

BINDING ENERGIES OF CH₄ AND H₂O-ICE SYSTEMS. R. M. Mastrapa^{1,2}, T. Cadarette³, and S. A. Sandford²
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Introduction: Previous results have shown that some volatile species have a higher surface binding energy to H₂O-ice than to themselves, [1-5]. In other words, materials such as CO and CO₂ “stick” to H₂O-ice for longer periods of time than they would “stick” to themselves. This means that these materials may be found stuck to H₂O-ice at temperatures higher than they would normally be stable. CH₄ is a simple organic compound that has been detected on Pluto and Kuiper Belt Objects on the edge of the Solar System. We performed a series of experiments to determine the surface binding energy of CH₄ to H₂O and to itself.

The Experiment: We completed measurements of binding energies of the following systems: CH₄-CH₄, CH₄-H₂O using a cryo-vacuum system and following the methods of Sandford and Allamandola [1, 2]. Briefly, for the CH₄-CH₄ measurements, we monitored the area of relevant infrared features with time at three different temperatures (<50 K) and used the results to estimate sublimation rates. For the mixture H₂O/CH₄ = 20, we carried out a series of experiments in which we deposited the mixtures at increasingly higher temperatures (starting at 15 K) until the infrared features of the more volatile component are no longer seen (usually at > 50 K). We then use the deposition rate of H₂O to estimate the residence time of the more volatile species (CH₄).

Results:

Pure CH₄. For the pure CH₄ experiments, we deposited CH₄ alone at 15 K. We then slowly heated the sample to 36, 37, or 39 K. We then monitored the area of the CH₄ features at 7.7 and 3.3 μm with time.

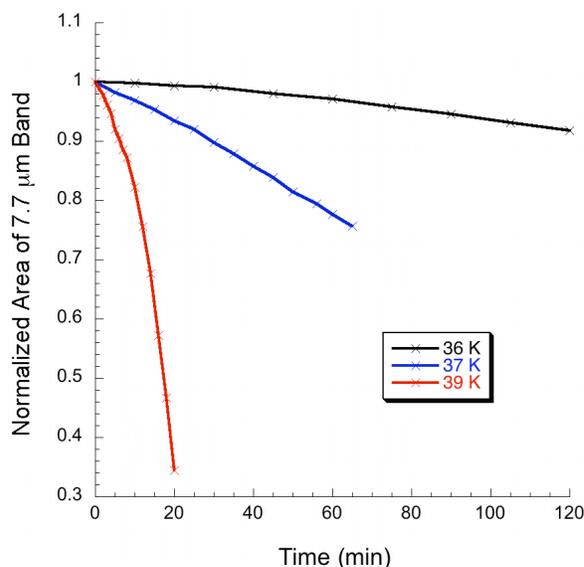


Figure 1 The area of the CH₄ feature at 7.7 μm with time at 36, 37, and 39 K.

H₂O/CH₄=20. We deposited the gas mixture of H₂O/CH₄=20 at a range of temperatures from 15 to 105 K. After each deposition we measured the areas of the H₂O and CH₄ features and noted how their abundance ratio changed with deposition temperature.

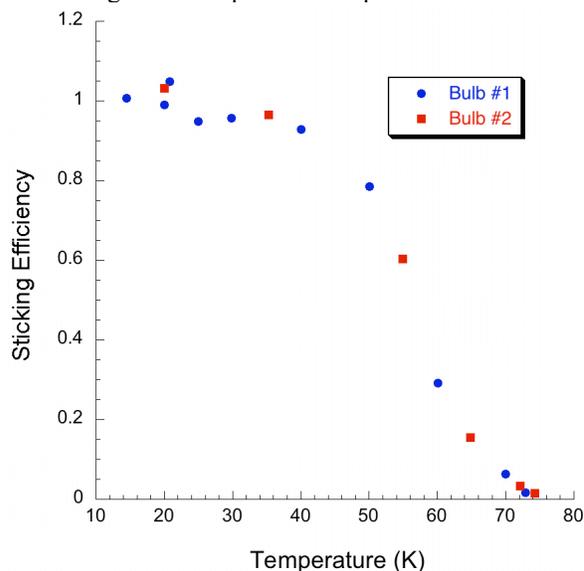


Figure 2 The sticking efficiency of the H₂O/CH₄ system with deposition temperature, calculated by taking the ratio of the molecular abundance of H₂O calculated from the 3 μm feature to that of CH₄

calculated from the 7.7 μm feature then normalized to 20. The scatter in the points at 20 K is from repeated experiments and represents the error in the measurement. The data are presented in circles and squares from two $\text{H}_2\text{O}/\text{CH}_4=20$ bulbs prepared separately and show good agreement.

CH₄ Residence Times: Note that the small change in binding energy, $\sim 750\text{K}$, results in a large difference in residence time. Not shown are the values at 10 K since they exceed the lifetime of the universe : $\text{CH}_4\text{-CH}_4$ $t = 10^{29}$ yr; $\text{CH}_4\text{-H}_2\text{O}$ $t = 10^{60}$ yr. However, the values quickly become relevant at 20 K where $\text{CH}_4\text{-CH}_4$ is stable for a mere 10^4 yr compared to $\text{CH}_4\text{-H}_2\text{O}$'s 10^{20} . These low temperature would be relevant to the interstellar medium and the outskirts of clouds and planetary disks. In the temperature range of Kuiper Belt Objects (40-60 K), the $\text{CH}_4\text{-H}_2\text{O}$ residence times are on the order of years to fractions of a year, while the $\text{CH}_4\text{-CH}_4$ stability is $10^5\text{-}10^8$ times shorter. The relative timescales approach within 10^4 years in the Saturnian system and 10^2 years for the Galilean satellites.

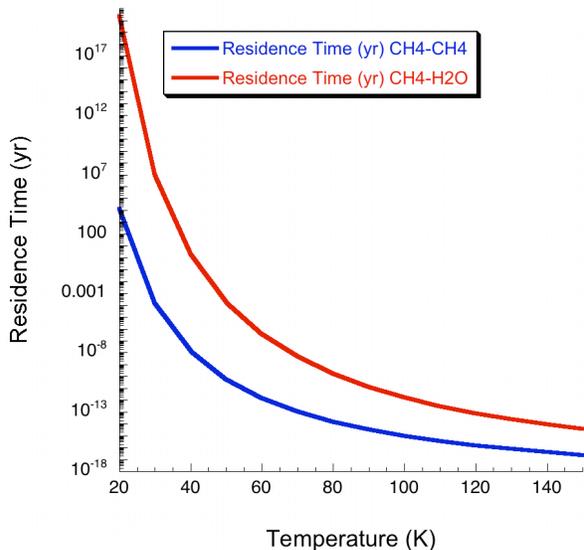


Figure 3 Residence time of CH₄ on CH₄ and CH₄ on H₂O in years. Calculated using the equation $t = \exp(\Delta H_s/kT)/\nu_0$ using values from the results and $\nu_0 = 2.0 \times 10^{12} \text{ s}^{-1}$.

Conclusions: The presence of solid H₂O greatly changes the residence time of CH₄ on the surface of objects in the Solar System. Since, H₂O-ice is ubiquitous on satellite surfaces, this greatly changes the possible distribution of CH₄. In other words, the “ice line” for CH₄ could be moved in closer to the sun. This also affects the stability of CH₄ in sub-nebulae that eventually formed the giant planets, depending on the interior temperature distribution.

One must use caution when considering these numbers, because they apply only to the residence time on the surface. It is therefore only applicable to surface condensations or sublimation. However, once the CH₄ is buried, it can be stable for even longer periods of time. Long term stability of CH₄ trapped in amorphous H₂O-ice or enclathrated in crystalline H₂O-ice is not well constrained, but is likely to be longer scale than the surface stability. These numbers must be integrated into atmospheric escape models to fully understand the stability of CH₄.

References:

- [1] Sandford S.A. and Allamandola L. (1990) *Icarus*, 87, p.
- [2] Sandford S.A. and Allamandola L. (1998) *Icarus*, 76, p. 201-224.
- [3] Sandford S.A., et al. (1988) *Astrophys. J.*, 329, p. 498-510.
- [4] Sandford S.A. and Allamandola L.J. (1993) *Astrophys. J.*, 417, p. 815-825.
- [5] Sandford S.A. and Allamandola L.J. (1993) *Icarus*, 106, p. 478.