Deuterium Fractionation in the Presolar Nebula: Kinetic Limitations on Surface Catalysis

DAVID H. GRINSPOON AND JOHN S. LEWIS

Lunar and Planetary Laboratory, Space Sciences Building, University of Arizona, Tucson, Arizona 85721

Models assuming low temperature equilibrium fractionation have previously been employed to explain the range of D/H values observed in the solar system and to make predictions of deuterium enhancement in the outer planets. While the reaction rates of the homogeneous partitioning reactions are prohibitively low at nebular temperatures, it has been suggested that catalysis on grains could shorten equilibration times sufficiently. This idea is quantitatively tested here. We find that under highly idealized conditions—the full cosmic abundance of nickel available for catalysis in pure 5-μm grains—the equilibration time constant becomes greater than the lifetime of the nebula at temperatures lower than 560°K. Even this firm lower limit is not cold enough to allow strong fractionation. Speculations are offered on alternative explanations for the distribution of hydrogen isotopes in the solar system. © 1987 Academic Press, Inc.

INTRODUCTION

Variations in the deuterium to hydrogen ratio (D/H) between different solar system objects may reflect fractionation which occurred very early, prior to or during planet formation. Observations have revealed a wide range of D/H values in the solar system. Essential to a correct interpretation of these observations is an understanding of the nature and rates of the fractionation processes.

The standard for terrestrial deuterium abundance is the standard mean ocean water (SMOW) value of D/H = 156 ppm. This represents an enrichment by about a factor of 8 over the value in the primordial solar nebula, which is inferred to be 2×10^{-5} (Geiss and Reeves 1981). Large deuterium enrichments of up to 30 to 100 times this "primordial" D/H have been observed in organic components of carbonaceous meteorites (Kerridge 1980).

One popular explanation for these enrichments has been low temperature equilibration fractionation in the presolar nebula (Geiss and Reeves 1981, Hubbard and Macfarlane 1980). In a solar composition gas, as the temperature drops, deuterium will be partitioned increasingly into heavier molecules from molecular hydrogen (Fig. 1). Equilibration at temperatures of 200°K or lower could result in the observed deuterium enhancements in SMOW and meteorites, if the partitioning reactions are not kinetically limited. A low temperature explanation for the meteoritic enhancements is problematical in the light of oxygen isotopic ratios which seem to require much higher equilibrium temperatures (Black 1973).

Due to the high cosmic abundances of O, C, and N, the primary deuteron recipients will be H_2O, CH_4, and NH_3. If equilibrium has prevailed, the ice will be extremely D-rich relative to the gas.

Theoretical models of Jovian planet formation, assuming that equilibrium fractionation has occurred, predict that Jupiter and Saturn should have D/H close to the primordial ratio. Greatly enhanced ratios are predicted for Uranus and Neptune due to
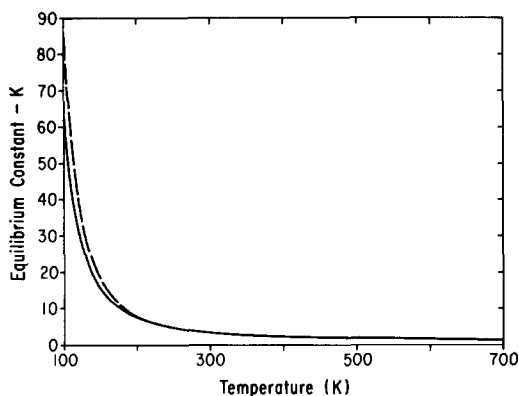
FIG. 1. The temperature dependence of reaction (1) and (2) in the text. Solid curve is K_{HDO}. Broken curve is $\frac{1}{2}K_{CH_3D}$, shown here to compensate for stoichiometric effects, representing the comparative partitioning capacity of these two reactions at a given temperature. After Reeves and Bottinga (1972); and Richet et al. (1977).

the larger ice-to-gas ratios expected in the formation of these planets (Hubbard and MacFarlane 1980). Observations of D/H on Jupiter and Saturn tend to confirm a roughly solar proportion for these planets. (Beer and Taylor 1973, Trauger et al. 1971, Macy and Smith 1978, Fink and Larson 1978, Owen et al. 1986).

Hubbard and MacFarlane (1980) have sought to explain early observations of CH_3D abundances on Uranus which did not show the predicted enhancement (Macy and Smith 1978). Barring systematic errors in observation or interpretation, they suggested that a stably stratified Uranus could sequester a deuterium enhancement in the "icy" core for the age of the solar system. Another possible explanation is that kinetic limitations on the deuterium partitioning reactions prevented low temperature equilibrium fractionation from occurring in the solar nebula. While this would negate the prediction of an enhanced Uranian D/H ratio, it would also eliminate a plausible explanation for the terrestrial (SMOW) enhancement. Recent findings of enhanced D/H on Titan support the hypothesis that outer solar-system icy planetesimals were

enriched in deuterium (Owen et al. 1986). Also, new analysis of CH_3D on Uranus has suggested values closer to the predictions of Hubbard and MacFarlane (1.65 ± 1.65/−0.8) × 10^{-4}, Owen et al. (1986). Thus, it may be that ices in the early solar system were deuterium rich, yet the kinetic limitations on the low temperature partitioning reactions cannot be ignored, and may impose severe constraints on equilibrium fractionation as an explanation for this enrichment (Fig. 2).

Beer and Taylor (1973) performed a kinetic analysis of the partitioning reactions summarized by

$$CH_4 + HD \rightleftharpoons CH_3D + H_2 \qquad (1)$$

and found that for temperatures below 450°K equilibration times are greater than the age of the universe. Similar calculations for

$$H_2O + HD \rightleftharpoons HDO + H_2 \qquad (2)$$

also yield extremely large equilibrium times (Steacie 1954, Geib and Steacie 1935, Farkas and Melville 1936), far too great to be relevant to the solar nebula at any temperatures low enough to provide a significant equilibrium partitioning effect.
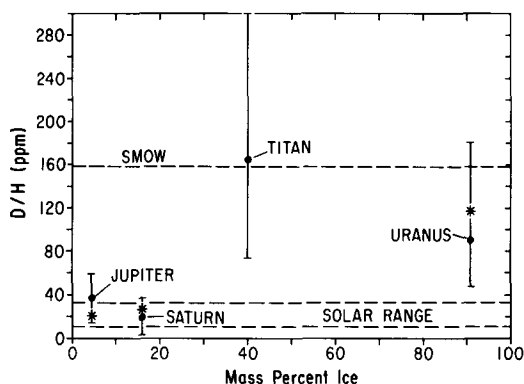

FIG. 2. Values of D/H for solar system objects plotted against modeled amounts of icy material incorporated in their formation. D/H values are from Owen et al. (1986). Asterisks are predicted D/H values from the model of Hubbard and MacFarlane (1980). Ice percentages are from Hubbard and MacFarlane (1980) and Pollack and Consolmagno (1984).

Surface catalysis of deuterium fractionation is a familiar industrial process. Several authors have suggested that reactions on grain surfaces could contribute to fractionation in the nebula, perhaps allowing more reasonable equilibration times (Beer and Taylor 1973, Geiss and Reeves 1981). This idea has not previously been quantitatively tested. We have undertaken a search of the experimental literature on surface catalysis for the relevant reactions and applied these results to conditions in the nebula in an effort to determine whether this mechanism could indeed overcome the kinetic barrier, allowing low temperature equilibrium fractionation in the nebula.

SURFACE KINETICS

The relative cosmic abundances of O, C, and N, and the relative volatility of their hydrogenated condensates dictate that, for regions of interest, the hydrogen containing ices will be largely H_2O. For this reason we have focused our analysis of surface kinetics on reaction (2).

We have identified two substances, metallic nickel and magnetite, that are both efficient catalysts for reaction (2), and likely components of nebular grains (Lewis 1972). Economic incentives have motivated a very thorough experimental search for efficient isotopic exchange catalysts, and thus it is unlikely that there are more important catalysts which would have been present in the nebula which have escaped experimental scrutiny. Nakhmanovich et al. (1963) and Temkin et al. (1961) studied the kinetics of reaction (2) on several catalytic surfaces, including Fe_3O_4 and metallic Ni. They found that the simple reaction scheme

$$HDO + (\ ) \rightleftharpoons HD + (O)$$
$$H_2 + (O) \rightleftharpoons H_2O + (\ ) \qquad (3)$$
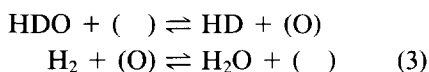
was adequate for derivation of a kinetic equation which agrees with experimental results over a wide range of conditions. ( ) represents a free surface site on the catalyst and (O) a chemisorbed atom of oxygen, or a

surface oxygen atom of an oxide. The actual mechanism may also involve intermediate chemisorbtion of hydrogen. This would have no effect on the reaction kinetics as long as rapid equilibrium is maintained between adsorbed and gaseous H_2, as seems to be the case.

Utilizing a logarithmic adsorption isotherm and assuming the reaction scheme (3), the following kinetic equation was derived and experimentally verified by Nakhmanovich et al. (1963),

$$W = k_1 P(HDO) \left(\frac{P(H_2)}{P(H_2O)} \right)^m$$
$$- k_2 P(HD) \left(\frac{P(H_2O)}{P(H_2)} \right)^{1-m}, \quad (4)$$

where $W = \partial P(HDO)/\partial t$ is the reaction rate, k_1 and k_2 are the rate constants for the forward and reverse reactions, and m is a constant which depends on the degree of oxygen coverage. At low oxygen coverage m goes to zero leading to the kinetic equation

$$W = k_1 P(HDO) - k_2 \frac{P(HD)P(H_2O)}{P(H_2)}. \quad (5)$$

For the comparison of different catalytic surfaces, and for the application of kinetic data to the solar nebula it is useful to introduce the specific reaction rate k_1^*, defined as the number of HDO molecules reacting per unit time per unit area of catalyst. It is easily seen that

$$k_1^* = \frac{1}{RT\sigma\rho} k_1 \text{ (mole/atm m}^2\text{sec)}, \quad (6)$$

where R is the gas constant, $\sigma(m^2/g)$ the specific surface area of the catalyst, and $\rho(g/cm^3)$ the bulk density of catalyst. The quantity $\sigma\rho(m^2/cm^3)$ is the available surface area per unit volume of catalyst. We will refer to this quantity as α. The temperature dependence of k_1^* for magnetite and nickel, as derived from the results of Nakhmanovich et al. (1963) and confirmed, for nickel, by Olariu and Margineanu (1967), is shown in Fig. 3.
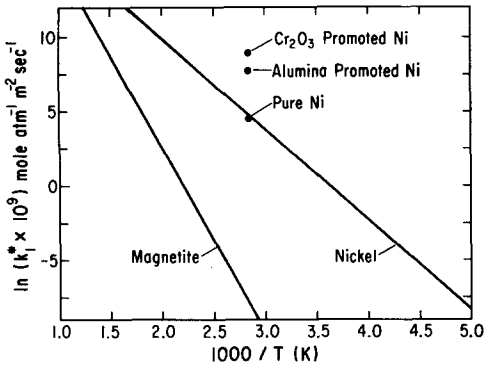
FIG. 3. Specific rate of deuterium fractionation on magnetic and nickel surfaces. Lines are from kinetic data of Nakhmanovich et al. (1963), points are from data of Olariu and Margineanu (1967).

APPLICATION TO SOLAR NEBULA

We present here a "best-case scenario" in which the most favorable catalyst is available, fully exposed in its cosmic abundance. Starting with the generous assumption (from the point of view of molecules wishing to rush toward equilibrium) that pure spherical nickel grains are present in the region of interest, we derive the available surface area for catalysis, per unit volume of solar nebula:

$$\alpha = 12A(\#/H)P/d\rho \, RT. \tag{7}$$

Here $6A/d\rho$ is the available area per mole of nickel grains with diameter d and density ρ. $A = 58.7$, the molar mass of nickel. This is multiplied by $2(\#/H) \, P/RT$ which is the number of moles of nickel per unit volume of nebula, where $\#/H$ is the atomic abundance of nickel relative to hydrogen.

Substituting Eq. (6) into (5) we obtain

$$W = -\frac{\partial P(HDO)}{\partial t} = k_1^*(T)RT\alpha$$

$$\left[P(HDO) - K(T)P_{HD} \frac{P(H_2O)}{P(H_2)} \right]. \tag{8}$$

$K(t) = \dfrac{P(H_2)P(HDO)}{P(H_2O)P(HD)}$ is the equilibrium constant for reaction (2) taken from Richet

et al. (1977). Thus, the term in brackets in (8) goes to zero at equilibrium.

The time constant for chemical equilibration,

$$\tau = \frac{P(HDO)}{(\partial P(HDO)/\partial t)}, \tag{9}$$

was calculated as a function of temperature, using a temperature–pressure profile and H_2O abundance from equilibrium calculations of Lewis (1972, 1974). The available surface area, and hence the absolute reaction rate, is inversely proportional to grain size. Metal particles in chondritic meteorites have typical diameters of 100 μm (Lewis and Prinn 1980). Figure 4 shows the result of our calculation with the extremely liberal assumption of 5-μm pure nickel grains.

As can be seen in Fig. 4, the calculated equilibration times, assuming highly idealized conditions, are greater than the presumed lifetime of the nebula for temperatures lower than 560°K. At this temperature the equilibrium partitioning is not adequate to produce the fractionation observed in SMOW, in meteorites, or the assumed fractionation in the Jovian planet model of Hubbard and MacFarlane (1980). These equilibration times should be regarded not
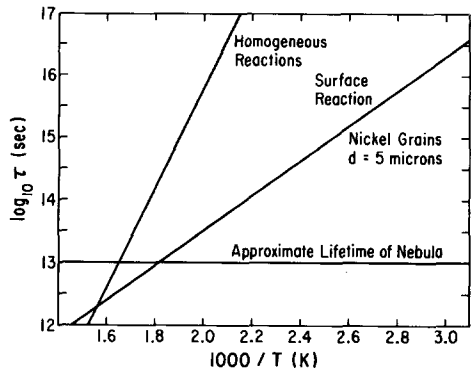

FIG. 4. Equilibration times for deuterium fractionation as a function of temperature for homogeneous reactions and for catalysis by nickel grains under highly idealized conditions.

as representative but as a firm lower limit. Thus, 560°K may be seen as a lower limit for an equilibration temperature for catalytically partitioned deuterium in the solar nebula.

Quantum molecular tunneling has been suggested as a mechanism for overcoming low temperature kinetic inhibitions in the interstellar medium (Goldanskii 1977, 1979, 1985). The low-temperature quantum limit of chemical reaction rates has been confirmed in the laboratory in the case of formaldehyde polymerization (Goldanskii et al. 1973), and this mechanism has been offered as a means of facilitating the formation of complex organic molecules in molecular clouds. Tielens (1983) modeled the surface chemistry of deuterated molecules on mantled interstellar grains with a complex reaction scheme including the effects of molecular tunneling. This mechanism appears to offer an alternative to the ion–molecule reaction scheme described by Watson (1976) for explaining the large deuterium fractionation observed in molecular clouds. It is interesting to consider whether this tunneling mechanism could help overcome the kinetic barriers we have discussed in the presolar nebula. The theoretical studies of Goldanskii and Tielens have been for conditions in interstellar clouds with characteristic temperatures of 10–20°K and lifetimes of 10^5–10^7 years, comparable to the lifetime of the solar nebula. The "tunneling temperature" at which reaction rates level off with decreasing temperature, departing from the Arrhenius exponential decline, is inversely proportional to the square root of the mass of the tunneling species. Characteristic tunneling temperatures for hydrogen and deuterium are 160 and 120°K, respectively (Goldanskii 1985), considerably higher than those for other species, and within the range of temperatures in most nebular models, at least for the extremities of the nebula. The calculations presented above appear to preclude the usefulness of tunneling for surface catalyzed deuterium fractionation in the nebula. A leveling off of reaction rate at

160°K does not help if the classically calculated rate at 560°K is already slow enough to preclude significant fractionation in a nebular lifetime. Nevertheless, we support the suggestion of Goldanskii (1979) that the consequences of this relatively new area of kinetics should be very carefully considered for chemical and prebiotic evolution in early solar system environments.

DISCUSSION

The results presented here indicate that low temperature equilibrium fractionation of deuterium did not occur in the presolar nebula. Even under unrealistically favorable conditions, the equilibration times are prohibitively long. Other explanations must be sought for the range of D/H ratios observed throughout the solar system. Predictions and interpretation of D/H ratios in the Jovian planets must be reconsidered in the absence of equilibrium fractionation. Likewise, the D/H values found in the terrestrial planets, meteorites, and Titan must be explained in a consistent fashion. Equilibration at 200°K, as invoked for meteorite phyllosilicates (Yang and Epstein 1983), seem to be ruled out.

Recently several theoretical discussions of the origins of cometary ices have proposed that the incorporation of mantled dust grains from molecular clouds could lead to large enhancements of D/H in comets (Vanysek and Vanysek 1985, Ip 1980). Eberhardt et al. (1987) determined D/H in Comet Halley from Giotto neutral mass spectrometer measurements. Their value (0.6×10^{-4} < D/H < 4.8×10^{-4}) is consistent with the terrestrial value, with a large uncertainty. The degree to which this represents an average cometary value, and the amount of heterogeneity to be expected in cometary D/H are unknown. Heavily deuterated cometary ices could provide a mechanical connection between the large deuterium enhancements observed in interstellar molecules and the range of enhanced (over solar) values observed in the solar

system. In this scenario, the suite of D/H values found in the solar system could represent a range of mixtures of "interstellar/cometary" and "solar/primordial" hydrogen. Impact of deuterium-rich cometary and meteoritic material may have assisted in producing the enhanced terrestrial D/H. Literature references to a "hundred-fold enrichment" of deuterium on Venus are common. This assessment may be unnecessarily geocentric, since the significance of the terrestrial value to which it refers, as a standard, is not understood. Escape of 0.003 to 1 terrestrial oceans of water has been invoked as a mechanism for providing the large D/H ratio observed on Venus (Kasting and Pollack 1983, Kumar et al. 1983, Kasting et al. 1984). While mass-selective escape of hydrogen has certainly contributed to this enhanced value, there is as yet no direct geological evidence for a paleo-ocean on Venus. Models of planet formation differ on whether Venus should have formed with a roughly terrestrial supply of water (Walker 1977) or in its present extremely dry state (Holland 1963, Lewis 1972). The Magellan radar mapper may reveal evidence for or conspicuous lack of evidence for ocean floor and shoreline morphology unless the whole surface of the planet is younger than the age of the putative ocean. In either case accretion of deuterium-rich material may have assisted in creating the large D/H observed. It has been shown that water on Venus is likely to be in a quasi-steady state, with comets possibly constituting the major source of water (Grinspoon and Lewis 1987). This differs from previous models which have assumed that water abundance on Venus is monotonically declining, and implies that D/H on Venus is strongly coupled to both the magnitude and time dependence of the cometary flux, and the cometary D/H ratio.

If comets are the remnants of a population of Uranus–Neptune icy planetesimals, then D-rich comets would be consistent with the observed deuterium enhancement on Uranus and suggest a predicted enhancement for Neptune as well.

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