Titan’s Interior: (I) A thermo-chemical assessment suggests $N_2$ is the dominate source of nitrogen near Titan’s surface; and (II) future studies on the effects of comet impacts on organic and surface chemistry.

W. M. Howard and S. Bastea
Extreme Chemistry Group
Lawrence Livermore National Laboratory

B. N. Khare and C. P. McKay
NASA Ames Research Center
Moffet Field, CA

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Use high-pressure chemical equilibrium models to predict the chemical interior of Titan

Moons of the solar system by size

Chemical equilibrium predicts $N_2$ is the dominant form of nitrogen near the surface and graphite (if not kinetically inhibited) maybe a dominant of carbon in the interior.
Use high-pressure chemical equilibrium models for Titan’s interior

- We use a high-pressure chemical equilibrium model to study the interior composition of Titan.
- We include a variety of CHNO molecules as well as metals to nickel and minerals and their oxides and a detailed carbon model.
- We use statistical-based thermo-chemical equilibrium calculations based on exp-6 fluid equations of state that are calibrated to both low and high pressures (~ 1 kbar to 1 Mbar) and low and high temperatures (~ 250K to 20000K).
- Multi-phase solids are modeled with a temperature-dependent Murnaghan form. (temperature-dependent heat capacities)
- Initial composition is taken as solar (Asplund, Grevesse and Sauval, 2006), except for depleted hydrogen as observed in comets (Delsemme, 1988).
- For the moment we do not include clathrates and some low temperature solids
We follow 80 species in chemical equilibrium, including multi-phase solids, via minimizing the Gibbs free energy.

- The following species were considered for the fluid phase: CH$_4$, H$_2$O, CO$_2$, N$_2$, SO$_2$, H$_2$, H, CO, NH$_3$, C$_2$H$_6$, CH$_2$O$_2$, C$_3$H$_8$, CH$_3$OH, C$_2$H$_4$, HCN, C$_2$H$_6$O, OC(CH$_3$)$_2$, C$_2$H$_2$, C$_6$H$_6$, C$_8$H$_{18}$, NO, C$_7$H$_{16}$, N$_2$O, Ni, Fe, Ni, O$_2$, O, Mg, N, NO$_2$, Ca, C, CaO, Si, SiO, SiO$_2$, Si$_2$, Si$_3$, S, CS$_2$, O$_3$, COS, S$_2$ and Al.

- The solids include, Mg$_2$SiO$_4$, SiO$_2$, Fe$_3$O$_4$, CaCO$_3$, Ni (solid, liquid), Al$_2$SiO$_5$, AlN (b1-solid, b4-solid), NiO, Al$_6$O$_{13}$Si$_2$, FeS$_2$, SiC, SiO$_2$, S(solid,liquid), CaO (liquid, b2, solid), Al$_2$O$_3$(liquid,solid), Al (liquid, solid), CaCO$_3$ (calcite, aragonite), FeO (solid,liquid), FeCO$_3$, Ca (liquid,beta,alpha), Fe$_2$O$_3$(solid-2, solid), FeS, MgAl$_2$O$_4$, S (solid,liquid), C (graphite, two phase liquid, diamond), Fe (liquid, solid), Fe$_3$O$_4$(solid-h), MgO(solid,liquid), FeO, Fe$_2$O$_3$ (solid,solid-2), Mg(solid,liquid), Si$_3$N$_4$, MgO (liquid), Si (liquid, solid-hcp,solid, solid-ii), and MgH$_2$O$_2$. 
Multi-phase and multi-species equations of state (EOS) are essential for modeling high pressure equilibrium.

![Shock Hugoniot of carbon](image1)

- Calculations
- Experiments

![Shock Hugoniot of synthetic Uranus](image2)

- Water, Methane & Ammonia

Diamond

Graphite
We replicate sound speeds for N\textsubscript{2} for pressures to 25 kbars and isotherms for NH\textsubscript{3} to 10 kbars.
We also replicate sound speed data for CH$_4$ to 35 kbars and isotherms for CO$_2$ to 10 kbars.
Assumptions in summary

1) Full chemical equilibrium
2) Ignore effects of chemical differentiation
3) Solar abundances except for depleted hydrogen
4) Do not account for clathrate formation and solid phases of some organic molecules. to be included in later studies
Chemical equilibrium as calculated at 7 kbars (~ 400 kms below surface) as a function of temperature.

\[ 2\text{H}_2\text{O} + 2 \text{graphite} \rightarrow \text{CH}_4 + \text{CO}_2 \]

Phase transition occurs at \( T \sim 450\text{K} \)

\( \text{H}_2\text{O}, \text{N}_2, \) and \( \text{CH}_4 \) dominate below \( T \sim 450\text{K} \)

\[ \text{NH}_3/\text{N}_2 \sim 0.02 \]
Chemical equilibrium as a function of pressure at $T = 300 \text{K}$ predicts $N_2$ dominant form of nitrogen below 20 kbars.

- CH$_4$, H$_2$O, CO$_2$ and N$_2$ dominate near the surface.
- CH$_4$ + CO$_2$ $\rightarrow$ 2 H$_2$O + 2 graphite phase transition occurs at 5 kbar.
- Ammonia only appears at higher pressures.
- 1.5 CH$_4$ + N$_2$ $\rightarrow$ 2NH$_3$ + 1.5 graphite phase transition occurs at 20 kbar.
Results with and without graphite formation predict $N_2$ is the dominant form of nitrogen near the surface.

$\text{CH}_4$, $\text{H}_2\text{O}$ and $\text{CO}_2$ dominate in the absence of graphite. Equilibrium $\text{NH}_3$ is suppressed at all pressures because $\text{CH}_4$ dominates hydrogen.
Benzene is a chemical equilibrium decomposition product of tholin \((C_4H_4N)\)

Tholins decompose to \(CH_4, N_2\) and graphite in equilibrium. If graphite is kinetically inhibited, then the products are benzene and molecular nitrogen, independent of pressure (dashed-lines)
Stability of a equal molar mixture of H₂O and NH₃ as a function of pressure (and temperature) without carbon.
$N_2/NH_3$ ratio is a function of C/N for pressures from 0.5 GPa to 2.0 GPa.

$N_2/NH_3$ ratio is a function of C/N for pressures from 0.5 GPa to 2.0 GPa.

$NH_3$ becomes unstable in the presence of carbon because the formation of $CH_4$ competes for $H_2$.
Implications for Titan’s atmosphere

- Stable form of nitrogen below a pressure 20 kbars is $N_2$
- A pure-ammonia-water ocean (in the absence of carbon) is stable in the interior of Titan
- However, if C/N ratio in the ocean exceeds unity ($C/N_{\text{solar}} = 4$) then ammonia is not stable and the stable form of nitrogen is $N_2$
- Cryovolcanism on Titan may be derived by $N_2$-gas exsolution in a primarily water mixture with negligible ammonia or from gases trapped in clathrates
- Tholins in Titan may decompose to benzene due to temperature and pressure enhanced kinetic effects
- Results may be applicable to Triton, the large moon of Neptune (radius 1350 km), but not to Enceladus, the tiny moon of Saturn (radius 250 km)
- Graphite may form in equilibrium at pressures above 5 kbars in Titan’s core
II. Organic chemistry during comet–ice impacts with equilibrium chemistry and hydrodynamics

Diamond anvil experiments for validating high-pressure models

Extreme chemistry modeling

Raman measurements for identifying chemical species
We will study the contributions of comet impacts to organic chemistry on Titan’s (and Earth’s) surface.

Hypotheses:

- Some comet material (ice and carbon) can be transformed into methane during a fireball collision and subsequent expansion as a vapor cloud.

  Use thermo chemical (chemical equilibrium) and hydrodynamic codes to model a comet impact sequence on the moon Titan and the earth.

- For interest of origin of life on earth, amino acids may be produced from comet material during comet impacts.
Methods (for a prototype model)

- We couple our high-pressure chemistry models with hydrodynamics to study comet impact (i.e., we follow the chemistry of the comet material assuming chemical equilibrium).
- We use the same statistical-based thermo-chemical model.
- We use Eulerian hydrodynamics to determine time histories of the pressure, temperature, and chemistry of the comet, while following multiple species (~30 to 40).
- We use a Steinberg-Guinin model the yield strength and shear modulus of the comet material and the impact surface.
Chemical equilibrium indicates CH$_4$ formation during impact

Comet impact creates a hot, dense fire ball, followed by a low-density hot vapor-cloud.
Example of equilibrium chemistry showing CH$_4$ appearing in expansion
Methane and carbon monoxide form in the subsequent comet impact vapor-cloud

Molecular abundances (by mass fraction) in comet vapor cloud
In the future we plan to study chemistry processes in high pressure comet impacts with non equilibrium chemistry

- Goldman et al. (Nature, 2010) have recently shown that it may be possible to construct glycine-containing complexes from comet material during high-pressure impacts.
- We can use our high pressure chemistry models, coupled with kinetic processes inferred from MD simulations, to follow the complex organic chemistry that may take place during high-pressure comet impacts.
- The following slide is from Goldman et al. (2010).

Goldman et al., Nature Chemistry, 2, 949-954, 2010

There is a postbox position available at Lawrence Livermore to continue this work.
We observe the formation of Glycine-CO$_2$ complexes from impacts of astrophysical ices.

Glycine-CO$_2$ complexes can react spontaneously with an H$^+$ source to form glycine:

\[
\text{Glycine-CO}_2 + \text{H}_3\text{O}^+ \rightarrow \text{Glycine (NH}_2\text{-CH}_2\text{-COOH)} + \Delta H = -24.2 \text{ kcal/mol}
\]
Summary

- Assuming chemical equilibrium, production of methane from comet impacts depends on the details of the freeze out and cooling of the hot vapor-cloud.
- This, in turns, depends on the details of the impact and the high-pressure and temperature chemistry at impact and chemistry of the expanding cloud.
- This is a prototype for a future study of organic chemistry process during comet impacts, using kinetic rates inferred from MD simulations.