidence for two distinct reservoirs. *Nature* **320**, 244–246.

OWEN T., MAILLARD J. P., DE BERGH C., and LUTZ B. L. (1988) Deuterium on Mars: The Abundance of HDO and the value of D/H. *Science* **240**, 1767–1770.

PINTO J. P., LUNINE J. I., KIM S. J., and YUNG Y. L. (1986) D to H ratio and the origin and evolution of Titan atmosphere. *Nature* **319**, 388–390.

PIZZARELLO S., KRISNAMURTHY R. V., EPSTEIN S., and CRONIN J. R. (1991) Isotopic analyses of amino acids from the Murchison meteorite. *Geochim. Cosmochim. Acta* **55**, 905–910.

PRINN R. G. and FEGLEY B., JR. (1989) Solar nebula chemistry: origin of planetary, satellite, and cometary volatiles. In *Origin and Evolution of Planetary and Satellite Atmospheres* (ed. S. K. ATREYA, et al.), pp. 78–136. Univ. Arizona Press.

RICHET P., BOTTINGA Y., and JAVOY M. (1977) A review of hydrogen, carbon, nitrogen, oxygen, sulphur, chlorine stable isotope fractionation among gaseous molecules. *Ann. Rev. Earth Planet. Sci.* **5**, 65–110.

ROBERT F. (1989) Anomalous Isotopic Fractionation: A Deuterium-Hydrogen Exchange Experiment. *Proc. 19th Lunar Planet. Sci. Conf.*, 571–576.

ROBERT F. and EPSTEIN S. (1982) The concentration and isotopic composition of hydrogen, carbon, and nitrogen in carbonaceous meteorites. *Geochim. Cosmochim. Acta* **46**, 81–95.

ROBERT F., MERLIVAT L., and JAVOY M. (1979) Deuterium concentration in the early solar system: a hydrogen and oxygen isotope study. *Nature* **282**, 785–789.

ROBERT F., JAVOY M., HALBOUT J., DIMON B., and MERLIVAT L. (1987) Hydrogen isotope abundances in the solar system. Part I: unequilibrated chondrites. *Geochim. Cosmochim. Acta* **51**, 1787–1805.

SHOCK E. L. and SCHULTE M. D. (1990a) Amino-acid synthesis in carbonaceous meteorites by aqueous alteration of polycyclic aromatic hydrocarbons. *Nature* **343**, 728–731.

SHOCK E. L. and SCHULTE M. D. (1990b) Summary and implication of reported amino acids concentrations in the Murchison meteorite. *Geochim. Cosmochim. Acta* **54**, 3159–3173.

WATSON W. T. (1973) Formation of HD molecules in the interstellar medium. *Astrophys. J.* **182**, 73–76.

WATSON W. D. (1976) Interstellar molecule reactions. *Rev. Mod. Phys.* **48**, 513–552.

WOOD J. A. and MORFILL G. E. (1988) A review of the solar nebula models. In *Meteorites and the Early Solar System* (ed. J. F. KERRIDGE and M. S. MATTHEWS), pp. 329–347. The Univ. Arizona Press.

WYCKOFF S. (1991) Comets: Clues to the early history of the solar system. *Earth. Sci. Rev.* **30**, 125–174.

YANG J. and EPSTEIN S. (1983) Interstellar organic matter in meteorites. *Geochim. Cosmochim. Acta* **47**, 2199–2216.

YUNG Y. L., FRIEDL R. R., PINTO J. P., BAYES K. D., and WEN J. S. (1988a) Kinetic Isotopic Fractionation and the Origin of HDO and CH_3D in the Solar System. *Icarus* **74**, 121–132.

YUNG Y. L., WEN J. S., PINTO J., ALLEN M., PIERCE K. K., and PAULSON S. (1988b) HDO in the martian atmosphere: Implications for the Abundance of Crustal Water. *Icarus* **76**, 146–159.