CHARACTERIZING PHASE TRANSITIONS FOR TITAN'S SURFACE MOLECULES: IMPLICATIONS FOR DRAMS AND *DRAGONFLY*. I. Madan[1], M. G. Trainer[2], G. C. Collins[1], K. K. Farnsworth[2]., K. Zacny[3]. [1]Wheaton College, Norton MA, [2]NASA Goddard Space Flight Center, Greenbelt MD, [3]Honeybee Robotics, Altadena CA.

Introduction: Part of NASA's New Frontiers Program, *Dragonfly* is a rotorcraft lander mission designed to assess Titan's potential prebiotic chemistry at various locations [1]. Two of the main scientific goals of the *Dragonfly* mission are to identify chemical components and potential processes responsible for the production of biologically relevant compounds, and to search for potential biosignatures. *Dragonfly's* Mass Spectrometer (DraMS) is a linear ion trap mass spectrometer that will measure the molecular composition of the acquired surface samples to address these mission goals [2].

There may be regions of Titan's surface in which the sampled materials have a large component of molecules that are sensitive to phase changes within the expected range of the sample handling chain, 94 - 165 K. A large abundance of such materials may therefore impact the capture efficiency and physical properties of the sampled materials within the system. In this work, we explore the potential for induced phase transitions of some of the most abundant organic molecules during the end-to-end sampling process.

DraMS works in conjunction with the Drill for Acquisition of Complex Organics (DrACO) system that acquires and delivers solid samples for analysis. While the surface temperature of Titan is around 94 K, the interior of the lander is held closer to 273 K. DrACO utilizes one of the two redundant drills to generate fines that are pneumatically transferred to the sample collection cups with the help of Titan's thick atmosphere (1.5 bar) [1, 3]. During this transport, the materials are held within ~10 K of Titan's ambient temperature to minimize phase changes. After the pneumatic transfer, the sample cups are moved around a Sample Delivery Carousel from which they can be delivered into one of the two ports for DraMS sample analysis. The two ports correspond to: Laser Desorption Mass Spectrometry (LDMS), broadly identifying solid sample composition, and Gas Chromatography Mass Spectrometry (GCMS), separating and identifying key prebiotic species and potential enantiomers [2]. As the instrument ports are within the enclosed space of the lander, there will be a temperature rise after the sample is captured in the cup and manipulated within the carousel region. The requirement is for samples to be kept below 165 K in order to preserve bulk ice samples and the medium- to high-molecular weight molecules of importance to the scientific investigation.

For the LDMS mode, the sample undergoes a series of steps that involve temperature and pressure changes. The following represents expected pressure and temperature conditions for a point design of the sampling process. Step 1 is the drilling process, during which there is an approximate limit of 10 K increase in temperature (95 K → 105 K). Step 2 is the transport process, during which there is a nominal pressure drop in the pneumatic system (1.5 bar → 1.40 (± 0.03) bar) which is then restored when the sample is delivered to the cup. Step 3 is the isobaric warming of the sample tray/spoon raising the temperature by ~60 K (105 K → 165K). Step 4 is the evacuation of the LDMS chamber which drops the pressure by ~1.46 bar (1.5 bar → 0.04 bar) [Depicted in Figure 1]. The sample is then maintained at these pressure and temperature conditions during the duration of the LDMS analysis.

Methods: Constructing Phase Diagrams. Using fundamental constants and the Clausius-Clapeyron relationship, we constructed phase diagrams for small and volatile species to track the possible phase transitions as samples are collected and analyzed by DrACO and DraMS. The fundamental constants included solid density, liquid density, molar mass, enthalpies of vaporization, fusion, and sublimation, triple point (temperature and pressure), and critical point temperature [4, 5]. Though, there were some constants missing in literature.

The Clausius-Clapeyron relationship characterizes discontinuous phase transition, allowing us to estimate vapor pressures at varying temperatures:

$$ln(\frac{P1}{P2}) = \frac{\Delta Hvap}{R}(\frac{1}{T2} - \frac{1}{T1}) \quad (1),$$

where P_2 was substituted with the triple point pressure and T_2 was substituted with the triple point temperature. $\Delta Hvap$ is the enthalpy of vaporization and R is the gas constant. Equation 1 was rearranged to solve for P_1 as a function of T_1:

$$P1 = Pt \cdot e^{((\frac{\Delta Hvap}{R})\cdot(\frac{1}{Tt} - \frac{1}{T1}))} \quad (2),$$

where Pt is the triple point pressure and Tt is the triple point temperature. $\Delta Hvap$ was used in Eq. 2 when characterizing the vaporization (liquid → gas). To characterize the sublimation (solid → gas), $\Delta Hvap$ in Eq. 2 was replaced by the enthalpy of sublimation

($\Delta Hsub$). To characterize melting (solid → liquid), $\Delta Hvap$ was replaced by enthalpy of fusion ($\Delta Hfus$).

Phase diagrams were constructed for the molecules listed in Table 1. Titan likely houses an inventory of these small and volatile molecules as measured by past missions and simulations [6, 7]. Since most of the listed molecules lacked concrete literature values for their solid density, a constant value of 0.125 g/cm^3 was added to the liquid densities to estimate the solid density. The position of the solid-liquid line was not sensitive to the assumed density.

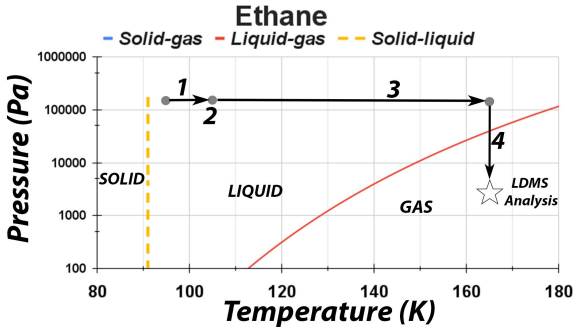

Figure 1. Example Phase Diagram: Ethane. The numbers correspond to the steps of the sample collection and transport process.

Results and Discussion: Different molecules experience phase changes during different steps of the sample collection process, largely as a function of chemical class and molecular weight. Methane, butane, isobutane, pentane, isopentane, and formaldehyde are predicted to experience a phase transition during step 3, the isobaric warming of the sample cup. Ethane, acetylene, and carbon dioxide are predicted to experience a phase transition during step 4, evacuation of the LDMS chamber.

Ethene experiences two phase transitions: the first during the isobaric warming (step 3) and the second during the evacuation of the LDMS chamber (step 4). Methane, ethane, ethene, acetylene, and carbon dioxide will likely transition into their gaseous phase during the end-to-end sampling process. Butane, isobutane, pentane, isopentane, and formaldehyde will likely transition into their liquid state during the end-to-end sampling process. No phase transitions are expected for propane, propene, benzene, toluene, hydrogen cyanide, acetonitrile, and water. Propane and propene will likely remain in their liquid state while benzene, toluene hydrogen cyanide, acetonitrile, and water will likely remain in the solid state after the sample collection and transfer process.

Conclusion: The process of assembling information from the literature to construct these phase diagrams has highlighted knowledge gaps about many molecules in Table 1 under Titan conditions. Understanding which potential phase transitions in DraMS sample handling are most sensitive to unknown molecular constants will help to prioritize future laboratory measurements. Other recommended future work could examine the interactions of mixtures of these molecules, as the phase diagrams in this study only examined the behavior of single compounds.

Table 1. Molecules and their expected phase change from initial to final state.

Molecule	M.W. (g/mol)	Expected Phase Change
Methane (CH_4)	16.04	Liquid → Gas
Ethane (C_2H_6)	30.07	Liquid → Gas
Ethene (C_2H_4)	28.05	Solid → Liquid Liquid → Gas
Acetylene (C_2H_2)	26.04	Solid → Gas
Propane (C_3H_8)	44.1	Remains as Liquid
Propene (C_3H_6)	42.08	Remains as Liquid
Butane (n-C_4H_{10})	58.12	Solid → Liquid
Isobutane (iso-C_4H_{10})	58.12	Solid → Liquid
Pentane (n-C_5H_{12})	72.15	Solid → Liquid
Isopentane (iso-C_5H_{12})	72.15	Solid → Liquid
Benzene (C_6H_6)	78.11	Remains as Solid
Toluene (C_7H_8)	92.14	Remains as Solid
Hydrogen Cyanide (HCN)	27.02	Remains as Solid
Acetonitrile (CH_3CN)	41.05	Remains as Solid
Formaldehyde (CH_2O)	30.03	Solid → Liquid
Carbon Dioxide (CO_2)	44.01	Solid → Gas
Water (H_2O)	18.02	Remains as Solid

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