$$C_n H_{2n+2} \xrightarrow{H^+ + Ga-oxide} C_n H_{2n} + H_2$$
 (9)

The ethene and higher alkenes are oligomerized and then dehydrocyclized to aromatics over the bifunctional zeolite catalyst:

$$C_2 \text{ to } C_4 \text{ alkenes} \xrightarrow{H^+} C_6 \text{ to } C_{10} \text{ alkenes}$$

$$\xrightarrow{H^+ + Ga\text{-oxide}} \text{ aromatics} \qquad (10)$$

The methane activation resulting from the presence of the higher alkane also involves the above reactions, but the alkane is first converted to alkene by Eq. 9.

Because of the very large change in free energy ($\Delta G_r > 48$ kcal/mol of benzene) that would be involved, the direct formation of benzene from methane at $\leq 600^{\circ}$ C is thermodynamically impossible. However, the thermodynamic barrier is drastically reduced or even eliminated as a result of the addition of alkenes or higher alkanes; the value of ΔG_r approaches zero or even becomes negative, depending on the additive, its concentration relative to that of methane, and the temperature. For example, for an n-butene/methane ratio of 1.0, $\Delta G_r =$ -4.1 kcal/mol at 500°C and -10.6 kcal/ mol at 600°C (11).

According to the stoichiometry of Eq. 8 (which is responsible for the methane activation), the rate of methane conversion should increase with an increasing alkene/CH₄ ratio. The results in Fig. 1 are consistent with this assumption. Further, the appreciable formation of butanes from *n*-butene, particularly at lower temperatures (Fig. 2), and that of propane from propene (Fig. 1), also indicate the occurrence of the hydrogen-transfer reaction. The observed high methane activation (at lower temperature and higher space velocity) resulting from the isobutene additive (Table 1) is consistent with the tert-butyl carbonium ions being more stable than the primary and secondary butyl carbonium ions. This interpretation also supports the involvement of carbonium ions in the methane activation by Eq. 5.

A comparison of the results of alkene aromatization in the presence of methane with that in the absence of methane (Table 2) shows a marked increase in H_2 production in the reaction when methane is present in the feed; the observed flow rate of the H_2 formed is quite close to that estimated from the composition of feed and products. Moreover, the methane conversion values estimated from the feed and product compositions are quite close to that obtained directly from the methane flow measured at the inlet and outlet of the reactor. Also, in general, there is a small but appreciable increase in the selectivity for aromatics because of the presence of methane (Table 2). All of these observations confirm the low-temperature methane activation over the zeolite as a result of the presence of the additives.

Our results show that methane can be highly activated, and hence converted to higher hydrocarbons and aromatics with high conversion rates at low temperatures (\leq 600°C), by its hydrogen-transfer reactions with alkenes over the zeolite. This method could provide an environmentally cleaner process, operating at much lower temperatures, for converting methane into higher hydrocarbons without the formation of undesirable carbon oxides.

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Dissociation of Methane into Hydrocarbons at Extreme (Planetary) Pressure and Temperature

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Constant-pressure, first-principles molecular dynamic simulations were used to investigate the behavior of methane at high pressure and temperature. Contrary to the current interpretation of shock-wave experiments, the simulations suggest that, below 100 gigapascals, methane dissociates into a mixture of hydrocarbons, and it separates into hydrogen and carbon only above 300 gigapascals. The simulation conditions (100 to 300 gigapascals; 4000 to 5000 kelvin) were chosen to follow the isentrope in the middle ice layers of Neptune and Uranus. Implications on the physics of these planets are discussed.

The high-pressure and high-temperature behavior of methane (CH₄), the most abundant organic molecule in the universe, is of great importance in planetary physics. Current models (1, 2) of the interiors of Neptune and Uranus are based on the existence of a middle ice layer made of CH₄, NH₃, and H₂O in solar proportions. In this layer, pressure and temperature (*P*-*T*) range from 20 GPa and 2000 K to 600 GPa and 8000 K. Shock-wave experiments indicate that, in spite of its stability at ambient conditions (3), CH₄ dissociates at these extreme conditions (4), possibly into H₂

and carbon, with precipitation of solid diamond (5). Here we present computer simulations that show a different, more complex, chemical breakdown.

The lack of direct information on the interior structure of Neptune and Uranus has restricted attempts to understand the behavior of CH_4 under extreme pressures to the interpretation of laboratory-based shock-wave experiments (4), where planetary *P*-*T* conditions are achieved. An alternative tool for such an investigation is computer simulation (6). Our simulations are based on a recently developed deformable-cell method for constant-pressure, first-principles molecular dynamics (7).

We set our simulation conditions at 100 GPa and 4000 K (8), which correspond to the P-T conditions at a distance of about twothirds of the planetary radius from the center. This pressure is also the highest reached in shock-wave experiments (4). In the first picosecond of the simulation, the initial configuration of 16 CH₄ molecules (Fig. 1A) under-

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Fig. 1. Snapshots of CH₄ dissociating at 100 GPa and 4000 K. The simulation cell contains 16 carbon atoms (green spheres) and 64 hydrogen atoms (white spheres) periodically repeated in space (gray spheres). (A) All-CH₄ configuration at 100 GPa and 600 K. (B) Dissociation products obtained after 2 ps of simulation at 100 GPa and heating at 4000 K.

went a dramatic breakdown. The final equilibrated configuration (Fig. 1B) consisted of a mixture of two CH_4 , four ethane (C_2H_6) , and two butane (C_3H_8) molecules, with the residual hydrogen atoms mainly in molecular form (9). Although the small number of particles that can be modeled does not allow a reliable stoichiometric analysis of the resulting hydrocarbon mixture, the tendency of CH₄ to dissociate, as well as the formation of saturated hydrocarbons of higher molecular weight, is evident (10). High-pressure and -temperature dissociation into mixtures of saturated hydrocarbons was proposed for benzene and polybutene (11) but is unexpected for CH_4 , the most stable hydrocarbon at ambient conditions. The hydrocarbons obtained in the simulation are neutral and insulating, with a calculated electronic gap of about 6 eV. These neutral species will not contribute to the conductivity in the middle ice layer; therefore, the picture that ionic currents generated by pressurized and ionized H2O-the main constituent of the middle ice layers-and NH₃ are responsible for the magnetic field of these planets (12) remains unchanged. We do not anticipate an important interaction of these ions with the (hydrophobic) hydrocarbons, except for possible hard-sphere packing compounds (13).

A second simulation was performed at 300 GPa and 5000 K. These *P*-*T* conditions still lie on the planet isentrope and correspond to a larger depth. The simulation, about 2 ps long, produced a change in the mixture composition, with the formation of a long alkane chain containing a methilic group (a total of 12 carbon units), two C_2H_6 molecules, and partially dissociated hydrogen. The comparison of both simulations indicates that the formation of C–C bonds is favored with increasing pressure. It suggests that the formation of diamond-like configurations is likely at slightly higher pressure, in agreement with

earlier predictions (5) and with empirical calculations (14) based on the equations of state for CH_4 , diamond, and hydrogen and their extrapolation to high pressures. Our results show that diamond formation is initially preempted by the appearance of hydrocarbon mixtures, which was not considered in earlier works.

These dissociation products were obtained in simulations at high temperatures. To test whether hydrocarbons are still favored at low temperature, where entropic effects become negligible, we quenched the dissociation products and compared the zerotemperature enthalpies of CH₄, H₂ plus diamond, and hydrocarbon mixtures (15). To this aim, we performed a set of low-temperature simulations of the hydrocarbon mixtures at 100 and 300 GPa, along with a low-temperature compression run on CH₄. A plot of enthalpy versus pressure (Fig. 2) shows that, in contrast with previous suggestions (5), complete dissociation of CH₄ into diamond and hydrogen is enthalpically disfavored up to at least 120 GPa. Moreover, at 100 GPa the enthalpy of the hydrocarbon mixture is lower than that of CH_4 by about 0.4 eV per CH_4 molecule (16). The low-temperature results therefore confirm that the dissociation of CH4 into hydrocarbons, before full conversion into diamond and hydrogen, is favored even on simple energetic grounds (17). High-temperature entropic contributions to the free energy are likely to further favor the mixture because of the increased disorder relative to the pure phases. At low temperature, full conversion to diamond and hydrogen only appears above 300 GPa, where the enthalpy of H₂ plus diamond becomes nearly identical to that of the mixture, their difference being within the accuracy of our simulation. Again, entropic contributions could favor the mixtures at high tempera-



Fig. 2. Enthalpy versus pressure for (solid line) CH₄, (dotted line) diamond plus H₂, and (squares) dissociation products (hydrocarbon mixtures) (T = 0). The diamond and H₂ were in a stoichiometric ratio of [C]:[H] = 1:4; the hydrocarbon mixtures were obtained as dissociation products in our 100- and 300-GPa simulations. The dashed line is a guide to the eye. The volume scale refers to the CH₄ equation of state. The mixtures appear to be more stable roughly in the 100- to 300-GPa range (26).

tures, as shown by the simulation at 300 GPa and 5000 K. Extrapolating to even higher pressures, we conclude that it is likely that significant amounts of diamond are formed at pressures higher than 300 GPa in the deep interiors of the outer planets; however, they should be buried under a layer of "ices" where CH_4 has dissociated into a saturated hydrocarbon mixture.

Because of convection, CH4 dissociation in the middle ice layer may have consequences for planetary atmospheres. The complete separation of CH_4 into H_2 plus diamond in the middle ice layer (5) would imply gravitational precipitation of carbon, which may lead to a depletion of the total amount of atmospheric carbon. Hydrocarbons, in contrast, do not precipitate. Rather, they may partly leak into the atmosphere. Current models, based on photochemical schemes, underestimate the C_2H_6/C_2H_2 ratio in the observable atmosphere of all of the outer planets, especially Neptune (18). It has been suggested that a C_2H_6 production mechanism is probably missing in these models (19). Our results show that a considerable amount of C_2H_6 could be present in the middle ice layer (20). The anomalous abundance of atmospheric C_2H_6 could then be understood in terms of a convective mechanism carrying C_2H_6 from the middle ice layer up to the observable atmosphere. Because convection in Uranus is reduced with respect to Neptune, possibly as a result of its greater proximity to the sun (2), this mechanism should be especially effective in Neptune.

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- This finding is consistent with shock-wave experiments (4), which reveal a discontinuity in the CH₄ equation of state at 20 GPa and 2000 K.
- 10. The time scale of our simulations is such that a few hundred C-H stretching oscillations and a few tens of molecular collisions take place in each run. Although this is typically a sufficient time scale for thermalization, and in fact dissociation took place in a fraction of a picosecond, processes like segregation and diffusion occur on a longer time scale. These processes are energetically minor in comparison with dissociation and will not significantly alter the dissociation picture as proposed.
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- 15. Mixtures, of course, do not represent a well-defined state at T = 0. Their enthalpy is an upper bound to that of the true low-temperature system, where single phases are likely to prevail.
- 16. In spite of the endothermic character of the zeropressure conversion 16 CH₄ \rightarrow 2 CH₄ + 4 C₂H₆ + 2 C₃H₈ + 8 H₂ (enthalpy of reaction $\Delta H^{\circ} = 0.37$ eV per CH₄ molecule), the volume reduction ΔV brought by the 100-GPa conversion leads to a $P\Delta V$ contribution of about 0.65 eV per CH₄ molecule and to an enthalpy gain of about 0.4 eV per CH₄ molecule.
- 17. Moreover, a comparison of simulated vibrational spectra of the mixture and of CH_4 shows a significant broadening of the C-H bending mode band around 800 to 1700 cm⁻¹ in the mixture. This fact, together with the presence of the H_2 stretching mode at 4200 cm⁻¹, should be looked for as the signature of the CH₄ dissociation in forthcoming low-temperature diamond–anvil cell experiments.
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with the same level of accuracy, for carbon (24) and for hydrogen (25).

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Burst Conditions of Explosive Volcanic Eruptions Recorded on Microbarographs

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Explosive volcanic eruptions generate pressure disturbances in the atmosphere that propagate away either as acoustic or as shock waves, depending on the explosivity of the eruption. Both types of waves are recorded on microbarographs as 1- to 0.1-hertz N-shaped signals followed by a longer period coda. These waveforms can be used to estimate burst pressures and gas concentrations in explosive volcanic eruptions and provide estimates of eruption magnitudes.

Since first photographed during the 1975 eruption of Ngauruhoe Volcano in New Zealand (1), atmospheric shock waves and condensation clouds marking their passage in the near field of the source have become wellrecognized features of explosive volcanic eruptions (2-4). Occurrences of shock waves were documented in video footage of the 1992 eruptions of Mount Spurr, Alaska, where the shocks were observed propagating through the column of ash in a series of flashes occurring within the plume (4). These flashes represent short-lived clouds produced by the propagation of shock waves through the local atmosphere, which momentarily condenses water vapor. A vigorous ejection of a mixture of hot gases and rock fragments characteristic of a vulcanian eruption followed the flashes. Air waves accompanying vulcanian eruptions are recorded on microbarographs as N-shaped signals followed by a longer period coda. Here we use numerical simulations to demonstrate how the amplitude and waveform of atmospheric pressure waves may be used to estimate both burst pressure (or preexplosion gas pressure) and gas concentration of ejecta for discrete, explosive eruptions. Recognition and analysis of such pressure signals may aid in the detection of explosive eruptions and subsequent ash plumes in remote areas.

The types of eruption signals recorded on microbarographs (Fig. 1, A to E) range from sharp N-shaped waves, such as that observed at the onset of the 1883 eruption at Krakatoa (5), to long-period oscillations, such as those recorded during the 15 June 1991 eruption at Mount Pinatubo (6). The spectral peaks associated with the latter type of disturbance have been interpreted as the characteristic periods of the acoustic and gravity modes of the atmosphere triggered by a continuous flux of thermal energy from a Plinian eruption (7-10). N-shaped waveforms are commonly associated with acoustic disturbances produced by discrete explosive eruptions (Fig. 1).

Within the past 25 years, a variety of numerical models have been used to estimate the burst pressures of vulcanian eruptions from observed maximum ejecta velocities (11–15). Early models based on the Bernoulli equation (11, 12) overestimated burst pressures by an order of magnitude because they neglected the compressibility of the gas phase (13) in the solid-gas mixture. In these and later models, the gas phase is H₂O, which makes up >90% by weight of total gas exsolved from magma situated at depths shallower than 3 to 4 km. More recent models have taken into account not only gas compressibility (13, 14) but also the relative motion of ejecta of variable sizes and the air through which the ejecta travel (15). In the most recent model (15), burst pressures were estimated as functions of gas concentration for a given travel distance, launch velocity, launch angle, and diameter of ejected fragments. Like the earlier models (11-13), this latter model was applied to the 1975 Ngauruhoe eruption, the classic example of a vulcanian eruption. Burst pressures ranging up to 10 MPa for gas concentrations of between 2 to 6 weight % H₂O were calculated for ejecta parameters measured in photographs. The accuracy of this model depends primarily on how well ejecta parameters are constrained. Here we introduce an alternative method for independently estimating the burst pressures and gas concentrations based on the wave-

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