INTRODUCING A NEW KIND OF GEOCHEMISTRY: THE THERMODYNAMICS OF CRYOGENIC FLUVIAL GEOCHEMISTRY ON TITAN.

C. R. Glein[1,2] and E. L. Shock[2,3], [1]Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC (cglein@ciw.edu), [2]School of Earth and Space Exploration, [3]Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ (Everett.Shock@asu.edu).

Introduction: The Cassini-Huygens mission has provided physical [1,2] and chemical [3,4] evidence for the presence of liquid hydrocarbons on the surface of Titan. This makes Titan the only body besides Earth where surface liquids are known to exist. Geomorphological observations show that liquids have physically modified Titan's surface [5], so it is natural to wonder whether liquids have also chemically altered the surface [6], in a manner analogous to aqueous geochemical processes on Earth and Mars. This leads to the following questions: (1) What are the compositions of liquids on Titan's surface? (2) What physical and chemical processes control liquid composition? (3) Can organic chemical evolution occur in cold hydrocarbon solvents? (4) What are the geological consequences of geochemical processes on Titan?

To help address these questions, we developed a model of phase equilibrium for liquefied natural gases on Titan [7]. The geochemical model can be used to predict the composition of liquids that are at equilibrium with Titan's atmosphere and minerals on the surface. It is useful to know what equilibrium looks like because it can serve as a reference point for understanding the geochemistry of natural systems.

Geochemical Model: The solubilities of gases and solids in liquids on Titan are predicted using standard-state fugacities, and the modified van Laar (MVL) model to calculate activity coefficients in the liquid mixture [7]. By convention, the standard states for solids and liquids (including supercooled liquids) are the pure phases at the temperature and pressure of the system, and that for gases is the ideal gas at the temperature of interest and 1 bar. The MVL model is rooted in regular solution theory [8], is mathematically simple, and can be extended to any number of components while maintaining thermodynamic consistency. The model uses a single adjustable parameter to account for non-ideal behavior in binary systems. Binary parameters are obtained by regressing experimental phase equilibrium data [e.g., 9]. Activity coefficients in multicomponent mixtures of nonpolar compounds are dominated by binary contributions, but the MVL model has the flexibility of allowing higher-order corrections to be included if ternary data are available.

Vapor-Liquid Equilibria: The solubilities of atmospheric gases in liquids on Titan are governed by vapor-liquid equilibria (VLE). To date, we have characterized VLE for all of the binaries in the CH_4-C_2H_6-C_3H_8-N_2 system. As an example, Fig. 1 shows that the

MVL model provides an accurate representation of experimental data for the CH_4-C_2H_6 system.
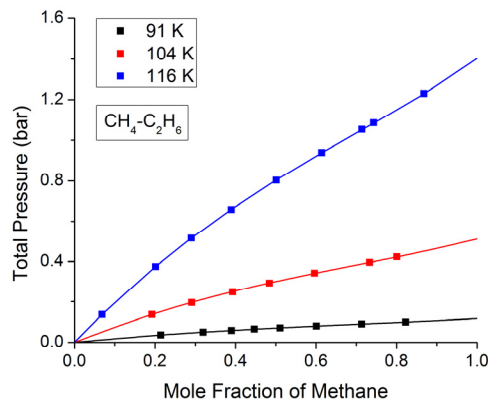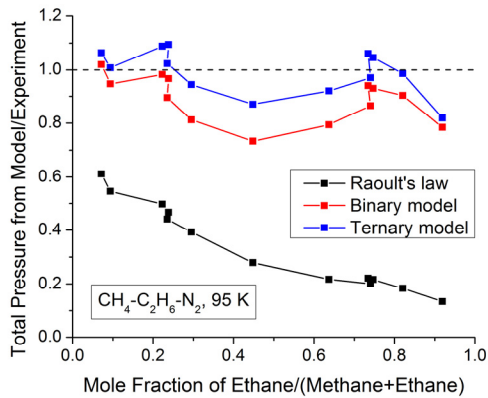

Fig. 1. Comparison of total pressures from the geochemical model (curves) to total pressures from experiments reported in the literature (symbols; see ref. 7) as a function of the composition of the liquid phase, for the CH_4-C_2H_6 binary at cryogenic conditions.

Model results for other binaries with CH_4 are also consistent with experimental data to within a few percent [7]. The MVL model shows greater but tolerable inconsistencies of ~10% for C_2H_6-N_2 and C_3H_8-N_2, because these systems exhibit substantial non-ideal behavior that is difficult to represent completely using a model with only one adjustable parameter.

It is vital to determine how well the geochemical model extrapolates to systems containing more than two components, such as liquids on Titan. Therefore, we used experimental VLE data for the CH_4-C_2H_6-N_2 ternary to test the model. Figure 2 shows that reasonably accurate results can be obtained using binary parameters alone. The results are much more accurate than those from Raoult's law, which demonstrates that this system is significantly non-ideal. Nevertheless, the accuracy of the MVL model can be improved to within ~10% of the experimental values if a ternary parameter is included (Fig. 2). Based on this analysis, we are confident that the geochemical model can be used to predict VLE on Titan with sufficient accuracy.

Solid-Liquid Equilibria: By analogy to Earth, minerals on Titan's surface may dissolve in liquids, leading to chemical weathering [6]. In arid regions, evaporation of the solvent may lead to the formation of evaporite deposits [10]. "Ore" deposits may form in

the subsurface if fluids are subjected to changes in physical or chemical conditions. Understanding how such processes might work on Titan requires knowledge of mineral solubilities in liquefied natural gases.

Fig. 2. Comparison of total pressures from models to experimental values [see 7] as a function of the C_2H_6 content of the liquid phase, for the CH_4-C_2H_6-N_2 ternary at 95 K. The dashed horizontal line indicates perfect agreement between model and experiment.

The MVL model is well-suited for computing the solubilities of solids in cryogenic fluids. As an example, Fig. 3 shows that the model accurately reproduces the measured solubilities of solid acetylene and benzene in liquid CH_4 to within ~10%. Both of these compounds have been detected on Titan's surface [11,12]. The dramatically different solubilities of acetylene and benzene imply that these compounds will exhibit different geochemical behaviors on Titan. The solubility of acetylene in liquid CH_4 at 91 K (67 ppm) is similar to that of calcite in groundwaters on Earth (~10^2 ppm). This suggests that the geochemical behavior of acetylene on Titan may be analogous to that of calcite on Earth [7]. Thus, dissolution of acetylene may lead to the formation of karst [13], if sufficiently thick deposits of acetylene-rich rocks exist on Titan. Conversely, the very low solubility of benzene in liquid CH_4 (e.g., 0.4 ppm at 91 K) suggests that grains of solid benzene may be resistant to dissolution erosion on Titan. It is striking that benzene is less soluble in liquid CH_4 than is quartz in surface waters on Earth (11 ppm at 298 K). This comparison raises the possibility of benzene beaches on the coasts of Titan's lakes and seas [2].

A key unknown is the concentration of C_2H_6 in the liquids [4]. The MVL model indicates that solid acetylene and benzene are ~10^2 times more soluble in liquid C_2H_6 than in CH_4. C_2H_6 on Titan is evidently the geochemical analogue of acid on Earth, since both substances can greatly increase mineral solubilities [7].
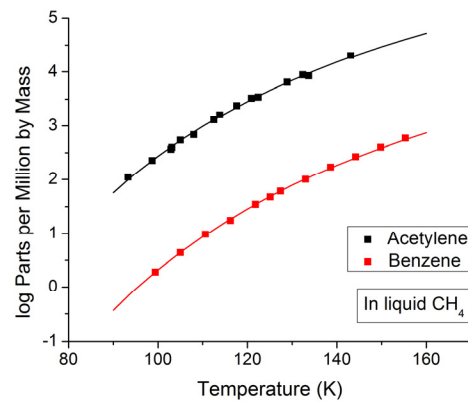
Fig. 3. Comparison of solid solubilities in liquid CH_4 from the geochemical model (curves) to solid solubilities from experiments reported in the literature (symbols; see ref. 7) as a function of temperature.

Conclusions: We developed a thermodynamic model for predicting equilibrium between solids, liquids, and gases on Titan [7]. The model is easy-to-use and consistent with available experimental data. We now have a framework for assessing hypotheses on the fluvial geochemistry of Titan in a quantitative manner. Potential applications of the geochemical model are numerous, and include studies of the composition of Titan's lakes, karst and evaporite formation, fluid mixing, cementation of sedimentary rocks, bioenergetics of weird life, and the development of soil horizons. A key concept is that the geochemistry of exotic materials on Titan can be understood by combining model results with knowledge of the geochemical behavior of analogous materials on Earth. Further progress in this area will require additional experimental data, such as solubilities in liquid CH_4, C_2H_6, and their mixtures.

References: [1] Tomasko M. G. et al. (2005) *Nature*, 438, 765-778. [2] Stofan E. R. et al. (2007) *Nature*, 445, 61-64. [3] Niemann H. B. et al. (2005) *Nature*, 438, 779-784. [4] Brown R. H. et al. (2008) *Nature*, 454, 607-610. [5] Lorenz R. D. et al. (2008) *Planet. Space Sci.*, 56, 1132-1144. [6] Lorenz R. D. & Lunine J. I. (1996) *Icarus*, 122, 79-91. [7] Glein C. R. & Shock E. L. (2013) *Geochim. Cosmochim. Acta*, in review. [8] Hildebrand J. H. & Scott R. L. (1950) *The Solubility of Nonelectrolytes*, Reinhold Publ. Corp., New York. [9] Hiza M. J. et al. (1979) *J. Phys. Chem. Ref. Data*, 8, 799-816. [10] Barnes J. W. et al. (2011) *Icarus*, 216, 136-140. [11] Clark R. N. et al. (2010) *J. Geophys. Res.*, 115, E10005. [12] Niemann H. B. et al. (2010) *J. Geophys. Res.*, 115, E12006. [13] Mitchell K. L. et al. (2008) *LPS XXXIX*, #2170.