

CRYOSTABILIZED PROPELLANT ADDITIVES

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Abstract

There exists a set of normally unstable materials that can be cryogenically stabilized and used for the purposes of propulsion to provide revolutionary improvements in propulsive efficiency. The criteria for selection and formation of cryostabilized additives (CSAs) is described. Paths to the production of these CSAs may include 1) the formation of atmospheric pressure van der Waals compounds, 2) the capture and stabilization of radical species, and 3) techniques to concentrate or separate the CSAs. These routes to CSA production are described in general and for specific cases. The van der Waals compound H_2Ne_2 is described, together with its fabrication. The production and storage of HO_2 is described. Specific techniques for separation and concentration of CSAs are described. The benefits and use of CSAs in combination with standard propellants are discussed.

Cryostabilized Additives

The hypothesis of this ongoing effort is that there exists a set of materials that are unstable at room temperature but which can be stabilized cryogenically to create high value, novel, propellant enhancers. These additives provide revolutionary improvements in propulsive efficiency. The characteristics of these cryostabilized additives (CSAs) can be defined and potential candidates identified. A critical element for the fabrication of CSAs is the path between its created state and its cryostabilized state. Specific paths to the scientific and engineering production of CSAs that are being investigated and described below include 1) the formation of room temperature van der Waals compounds, 2) production of cryostabilized radical species, and 3) techniques to concentrate or separate CSAs. This publication is not a review of previous relevant work, and focuses on experimental rather than theoretical or computational approaches. Analytical experimental techniques for determining material properties, while critical, will not be discussed.

The overall objective of the effort is to establish experimental results that demonstrate or disprove the validity of each of the CSA production paths for a specific case as follows. For the CSA production path of forming a room temperature van der Waals compound, the specific objective will be to form H_2Ne_2 . For the production path of choosing a radical species as a CSA, HO_2 will be formed and stably stored. For the production path of CSA concentration, the technique of

cryogenic sublimation concentration will be demonstrated. The most obvious host materials for CSA propellants are O_2 and H_2 , but any propellant material can be cooled to cryogenic temperatures - typically below 100 K - to provide stabilization.

The two primary classes of CSAs are those that are stable at cryogenic temperatures at 100% concentration, defined as CSA100s, and those that can only be stabilized at a lesser concentration. CSA100s are most easily formed and stabilized. An example of a CSA100 is an O_2/H_2 mixture at 10 K. Typical CSA densities for energetic fuel enhancement are on the order of 10 mole %¹; a catalytic CSA may be useful in significantly lower concentrations.

CSA Stability A stable material at a specified temperature is defined as a material that will not spontaneously change state in response to its thermal environment. A metastable material (MM) is one that does not change state over some reasonably long period, but does eventually change state. For CSAs, a CAMM99, or Commercially Applicable MMs is defined as a material with 99% of its original CSA concentration over a period of 3×10^6 s (1 month); a usable propellant material. LAMM50s are stable to at least 50% concentration over 3×10^4 s (10 hrs) and useful for Laboratory Applications. LDMM are stable over 3×10^2 s for easy Laboratory Diagnosis. ADMM are stable over 3×10^2 s for easy Laboratory Diagnosis.

A common misconception is that CSAs cannot exist in useful concentrations because the probability of two reactive atoms being adjacent approaches unity as the reactive atom fraction in the host material approaches 10%¹. When diffusion processes, particularly diffusion along grain boundaries, are taken into account, the estimated limiting concentration falls to 1-2%; work in radical trapping within solid matrices imply limiting concentrations of less than 1%.

This only applies for species that have a zero potential barrier to reaction along the spatial coordinate between the molecules. There are a number of species (including radicals) of interest that have non-zero but small potential energy barriers to reaction. There are a smaller set of CSAs with potential barriers only in specific directions; these might be stabilized in an external field or a van der Waals compound.

Detailed investigation of complex reaction potential energy surfaces is a modern science, although binary potential work is extensive (e.g. the H_2 potential²). Compilations exist for a variety of element pairs in their ground state (e.g.³ for alkali-inert pairs). The difficult problem in solid state compounds is to

define and model the many-body and long range effects. Here, self reaction barriers are of importance. These barriers, as others, arise from both molecular geometry effects, reaction intermediates, electron configuration effects, and others.

One can define approximately the needed potential energy barrier height. Energy stability in the solid phase is quite different from that in the gas phase because there is no high-energy tail of the vibration distribution to initiate reactions. The energy cutoff is $k\Theta_D$, where k is the Boltzmann constant (10^{-16} erg/K) and Θ_D is the Debye temperature of the solid. For Ne this energy is 6×10^{-15} ergs or 0.004 eV, so species with this reaction barrier height will presumably be CSA100s in this host. This is about a factor of 1000 below the normal chemical heat release/enthalpy difference between common reacting species; relatively small reaction barriers become important.

CSA Formation Given the generic reactivity /instability of the species that are potential CSAs stability issues are secondary to formation issues. Theoretically stable CSAs may have no path to their formation, since they cannot be formed in situ in the cold solid matrix. Aside from the problem of reaction due to natural concentration fluctuations, there is the problem that during the process of high concentration deposition the addition of the reactive species to the solid leads to reaction as a result of the energetic interaction between molecules being added and those in the solid. This can occur both in the gas phase and in the accretion layer on the surface of the solid.

Candidate CSA Materials. There are a wide variety of materials that can be chosen for deposition into a solid matrix. These materials fall into number of different classes according to the type of van der Waals solid crystal structure that is formed by the mixture. The important characteristics of the CSA species are its size/radius relative to the size of a matrix molecule, its outer electronic structure, and whether the activation energy for self reaction is zero, or significantly greater than zero. The CSA can form an interstitial impurity as small atoms in a large atom/molecule matrix, it can form a substitutional impurity for CSA and matrix species of comparable size, or it can be an impurity that displaces a significant number of matrix molecules in the lattice. Attention is usually focused on the light atom group Li, B, Be, and C because these isolated atoms provide a very high heat release upon combustion; light atoms are energetically favored for propulsion. Most, if not all, of these species have zero reaction barrier energy.

The Host Matrix This discussion will concentrate on H_2 and to a lesser extent O_2 and the case where a matrix is necessary for the formation of the CSA. The discussion here is necessarily condensed.

Solid H_2 has been chosen as the primary initial host matrix because: 1) it is the most well known of the

cryogenic solids with a simple, spherically symmetric molecule, with a single, simple phase, 2) it has been and can be theoretically described to a much greater degree than other cryogenic solids, 3) knowledge gained of its properties is likely to have fundamental importance for physical chemistry, 4) it is a common, simple, standard propellant.

Para H_2 is a quantum solid with significant zero-point energy where anharmonic effects in the lattice dynamics have increased beyond the treatment of perturbation theory. Although H_2 and Ne have similar σ and ϵ parameters, an H_2 molecule is significantly larger than a Ne atom.

The engineering properties of solid cryogenic H_2 has been compiled⁴ in contrast to standard thermodynamic properties⁵. From this point on the term solid H_2 is assumed to refer to pure para- H_2 . Experimentally, standard catalysts convert normal H_2 to para- H_2 .

Diffusion processes in the lattice control whether a CSA atom/molecule will move to and react with another CSA atom/molecule. In all cases, since the impurity is much more massive than the H_2 molecules in the lattice, its fundamental diffusion rate is much lower. However the much more mobile H_2 molecules can move around it and provide an additional driving force for its motion through the lattice.

Solid H_2 Surfaces Experiments involved with deposition on solid H_2 surfaces consider that at temperatures above 3 K, there is a high mobility H_2 layer on surface of the solid⁶. This means that true gas-to-solid deposition on H_2 can only take place at temperatures below 3 K. At higher temperatures there is a build-up of a smooth, homogeneous film up to a limiting thickness d_l of 3 to 4 monolayers, beyond which the condensing molecules aggregate to form bulk crystallites (Stranski-Krastanov growth). H_2 mixtures will thus normally produce pure crystallites of the depositing species at temperatures over about 3 K. Since the wetting behavior is determined by a delicate competition between adsorbate-adsorbate and adsorbate-substrate forces, it is probable that some substrates will exhibit complete wetting even below the triple point temperature, including perhaps more complex, multilayer systems.

Solid Behavior The diffusion rate of species within a cryogenic matrix or compound is not well known in general. Assuming the basic classical diffusion law $D = D_0 \exp(-E_D/k_B T)$, for self-diffusion, D_0 values are estimated to be 3×10^{-3} for H_2 and 4×10^{-4} for D, with activation energies E_D/k_B of about 200 K⁷ at zero pressure. This would imply $D(4 K) = 6 \times 10^{-25}$ cm²/s. At low temperatures quantum diffusion (tunneling) leads to much high actual diffusion rates; $D(H_2) = 2 \times 10^{-6} e^{-112/T}$, so that $D(H_2, 4 K) = 1.4 \times 10^{-18}$ cm²/s. The absolute numbers are very small; quantum diffusion is difficult to measure experimentally. For

planar diffusion from 100% concentration into a semi-infinite body at 4 K, the concentration would reach 50% 1 nm away in 2 hours. Diffusion proper is quite different from short-range relaxation, which is also called reclusterization or configurational relaxation. Microscopic concentration differences smooth out in a macroscopically homogeneous mixture.

The case of more interest is that of a larger species than H₂ moving toward another of its kind as a result of attractive forces between these two atoms. In this case the heavier and larger molecules must essentially plow through a mass of H₂ molecules, and the diffusion rate would be expected to be much slower than the movement of light and small H₂ molecules. Diffusion in practical materials is strongly dependent on lattice imperfections - vacancies and a variety of structural imperfections. Impurities in solid H₂ are thought to have important effects on the nearest neighbor sphere of surrounding H₂s. The displacement of nearest neighbor shells would be expected to have major effects on solids with high impurity concentrations, but these effects would be very different in a regular crystal compound.

Vacancies in solid H₂ are equilibrium lattice defects and their concentration is unambiguously determined by temperature and pressure. At the triple point (T = 13.81 K) of H₂ the concentration of vacancies is from 0.1 - 0.01 %, decreasing rapidly with decreasing temperature. Dislocations and packing defects are the main defects in single crystals and polycrystalline samples (with respectively large grains) of pure H₂. The density of dislocations can be decreased from 10¹⁰ cm⁻² to values as low as 10² - 10³ cm⁻² in well annealed samples⁸. One would thus expect diffusion in solid H₂ to be strongly dependent on the history and preparation of the sample.

The O₂ Host Solid O₂ exhibits a number of unusual solid behaviors associated with the molecule's magnetic field. There are major solid phase changes versus temperature with associated changes in diffusion and major changes in specific volume. The strength # and thus solid binding forces increase with decreasing temperature with significant asymmetries in the crystal lattice. This implies that there will be significant energy and reactivity differences with the lattice position of the CSA.

Atmospheric van der Waals Compounds

The creation of vdW compounds allows the formation of a stable crystal with high relative concentrations of separated species, and it allows the formation of this crystal at low temperature with low kinetic /thermal energy species. The existence of vdW compounds has been conclusively demonstrated at high pressures⁹, and various stability arguments and experimental data imply that these or related

compounds can be created at pressures on the order of 1 atm or less, at least in a long-term metastable form.

van der Waals Crystal Compounds A significant number of binary vdW compounds have been found to exist experimentally at high pressure. The list includes Ne(He)₂, A(H₂)₂, CH₄(H₂)_x, N₂-CH₄ system, and He(N₂)₁₁. Their crystal structure can also be plausibly predicted based on free energy calculations and by hard shell packing models¹⁰.

Van der Waals Epitaxy. Van der Waals epitaxy has only been investigated relatively recently¹¹ and has since lapsed. Epitaxial crystals can be deposited with large lattice mismatches compared with the few per cent typical of standard epitaxial growth. Critical to this process is the creation of substrates without dangling bonds. Such surfaces are usually created using planar materials that can easily be cleaved, or ionic materials. There seems to have been almost no previous work done on epitaxial growth of cryogenic crystals.

Crystal Packing The intermolecular interactions of vdW compounds, mixtures, and impurities with vdW solids are by definition small compared with those of common materials; the approximate binding energy¹² of an H₂-H₂ cryogenic dimer is 2.9 cm⁻¹ compared with the binding energy of H₂ itself - 104 kcal/mole, or 36,400 cm⁻¹. Since interactions between vdW molecules during solidification remain unchanged except for small perturbations, these interactions can be treated for some purposes as interactions between spheres whose size is determined by some consistent measure of the size of the molecule/atom. In assigning a size, quantum species have a size larger than that implied by their potential energy as a result of the effect of the zero-energy vibrations of the molecules.

The fact that high-pressure vdW compounds are often of the AB₂ stoichiometry with a Laves phase crystal structure is often explained as a natural consequence of the packing stability of a binary mixture with a certain relative species size (close to 1.2), using as a reference metal lattice formation¹⁰. In general, sphere packing has been shown to generate both simple and highly complex structures. Some (AB₁₃) are formed purely as a result of entropy-driven formation, rather than by free energy minimization. The most commonly found AB₂ structure is made up of alternating hexagonal layers of the small and large particles. The large spheres (A) form close packed layers aligning directly above each other along the c axis while the small spheres (B) occupy trigonal prismatic sites between these layers and form planar hexagonal rings. This structure would be appropriate for epitaxial growth. It should be noted that this structure is not the structure of high pressure vdW compounds found experimentally. X-ray results¹³ show these to be a closely related Laves phase structure. General packing investigations¹⁴ imply that the

diameter ratios (d_A/d_B) need to be in the range 0.5 - 0.8, with possible islands of stability at higher d_A/d_B . Larger d_A/d_B leads to a random alloy with fcc structure. Packing arguments provide a partial guide to the effects of adding impurities to a vdW solid.

Once H_2 has been chosen as the host matrix, the choice of a compounding species is critical, and should be one that leads to a combination of the highest chance of experimental success with the most general application. Ideally the chosen species would be highly reactive, capable of 1) stabilization and 2) implantation, and easily diagnosable. To date no highly reactive species been found that can be combined with H_2 in high concentrations. The experimental complications of using a reactive species are formidable. Reactive species have very complex vdW interactions, both short range and long range, probably only a few specific compounds are viable. A first effort has been dedicated to creating a low pressure vdW compound based on species related to those formed at high pressure.

Given the goal of creating a H_2X vdW compound, where X is an inert species, one must assess which species is most likely to lead to successful compound formation. X must behave as a vdW species, which means that it must have self-reaction and H_2 reaction activation energies that are greater than the thermal and quantum mechanical activation energies it encounters. Some atomic species are thus excluded. For example C reacts with H without a barrier, whereas B forms a vdW complex with H_2 because significant energy is required¹⁵ to form H-B-H, the stable product of B and H_2 . Finding which species have $E_{act} > 0$ is difficult because the relevant reaction energy surfaces are often 3-D, reaction intermediates are not well known, and reactions in general have not been studied at low temperatures. The noble gases such as Ne, Ar, and Xe, as well as the common cryogenic gases N_2 , CO_2 , CO, and CH_4 are more obvious candidates for initial experiments. These materials form vdW compounds naturally only at high pressures, indicating that crystallization from a liquid mixture will not lead to low pressure equilibrium compounds.

The concept that will be investigated in this work is to use vapor phase deposition to form the crystal. In this case (meta)stable crystals could be formed either through epitaxial growth on a substrate, or as a result of configurational relaxation from a more amorphous, but compositionally identical solid mixture. To perform epitaxial growth of a crystal with weak bonds or a locally uniform amorphous mixture using vapor phase deposition, the vapor molecules should be deposited at as low a temperature with as narrow a thermal dispersion as possible. This also minimizes the temperature rise of the solidifying substrate, since the heat release is smaller during condensation. Minimizing heat release is very important for the deposition cryogenic solids, as a result of their poor

solid thermal conductivity. The gas (aside from He and H_2) with the lowest condensation temperature and lowest heat of solidification (by far) is Ne.

Neon has a number of other advantages for this purpose. Its molecular volume is small enough relative to H_2 that it falls in the proper range of relative species sizes to form a Laves phase crystal¹⁶ of the form $H_2(Ne)_2$ similar to the vdW compounds formed at high pressure. Ne can also be considered an isotopic impurity in H_2 with very similar Leonard Jones potential parameters; the species size difference occurs mostly as a result of the large zero point energy of H_2 . H_2 is a quantum solid, whereas quantum effects in Ne are much smaller. Ne has the added advantage (for this approach) that it is not soluble with H_2 to a significant degree either as a liquid or as a solid¹⁷. For this reason partial solid mixtures that might obscure the detection of the vdW compound are very unlikely to occur, as opposed to the alternate possibilities. Furthermore, H_2/Ne mixtures have been extensively studied and characterized.

Crystal Structure and Stability. The existence of high pressure vdW compounds implies the stability of a related $H_2(Ne)_2$ compound. Such Laves phase compounds form when the size ratios of the component species are near 1.20^{10,14}. The hcp lattice spacing of H_2 is $a_0 = 3.76$ Å, which is also the effective molecular diameter in a hcp lattice, whereas the spacing of Ne at 16 K is $a_0 = 4.88$ Å¹⁶. Like related rare gas solids, Ne is a solid with the fcc structure, so that its effective atomic diameter is $4.88/\sqrt{2} = 3.17$, and the H_2/Ne effective diameter ratio is about 1.19. The σ parameters for H_2 and Ne potentials are 2.96 and 2.79⁷ respectively to give a ratio of 1.06; the reduced molar volume¹⁸ of H_2 relative to Ne resulting from quantum effects implies a further size factor of 1.09 to give a ratio of 1.16, which is consistent with the relative lattice parameters. Since the proposed H_2Ne_2 structure arises from alternating layers of larger (H_2) and smaller (Ne) species, there should be a number of ways to create this (meta)stable lattice using gas phase deposition. The compound cannot be formed from the liquids because they are not miscible at low pressure, or by deposition onto the H_2 solid above 3 K as a result of the liquid layer on its surface. H_2/Ne is designated by its probable stoichiometry: H_2Ne_2 .

The general reason that H_2Ne_2 has not been created previously is that there is no simple or natural dynamic route to its formation. Ne is not soluble in H_2 to any significant extent, preventing the solid solution route. Most previous experimental work has also been done at temperatures higher than 3 K, so the mobile surface layer prevents the formation of H_2Ne_2 via condensation from the gas. There is also a narrow concentration range for stable formation of the H_2Ne_2 crystal such that the small concentrations of a H_2Ne_2 crystal that may have been created are very difficult to

detect.

Material Properties. The basic description of the postulated H_2Ne_2 crystal is that of a fcc or hcp crystal with alternating layers of light and heavy species. The complexity of the crystal description in terms of its detailed properties arises from the quantum mechanical behavior of the H_2 molecules. Ne is a closed shell atom, with negligible dipole or higher order moments. H_2 molecules, even with their inherent nuclear asymmetry, have a nearly spherical potential surface. H_2 also has significant electronegativity. The material is expected to be highly sensitive to impurities; the effect of Ne isotopes is unclear. Macroscopic properties of the crystal such as specific heat and thermal conductivity can be measured, and microscopic properties such as optical properties can be measured using only a thin layer of the crystal or micro crystals spread throughout a solid. As a result of the delocalized nature of the electron structure of H_2 , a H_2Ne_2 crystal will have some very unusual electronic and optical properties.

A generic experimental problem that must be overcome is the deposition of species at low temperature. In the past implanted species had high energy (furnace vapors, laser ablation, nozzle expansion).

The approach will center on van der Waals epitaxial growth using vapor deposition, based on experiments using an existing Janis Supertran VP cryostat. This is a standard liquid He cryostat that controls sample temperature down to liquid He temperatures. Temperatures below 4 K can be achieved in this cryostat by pumping on the liquid He in its reservoir. Opposed optical access to the sample is provided from two orthogonal directions.

Apparatus A schematic of the crystal growth cell to be used for this work is shown in Fig. 1. It consists of an axial tube supplying H_2 , Ne, or mixtures with a tip directed toward a substrate, a thermally insulating deposition cell with a rotatable attachment fixture to the cryostat sample holder, windows (sapphire or beryllium) in the cell, temperature sensors, and a substrate if necessary for the epitaxial growth process. Sapphire windows provide optical access to the film; Be windows will be used for x-ray studies.

Gas Phase Deposition There seem to be three basic possibilities for forming a H_2Ne_2 crystal: alternating deposition of monolayers of H_2 and Ne, epitaxial growth of H_2Ne_2 on a substrate that facilitates its growth, or deposition of a 1/2 stoichiometric gas mixture of a H_2 and Ne onto the solid followed by high temperature annealing or plastic deformation plus annealing. In all cases the deposition must take place below 3 K to avoid separation of the pure substances in on the solid H_2 surface. The goal is to achieve a solid structure that forms as H_2Ne_2 or a

closely related structure that relaxes H_2Ne_2 .

The most common route to add atoms to solid H_2 has been to implant them from thermal sources, and rely on the low diffusivity in H_2 to create a stable matrix. This works well for low concentrations and can be used for studying the properties of these isolated atoms¹⁹. At concentrations approaching 1% implantation fails because the high thermal energy tracks of the implanted atoms intersect with atoms already implanted and reactions result from the energy of the newly implanted atom, a fundamental limitation of all related techniques.

The achievement of a stable crystal structure will be achieved by relaxation of a slightly more energetic, slightly amorphous solid structure into a regular crystal compound. The experimental task will be to find a viable route for this process. There are a number of crystal structures that could be formed; three closely related Laves phases are possible¹⁴. The lowest energy structure of these¹⁶ has alternating layers of small and large species, where the small species forms in hexagonal rings without the center atom that would make the layer close packed. This is the structure that lends itself to the alternating species monolayer approach. The structure that forms from the liquid mixture at high pressure in the Argon/ H_2 system is yet another, more complex and slightly higher energy

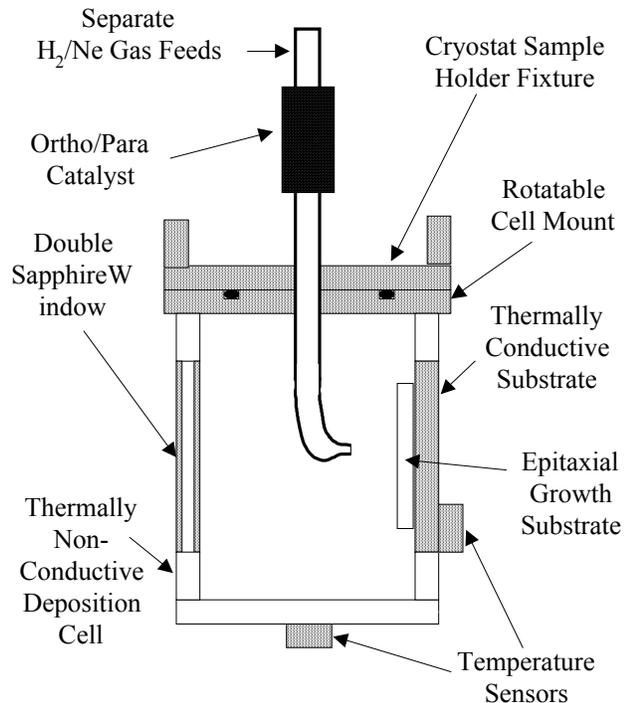


Figure 1. van der Waals condensation apparatus.

structure. It is not clear and not explained why this structure forms in preference to the lower energy alternating layer structure.

The proper condensation rate will depend on the

thermal conductivity, k , of the deposited material. For solid para- H_2 , k is near its maximum of 1.5 W/cm-K at 3K, and decreases with Ne content⁷. Assuming a sublimation heat release of 89 K/molecule and $k = 1.5$ W/cm-K, a 1 mm thick layer maintaining 3 K at its surface and 2.5 K at its rear cooled surface could support a deposition rate of 0.3 moles/cm²-s and a film growth rate of 7 cm/s; the actual deposition rate will be much lower. Related experiments²⁰ report that a deposition rate of about 10^{-5} mol/cm²-min of oxygen leads to snow formation.

The dewetting phenomenon prohibits the use of temperature induced reorganization of thin films. Growth conditions must cause the species to rearrange or arrange in an ordered lattice, rather than randomly stick to the surface. This may be done by depositing a layer of H_2 that preferentially locates at half of the H_2Ne lattice sites, then adding Ne to fill up the other lattice sites to complete a full layer of the H_2Ne crystal. The initial layer would presumably be guided by the properties of the substrate. Plastic deformation can perturb the crystal structure for improved stability.

The successful formation of a H_2Ne_2 crystal using van der Waals epitaxy may depend on finding a suitable deposition substrate. Silicon and sapphire are inappropriate due to their small atomic spacing. A pure single-crystal of H_2 is another material that will be tried, certainly for the alternating H_2/Ne monolayer approach, since the spacing between H_2 and Ne sites is expected to be on the order of 3.5 Å. Covalently bound substances have too small an interatomic distance. Ionically bound materials appear to be the best candidates. LiI has a 3.5 Å spacing for a bcc lattice. CsF would be another, similar candidate. Since H_2 has a negative electron affinity and is larger than Ne, then CsF would probably be a better choice, where the larger H_2 would be attracted to the positive Cs ion.

Cryostabilized Radicals

Radicals are generally thought to be unstable, but they may be metastable at cryogenic temperatures. They normally exist in low concentrations on short time scales, and are most typically observed in combustion environments where they occur as integral steps in the combustion process. Optical diagnosis of radicals is now common, as is their mass spectroscopy.

Among important radicals there are many candidates that may be appropriate for large-scale generation and cryogenic storage. Extensive research on stabilized free radicals was performed in the 1950s²¹ to overcome the fundamental problem of premature radical recombination and energy release as the stored radical number density is increased and the unstable atoms/molecules come close enough for their electron shells to overlap and reaction to occur. The difficulty lies in finding a radical that can both be produced in

relatively large amounts and then be stabilized cryogenically. The HO_2 radical is believed to be such a cryogenically stable radical.

The hydrogen-oxygen system has been the subject of many investigations by diverse methods. There are only nine known neutral chemical entities in this system: H , H_2 , O , OH , H_2O , O_2 , HO_2 , H_2O_2 , and O_3 . The oxygen-containing radicals O , OH , and HO_2 may be destroyed by single, or perhaps only a few, collisions with the walls of an ion source generating them. This does not imply that these radicals are intrinsically much more reactive than organic free radicals, only that metal surfaces comprising the ion-source electrode structure are excellent catalysts for the destruction of simple oxygen-containing radicals.

The hydroperoxo (HO_2) radical, an important intermediate in theories of oxidation, combustion, and explosions, has been investigated by mass spectrometry, optical spectroscopy, microwave spectroscopy, and electron spin resonance. HO_2 radicals are typically present in relatively significant concentrations in hydrocarbon processes involving oxidation steps. The main reason for this relative abundance is that the diffusion controlled

$H + O_2 \rightarrow HO_2$ reaction is very fast relative to its rate of decay in recombination: $2 HO_2 \rightarrow H-O-O-O-O-H \rightarrow H_2O_2 + O_2$ and H-abstraction: $HO_2 + RH \rightarrow H_2O_2 + R$. A technique has already been developed and achieved production of relatively high concentrations of HO_2 in a simple apparatus²². The goal is to create and store a stable radical that can be used as a fuel additive to enhance chemical propulsion.

The current effort includes 1) defining the fundamentals of the HO_2 chemical generation process, 2) defining the advantages of the HO_2 additive and amounts/concentrations needed to make it a useful CSA, 3) designing experiments to generate and store it, 4) performing the relevant experiments, and 5) designing a large-scale manufacturing process.

Reactions For Production of HO_2 The principal mechanisms for producing HO_2 radicals²² can be divided into two classes: (1) addition reactions, $H+O_2+M \rightarrow HO_2+M$ and $OH+O+M \rightarrow HO_2+M$, and (2) bimolecular abstraction reactions, Such as $OH+H_2O_2 \rightarrow HO_2+H_2O$, $CH_4+O_2 \rightarrow CH_3+HO_2$, etc. The requirement of a third body M to remove excess energy in an addition reaction makes this process relatively inefficient at low gas pressures. Bimolecular abstraction reactions are not limited by the requirement of a third body, and can be employed for the production of HO_2 in homogeneous gas phase reactions at low pressures. The latter case is favored for the detection and analysis of a radical by mass spectrometry.

A number of reactions readily produce hydroperoxo radicals: (i) reaction of H atoms with O_2 , (ii) reaction of H atoms with H_2O_2 , (iii) reaction of O atoms with H_2O_2 , (v) reaction of OH radicals with H_2O_2 ;

(v) ultraviolet photolysis of H_2O_2 , and (vi) electrical discharge in H_2O_2 . These various routes have already been surveyed²³.

HO₂ Production from Hydrogen Peroxide. When hydroxyl radicals, produced by an intense electrical discharge in H_2O or H_2O_2 , are mixed with H_2O_2 it is found that the OH radicals were very quickly destroyed. The production of HO₂ radicals is comparable to the amount of OH destroyed²³. These observations are consistent with the generation of HO₂ radicals by the reaction: $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$. The maximum concentration of HO₂ obtained by this method was about 0.3%, which is a few hundredfold higher than obtained in the reaction of H with O₂.

Photolysis of H₂O₂. The production of HO₂ by photodecomposition of H_2O_2 was expected since the primary photolytic step is $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}$, and the reaction of OH with H_2O_2 to form HO₂ had been established. In this experiment, the reactor was a Vycor tube 3.4 cm in diameter through which H_2O_2 at a pressure of 0.4 mm Hg flowed at a speed of 100 cm/sec. Small concentrations of HO₂ were obtained at the mass spectrometer, located 30 cm (0.3 sec) downstream, when a 15W GE mercury resonance lamp placed parallel to the Vycor tube was excited with about 300 w of 6 MHz RF power²². The photolytic method probably would be more suitable to higher-pressure experiments, in which case more of the UV radiation would be absorbed by the gas.

Low-Power Electrical Discharge in H₂O₂. A confined low-power glow discharge in a rapidly flowing stream of H_2O_2 vapor was found to be an excellent source of HO₂ radicals. The electrodeless discharge used for this purpose restricted the discharge to a small volume, eliminated the possibility of decomposition at electrodes, and permitted the position of the discharge to be easily changed.

The apparatus consisted of a Pyrex or quartz tube with two aluminum or wire loop electrodes wrapped around the tube, spaced 1 cm apart and connected to an RF generator. Substantial quantities of HO₂ radical are produced at power levels of the order of 1 W in the discharge. It is essential to be able to operate the discharge at low power levels in order to avoid completely decomposing the H_2O_2 .

The yield of HO₂ as a function of H_2O_2 decomposition in a 1 cm diameter tube reaches a maximum of 0.4% 3 ms after passing through the discharge at a corresponding decomposition fraction of 17%²². The gas velocity was about 1250 cm/s. The HO₂ radical concentrations were computed from measurements taken near the ionization threshold assuming an ionization cross section of HO₂ halfway between O₂ and H_2O_2 . The production of HO₂ is relatively insensitive to H_2O_2 decomposition over the range of 5% to 40% decomposition, changing by less than a factor of 2. The data was taken at 0.003 s and

0.006 s after the gas passed through the discharge by placing the electrodes at the corresponding distance from the molecular beam entrance aperture. OH was not observed at 0.003 s for H_2O_2 decomposition less than 60%, and at 0.006 s the OH produced at 80% decomposition had been completely destroyed. This indicates how fast OH reacts with H_2O_2 . Assuming that the principal radical constituent in the discharge is OH which then reacts with H_2O_2 to produce HO₂, the lack of OH at 0.003 s for low decomposition % implies a lower limit of 4×10^{-13} cm³/molecule-s for the rate constant of the reaction $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$. Oxygen atoms formed in the discharge are considerably less reactive than OH, as is evident from their persistence for times in excess of 0.006 s.

From the mass spectrometric standpoint, the low-power electrical discharge in H_2O_2 is an exceptional source of HO₂ because very little O₂ is produced in the reaction so that interference at mass 33 from the O¹⁶O¹⁷ isotope is virtually absent. The usual condition of operation was 5-10% decomposition of H_2O_2 , representing a compromise between loss of H_2O_2 and generation of HO₂. This also applies to any large-scale mass-spec type of separation process.

Assessment of HO₂ Production Mechanisms. An assessment of the various non-ionic techniques to produce HO₂ has already been performed²³. Based on this work, the initial effort will use an RF discharge technique as the primary experimental method to generate HO₂ radicals, and further testing of the photolysis route will be done. Various ionic routes and devices will also be studied as a result of the ease of separation of charged species.

Properties of H₂O₂ H_2O_2 , hydrogen peroxide, is a stable, widely used and inexpensive chemical; all of its major properties are well known [H2O2.com web site]. The H_2O_2 molecule is shown in Fig. 2, where the steric angles shown are $\theta(\text{H-O-O angle}) = 95^\circ \pm 2^\circ$, and $\phi(\text{Dihedral angle}) = 120^\circ \pm 3^\circ$. It is a liquid at room temperature, with density of 1.45 g/ml and a significant vapor pressure. H_2O_2 freezes at -9°C and boils at 160°C . Its room temperature vapor pressure is about 200 Pa, or 2 torr.

Properties of HO₂ Whereas the thermo-dynamical data on H_2O_2 is easy to find, the same can not be said for the kinetic data, especially concerning its reaction to form HO₂. The ionization potential and relevant thermochemical energies of HO₂ have been measured²³ and a variety of thermodynamic data are available from current databases (e.g. NIST). The NIST database also provides data on the ion reactions that lead to the formation of HO₂. Of course, there is no data on the properties of bulk HO₂. The HO₂ radical is planar, and the extra electron tends to be associated with the O₂ dimer.

H₂O₂/HO₂ Reaction Kinetics. The kinetics of some of the primary reactions associated with H_2O_2

formation and destruction are known, but cannot be compiled here. For the recombination reaction $2\text{HO}_2 \Rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ the rate constant is $\log_{10}k = 12.25$ at room temperature²⁴.

HO₂ Self Reaction Barrier The critical issue for HO₂ metastability is the existence of significant potential energy barrier to self-reaction. Such a barrier has not previously been found, either theoretically or experimentally, due to the difficulty of both efforts.

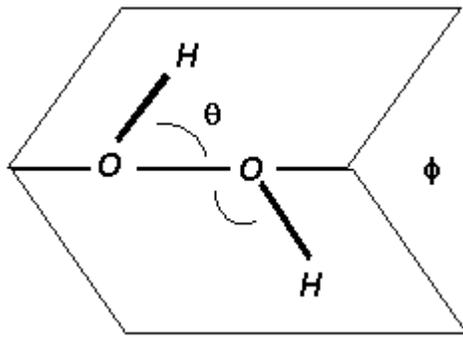


Figure 2. H₂O₂ molecular geometry.

That it exists is strongly suggested both by the slow rate constant and the geometry of the molecule and its reaction

intermediate, H-O-O-O-O-H.

Experiments. The goal of experimental design is twofold: to generate and store HO₂ stably, and to separate HO₂ from its H₂O₂ precursor so that it can be stored in high concentrations. The most important effort is to demonstrate the long-term stability of HO₂. The basic technique is to generate the HO₂ in a weak plasma discharge and expand the radical-laden gas to impinge on a cryocooled surface²⁵.

The apparatus is shown in Fig. 3. The reaction products will be cooled and captured by particles passing through the discharge. The reaction products can be easily accumulated and concentrated for engineering production.

The primary species collected will be H₂O₂, with a small fraction of HO₂ present. Frozen N₂ or Argon droplet will be used to quench and capture the H₂O₂/HO₂ mixture. The condensed material will form as a snow that can then be collected (it may float or sink) that can then be collected and examined optically; its presence and concentration will be immediately identified by its IR signature.

Separation Design. Separation of the HO₂ from the H₂O₂ is more difficult. One way to do the separation is to ionize the gas mixture using a low energy electron beam, then expansion-cool the HO₂ radicals in the H₂O₂ carrier gas. Once the charged gas is expanded and cooled it enters an ion drift chamber. The drift chamber is configured with electrodes that create a divergent electric field that forces the charged HO₂ particles to move relative to the H₂O₂ molecules as a result of their different ion mobilities. A cross-flow of cold helium would sweep the H₂O₂ molecules out of the drift chamber before they reached the liquid

cryogen collection location. A film of concentrated HO₂ molecules would condense on the liquid cryogen and could be collected by draining the liquid. The design of this apparatus is under development at Thoughtventions.

HO₂ Value. The primary benefit of a HO₂ CSA would probably be to catalyze an oxidation reaction. The other benefit would be in added heat release of the reaction. A fuel of H₂O₂ with a significant of HO₂ fraction may be very valuable.

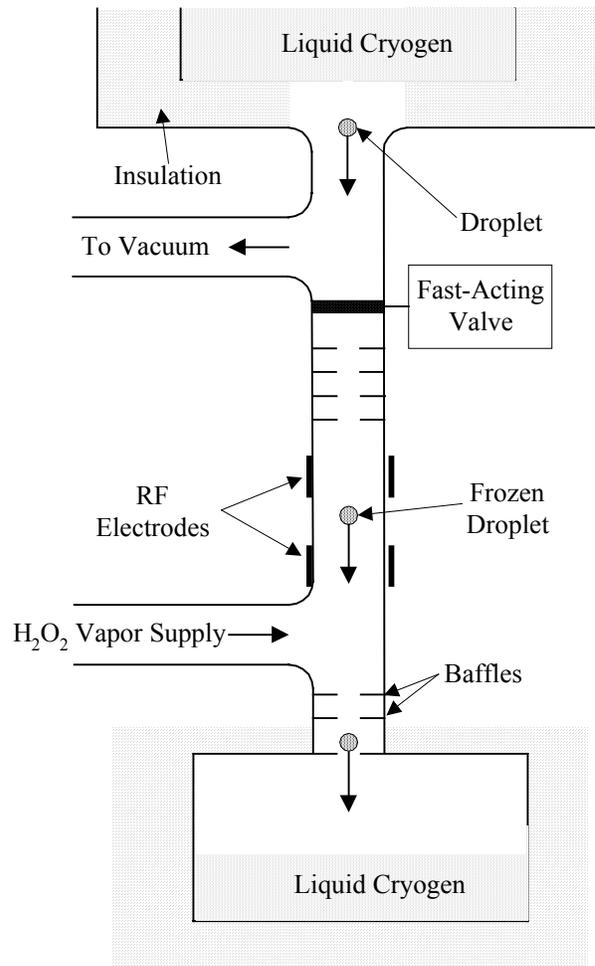


Figure 3. Schematic of apparatus to be used to generate, capture and stably store HO₂.

CSA Sublimation Concentration

Sublimation concentration refers to the process by which a condensed van der Waals gas that provides a matrix for a CSA can be sublimed to concentrate the CSA. The essential advantage of this process is that the CSA is stabilized chemically against thermal reaction by the low temperature of the matrix, and it is stabilized geometrically by being trapped in the matrix, preventing contact reaction with itself or other nearby CSAs. The advantage of sublimation concentration is

that the CSA can be captured by relatively high temperature processes at concentrations low enough that it does not come in contact with any species but the matrix and is prevented from reacting at the elevated temperatures by this isolation. Once captured and stabilized in the matrix at a low concentration, its concentration can be increased to a level that provides a CSA/matrix that is useful as an engineering material. In general, CSAs can be diluted by energy-limited mixing or concentrated (Table 1) by removing the matrix or solvent material.

To demonstrate the practicality of sublimation, a worst- case of CSA sublimation concentration was examined; the case of a solid matrix of H₂ at 3 K. The parameters associated with the sublimation of solid H₂ are reasonably well known. Solid H₂ has a vapor pressure of 5×10^{-11} torr at 3.0 K⁵, so the sublimation of H₂ at this temperature would require a vacuum pumping system that supplies this level of vacuum. A 10^{-11} torr vacuum can be and has often been achieved with care using a hard-sealed vacuum system and either a cryopump, a cryosorption pump, an ion pump, or a variety of gettering techniques. An external vacuum pump must supply a base pressure of about 1×10^{-11} torr to provide the sublimation pumping. A simpler technique is to use local cryosorption pumping or to use the chamber walls as high speed cryopumps by keeping them at 3 K.

In order to practically concentrate a widely dispersed CSA in H₂, enough lattice layers of solid H₂ must be removed to greatly increase the surface concentration of the CSA. If, for instance, the CSA is present in volume concentrations on the order of 0.1%, there will be one CSA atom/molecule for every 1000 H₂ molecules, assuming that the CSA specie is not large compared with the H₂ molecule. This also means that there is one CSA atom/molecule somewhere in each cubic volume of H₂ that has 10 H₂ molecules on a side. To achieve CSA densities on the order of 10%¹ needed for fuel enhancement, concentration by a factor of 50 would be required. To create a 5% concentration surface layer from a material with a 0.1% volume concentration would require the removal of 55 lattice layers on average. Each 10 molecule layer set that was sublimed would bring 1 CSA molecule to a 10×10 H₂ molecule area at the surface.

Assume, laboratory experiments, that a circular surface film of H₂ 5 mm in diameter is grown. This film has an area of about 0.2 cm². The effective cubic lattice spacing for H₂ is about 3.5×10^{-8} cm. This can be deduced from the density of solid H₂ of 0.088 g/cm³, which implies a volume density of $0.088/(3.3 \times 10^{-24})$ molecules/cm³ or 2.5×10^{22} H₂/cm³, and a lattice

spacing as estimated. This lattice spacing is also consistent with the hcp Van der Waals radius for H₂ of 1.9 Å. A surface area of 0.2 cm² thus contains about 1.7×10^{14} H₂s in each lattice layer. The time taken to sublime 50 lattice layers and concentrate the impurity is then determined by the pumping rate, or, in the case of cryopumping, by the heat absorbed in the cryosurfaces.

In the case of cryopumping, higher pumping speeds are possible even at very low pressure, only limited by the surface area that can be cooled to below 3 K. It will be better to use cryopumping because there is greater flexibility in temperature; a cryopanel at 2 K can provide a potential base pressure in H₂ of 4×10^{-18} torr, which is unattainable in real systems with small vacuum leaks. Taking the heat of sublimation of H₂ to

Table 1.		Assessment of possible concentration techniques.		
		Concentration Technique		
CSA Stability	Sublime	Evaporate	Liquid Phase Separation	Gas Phase Separation
Stable, in a host	Yes	Yes	Yes	Yes
CAMM99	Probable	Possible	Possible	Yes
LAMM50	Possible	Possible	Possible	Yes
LDMM	Unlikely	Unlikely	Unlikely	Yes
ADMM	No	No	No	Yes

be 240 cal/mole, a heat input of 4×10^{-22} cal per H₂ molecule is required. For each lattice layer considered above, 1.2×10^{-10} cal/s is required for sublimation. The heat of vaporization of LHe at 3 K is 22 cal/mole, so 10 times as many molecules of helium must be vaporized to provide the cooling to condense each H₂ molecule. In the present case the amounts are very small, since the total amount of H₂ sublimed is small. It is easy to provide a pumping surface 100 times as great as the surface area of the H₂. Another factor to be considered in cryopumping is the thermal shielding effect of the condensed gas on the metal cryopump surface. Solid H₂ has a low thermal conductivity, so pumping speeds become limited by the rate at which heat can be removed through the H₂ to maintain its temperature. Again, this is not a problem for the proposed experiment since the volume of H₂ sublimed is small and the surfaces are large - no thick layer is built up to hamper the pumping process.

Assuming that the cell is used as a cryopump, one can estimate the time to perform a concentration experiment. The sample surface is 5 mm diameter; a cryopumping area 100 times larger would consist of a 4×4 cm area, somewhat smaller than the cell internal surface area. Assuming the deposited sample to be about 100 lattice layers thick, or 200 Å, implies only a 1 Å layer of H₂ condensed on the cell. The thermal diffusivity of solid para-H₂, α_{H_2} is 8.25 cm²/sec, such that temperature equilibrium (90% T) in a 100 Å thick layer would be reached in a time, t, such that $x/[2(\alpha_{H_2}t)^{0.5}] = 1$, or $t = x^2/16$ seconds, where x is in cm.

This implies that the surface of the cryopumped H₂ reaches 2.5 K very rapidly; the experiment time will be determined by the time it takes to cool the helium bath from 3 K to 2.5 K by pumping on it. This will probably be on the order of 30 min, given the vacuum setup. It is expected that a typical sublimation concentration process will take on the order of 30 min, not limited by the fundamentals of the process and an overall test, including deposition, will probably take a few hours.

Further consideration of the sublimation process at the surface implies that a much higher sublimation temperature can be used in the case of H₂. The key is to be sure that the material loss rate from the surface is high enough that the any liquid layer that forms on the surface does not have sufficient time to provide mobility to the CSA species at the surface of the solid. This mobility should be small, given the small mass of the H₂ molecules compared with the CSA. The practical sublimation temperature should be a much higher temperature than 3 K. The approximate temperature will be calculated as a subtask and measured in experiments.

Experimental Design Experimental demonstration uses a cryochamber that 1) will allow the appropriate base pressure to be achieved, 2) can be liquid helium cooled to below 3 K, 3) will provide a highly thermally conductive, optically transparent mount on which films of solid cryomatrix can be grown, 4) will include a means for codepositing a CSA or CSA analog as the solid CSA/matrix film is grown, and 5) will provide a means for providing optical access to measure sublimation concentration.

A Janis Supertran VP optical standard cryostat will be for used for this research. A schematic of the proposed deposition test cell is shown in Fig. 3. It consists of a catalyzed low temperature (25 K) H₂ gas supply, a thermal CSA atom source, and an optical cell with an attachment fixture to the cryostat sample holder. The optical cell consists of a relatively low thermal conductivity metal shell with two sapphire windows brazed in opposite walls. Sapphire is an ideal substrate for deposition. It has the extremely high thermal conductivity at low temperatures (better than copper) and a wide transparency bandwidth (UV to mid-IR) for spectroscopic sample inspection. The cell attachment plate will be sealed to the cryostat sample heater with a high vacuum indium seal to prevent He from getting into the cell. The sapphire windows have a widely spaced heating coil attached to their inner surfaces. There are temperature sensors on the bottom of the cell and the substrate window for sensing the temperature of deposition and sublimation.

The H₂ gas passes through a cold bed of catalyst particles for conversion to para-H₂ using commercial ultrapure gas cylinders. The H₂ gas jet will be pointed onto the substrate from above and the thermal CSA source (flash vaporization) from below to avoid

interfering with the optical access to the sample. Deposition of the sample can be done in multiple steps at much higher temperatures than that at which the sublimation concentration takes place. Concentrations of the CSA will be low enough to avoid reactions nearer the melting point of H₂, but still high enough to be successfully concentrated by sublimation. For H₂ sublimation the sample substrate will be held at 3.0 K, and cryopumping the H₂ onto the rest of the cell surface. The sample substrate will be warmed slightly by a resistance heater to provide the 3 K temperature, while the remainder of the cell is immersed in LHe at temperatures of 2.5 K or below. The sublimation can be initiated or stopped by heating the substrate. Substrate temperature is kept uniform by the very high thermal conductivity of the sapphire. Due to the relatively low thermal diffusivity of cryogenic van der Waals solids care must be taken that the solid does not further cool so that sublimation effectively ceases.

Concentration Diagnostics. There are four basic techniques that are used to probe cryosolid matrix/CSA crystals: spectroscopy, electron diffraction, x-ray diffraction, and calorimetry. Electron diffraction is appropriate when the equipment is available and the X-ray response of the CSA differs significantly from any host that is also present; H₂ has a small scattering power. XAFS can be used to examine nearest neighbor characteristics and is more widely available. Matrix isolation spectroscopy studies of impurities in H₂ and other matrices has a long and detailed history²⁶.

Sublimation Concentration Engineering The process of sublimation concentration is basically a surface process. The use of surface processes for large-volume production is common in the chemical/materials processing industry. As a start-up process, 1 m³ of the propellant would be produced in a minimum time on the order of a week. This also implies that a volume of about 50 m³ of solid must be pumped away for low initial CSA concentrations. Deposition of the film is rapid; pumping away the solid matrix molecules to concentrate the film is the rate limiting process. Ten apparatuses operating during a week (6 x 10⁵ s) implies a volume rate of 10⁻⁵ m³/s, or 10 cm³/s of the solid must be carried away. Again, assuming a worst case, for H₂, with a lattice spacing of about 3 x 10⁻⁸ cm, there are about 3 x 10²² molecules/cm³, and 10²⁵ molecules/s must be evaporated. Based on a standard evaporation rate $r_{\#}$, the rate of evaporation in molecules or atoms per cm²-s, $\text{Log } r_{\#} = 19.5458 - \log P_{\mu} - 0.5 \log (MT)$, where, P_{μ} is the pressure in microns, M is the gram-molecular weight, and T is the temperature (K). For a drum 1 m long and 1 m in diameter, the area evaporating is about 1 m² = 10⁴ cm², so a vaporization rate of an average of about 10²² molecules/cm²-s is required. This implies a vapor pressure on the order of 100 microns and a temperature of between 7 and 8 K. For O₂ this vapor

pressure occurs at about 45 K, 10 K below its melting point. This approach appears to be practical.

Conclusions

There exists a set of normally unstable materials that can be cryogenically stabilized and used for the purposes of propulsion to provide revolutionary improvements in propulsive efficiency. The criteria for selection of cryostabilized additives (CSAs) depends on the concentration needed, the stability of the solid, and the self-reaction barrier of the CSA. The introduction of a CSAs into a host matrix is the critical step, requiring low energy processes for concentrated CSAs, especially on accretion surface layers as the multispecies solid is formed. Paths to the production of CSAs that are appear feasible and that are currently under investigation include 1) the formation of atmospheric pressure van der Waals compounds, 2) the capture and stabilization of radical species, and 3) techniques to concentrate or separate the CSAs. These routes to CSA production are being explored for the specific cases of the van der Waals compound H_2Ne_2 , the production and storage of the HO_2 radical, and for the separation and concentration of CSA's by sublimation. Realized on an engineering scale, CSA's are expected to create revolutionary new propellants.

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