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Manufacture and Deflagration of an Atomic Hydrogen Propellant

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It is observed that the use of very low temperatures (in the range 0.1°K to 1.5°K) produced by advanced cryogenic apparatus and the use of very strong magnetic fields (in the range 50 kG to 100 kG) produced by superconducting magnets can yield a significant improvement in the atomic hydrogen trapping effectiveness of an H_2 matrix. The use of a radioactive β-ray emitter isotope may yield H-H_2 propellants (with $I_{sp} \cong 740$ sec) by secondary electron impact dissociations of H_2 in an impregnated matrix maintained below 1°K in a strong magnetic field. Another method for manufacturing an H-H_2 propellant involves bombardment of supercooled solid H_2 with a cyclotron-produced beam of 10 Mev hydrogen atoms. The matrix-isolated atomic hydrogen must be used directly without prior melting as a solid propellant, and an analysis of the steady deflagration is presented.

I. Introduction

CONSIDERABLE interest has been attached to the research and development of an atomic hydrogen fuel for use as a rocket propellant, because markedly superior performance is predicted theoretically for such a propellant. It is well-known that the maximum for specific impulse with the best conventional chemical propellants is in the neighborhood of 500 sec. On the other hand, values for the theoretical specific impulse in the neighborhood and above 750 sec are predicted if it is possible to employ an atomic hydrogen propellant which contains at least 15% free H atoms by weight. Such a 50% increase in specific impulse would engender a dramatic concomitant increase in payload and a decrease in the number of stages in space vehicles.[5,35]

Free hydrogen atoms are known to be produced by a large variety of physical and chemical molecular dissociation reactions. Except under rather special conditions, however, atomic hydrogen cannot be produced in high concentrations and/or in large amounts, as required for propellant manufacture. Moreover, for the storage of free H atoms only one effective method is known, the so-called *matrix-isolation* technique in which the reactive species are trapped as isolated entities in an inert solid at a cryogenic temperature. Atomic hydrogen produced in a gas or liquid must be rapidly condensed and trapped by being frozen into normal or interstitial sites in an inert cryogenic lattice, while immediate storage of the species may be afforded by so-called in situ production methods which involve dissociation processes that take place exclusively within a preformed matrix.

A review of current experimental work related to the manufacture of an atomic hydrogen propellant is presented in Sec. II, where the two main technical aids now being employed to achieve higher concentrations of free H atoms with matrix-isolation, the use of very low temperatures and very strong magnetic fields, are described. It is shown that important progress toward the development of an atomic hydrogen propellant appears imminent with conventional methods of production and storage being augmented by these new technical aids. In Secs. III and IV it is observed that the manufacture of an H-H_2 propellant, 15% atomic hydrogen by weight, appears feasible by ultra-energetic hydrogen atom bombardment of solid H_2 or by impregnation of solid H_2 with radioactive phosphorus. The theoretical estimates given in Sec. V show that matrix-isolated atomic hydrogen must be used directly without prior melting as a solid propellant. Finally, the steady deflagration of an H-H_2 solid propellant, 15% atomic hydrogen by weight, is analyzed in Sec. VI.

II. Current Experimental Work and New Proposals

To achieve the high concentrations of atomic hydrogen required for useful propellants, it appears necessary to augment the conventional matrix-isolation method[11–14,17–25,27–29,33,34]

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with supplementary technical aids that assist in the stabilization of the reactive species. Two main supplementary technical aids are now being employed in experiments, namely, the use of very low temperatures (in the range 0.1°K to 1.5°K produced by advanced cryogenic apparatus) and the use of very strong magnetic fields (in the range 50kG to 100kG produced by superconducting magnets). At temperatures below 1.5°K, one can expect a dramatic improvement in the trapping effectiveness of a matrix compared to what it is at 4.2°K, the liquid helium temperature of earlier matrix-isolation experiments. In particular, for hydrogen atoms in a nearly perfect H_2 lattice, the lower edge of the band of critical temperatures for the escape of atoms from traps is somewhat greater than 2°K, which implies that the trapping processes should proceed favorably at temperatures below 1.5°K. Very strong magnetic fields can saturate the alignment and make parallel the spins of unpaired electrons in free hydrogen atoms, thereby inhibiting the $H + H \rightarrow H_2$ recombination reaction.

The use of strong magnetic fields to assist in the stabilization of matrix-isolated free radicals is not a new idea (see, for example, Refs. 3, 8, 15, 35, 36), but only recently has the cryogenic and superconducting magnet technology been available for the attainment of conditions favorable for the stabilization of atomic hydrogen, according to quantum mechanical theory. Table 1 shows the low temperature-strong magnetic field combinations predicted theoretically (see Ref. 15, p. 25) to yield substantial saturation† of electron spin-alignment in atomic hydrogen and thus to inhibit the recombination reaction $2H \rightarrow H_2$ (with only a total electron spin zero bound-state admissible for molecular hydrogen). However, the combinations of low temperatures and strong magnetic fields in Table 1 are neither necessary nor sufficient, for atomic hydrogen trapping in an H_2 matrix will assist stabilization, while the small interaction between the magnetic dipoles associated with the electron and proton spins in a hydrogen atom[15] and electron-spin multipole radiative transitions[26] may promote recombinations by electron spin-flips in the course of interactions between atoms with electron spins parallel initially. The rate of the latter phenomenon is quite difficult to estimate for electron spin-aligned hydrogen atoms in an H_2 matrix.

Exciting positive experimental results for atomic hydrogen stabilization have been reported recently. In a painstaking research program, Hess[9] has produced significant concentrations (apparently about 10% molar) of atomic hydrogen in the matrix-isolated condensate from a hydrogen glow discharge cooled very rapidly to about 1.3°K in a magnetic field of approximately 50 kG.‡ A copy of the Hess apparatus has been constructed at NASA's Lewis Research Center and experiments now in progress will clarify the effectiveness of this method for atomic hydrogen propellant manufacture and storage. In a thermal sensing experiment, a mixture of H and H_2 (or dissociated and molecular deuterium) is deposited on a nearly thermally isolated collector at about 1.2°K in a magnetic field of 100 kG; the recombination of atomic hydrogen is induced by electrical heating and the energy release is measured by a carbon thermometer. In a mass spectrometer sensing experiment, the beam of particles from either the H-H_2 source or the collection region is chopped by a toothed wheel and phase-sensitive detection is possible with an in-line-of-sight quadrupole mass spectrometer which is capable of recording particles with molecular weight 1. Results from these experiments are expected to be available in the near future.[4]

Table 1 Combinations of low temperatures and strong magnetic fields predicted theoretically to stabilize atomic hydrogen by nearly complete alignment of electron spins

Temperature (°K)	2	1	0.5	0.1	0.05
Magnetic field (kG)	570	285	142.5	28.5	14.25

Work in progress will also determine the effectiveness of *internal* in situ free radical production at ultra-low temperatures in a strong magnetic field. Here the idea is to use the β-ray electrons emitted in the decay of tritium to produce atomic hydrogen by electron impact. In experiments now being performed at the NASA Lewis Research Center, ordinary H_2 (molecular weight 2) and tritium molecules (weight 6, half-life 12.26 years, mean energy of β-ray electrons 5.7 kev) are frozen together in a dilution refrigerator at 0.1°K and a 35 kG magnetic field is applied to the sample, thus providing very favorable conditions for stabilizing H atoms that result principally from secondary electron impact dissociations of H_2 molecules in the matrix (see Sec. IV). Measurement of the atomic hydrogen concentration is accomplished by determining the magnetic susceptibility of the solid. This experiment will also yield results presently.[4]

In addition to the methods of manufacture and storage of an atomic hydrogen propellant that are under current investigation, there are two alternative schemes which also appear to warrant experimental study. The first involves the use of a cyclotron to produce a 10 Mev hydrogen atom beam which bombards solid H_2 at a temperature below 1°K in a very strong magnetic field. This possible method for the manufacture of an H-H_2 propellant (about 15% atomic hydrogen by weight) has been worked out in a preliminary theoretical fashion by the author and is described in Sec. III. The second scheme involves the use of the radionuclide P^{32} (with more than 300 times the specific activity of tritium) to produce an H-H_2 propellant through secondary electron impact dissociation reactions. Secondary electrons will be proliferated by β-ray electrons (mean energy 690 kev) in an H_2 matrix impregnated with 0.002% molar P^{32} atoms, and conditions will be favorable for the trapping of free hydrogen atoms that result from H_2 dissociations if the solid is maintained below 1°K and a strong magnetic field is applied during the radioactive "curing" of the propellant. Essentially an extension of the tritium H-H_2 propellant concept to higher energetics and production rates, this possible method for the manufacture of an H-H_2 propellant (at least 15% atomic hydrogen by weight) has been worked out by the author and is described in Sec. IV. Both of these two schemes offer promise of providing an atomic hydrogen propellant that will yield a specific impulse of about 740 sec for rocket engine conditions that make the specific impulse formula (A6) in the Appendix applicable.

III. Manufacture of an H-H_2 Solid Propellant by Ultra-Energetic Hydrogen Atom Bombardment

A conventional cyclotron of 1950 vintage, with a magnet of 100 in. diam and radiofrequency power supplied at about 250 kw, will deliver an external (extracted) beam of 10 Mev protons at a steady current of about 0.2 ma $\cong 1.2 \times 10^{17}$ protons/sec (implying a beam power of about 192 kw). Such a beam of high-energy protons can be made to have a uniform flux over a cross-sectional area of about 3×10^3 cm^2 (by electric or magnetic field dispersal focusing) and to pass from vacuum through a chamber filled with cesium vapor at a density of about 10^{17} cesium atoms/cm^3. Since the total cross section for the charge-exchange process leading to any neutral (possibly electronically excited)

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† For free hydrogen atoms at temperature T in a strong magnetic field of magnitude B, the recombination rate is suppressed by the Boltzmann probability factor for nonalignment of the electron spin in a hydrogen atom, given by $e^{-2\mu B/kT}$ where $\mu/k \cong 1°\mathrm{K}/15$ kG is the spin-magnetic moment of an electron divided by Boltzmann's constant. The values in Table 1 obtain if the probability factor is required to equal 0.25×10^{-16}, a number that makes the lifetime of the atomic hydrogen sufficiently long for practical utilization (Jones[15]).

‡ Hess[9] has conjectured that large clusters of spin-aligned atomic hydrogen may have formed and precipitated out in the condensate as atomic hydrogen domains, but this seems unlikely in view of recent theoretical estimates made by Etters.[7]

state of hydrogen, $H^+ + Ce \rightarrow H + Ce^+$, can be estimated for 10 Mev protons by extrapolation of lower energy data[31] to be at least 10^{-16} cm^2, it follows that almost all of the protons will be converted to neutral hydrogen atoms if the cesium vapor neutralizing chamber has a length along the beam of about 10 cm (see Ref. 10 for a detailed discussion of the technique). In this manner it is possible to produce a beam of 10 Mev hydrogen atoms with a uniform flux of about 4×10^{13} particles/cm^2-sec over a cross-sectional area of about 3×10^3 cm^2.

Now suppose that a 10 liter volume (equivalently, 0.71 kg) of liquid H_2 is cooled gradually through its freezing point and down to a temperature below 0.5°K to yield a wafer of solid H_2 about 3×10^3 cm^2 in area and 2.7 cm in thickness. The wafer of solid H_2, a rigid lattice composed of about 2.14×10^{26} H_2 molecules, will have a nearly perfect crystalline structure, good thermal conductivity, very low specific heat, and thus very high thermal diffusivity.[6,16]

Let us consider bombardment of the ultra-cold wafer of solid H_2 by the beam of 10 Mev hydrogen atoms described above. Having a velocity of about 4.4×10^7 m/sec, the 10 Mev hydrogen atoms will enter the solid without the significant backscatter and reflection observed experimentally at much lower bombardment energies.[3,8] This is because at the high velocities of atoms in the beam the cross sections for H-H_2 scattering and reaction processes are very small (i.e., well below the geometrical 4×10^{-16} cm^2) and scattering amplitudes are sharply peaked in the forward direction. Because the H_2 molecules in the solid lattice are separated by a distance (about 3 Å) which is roughly three times the diameter of an H_2 molecule, a 10 Mev hydrogen atom§ will travel about 2.0 cm in the solid H_2 before being brought to rest by energy-absorbing processes. Most of the energy of the 10 Mev atoms will be absorbed by ionization reactions which take on the average 38 ev per ion-electron pair and yield energetic free electrons that move preferentially in the direction of the hydrogen atom beam. There will also be knock-on dissociation reactions $H + H_2 \rightarrow 3H$ by the primary hydrogen atoms, yielding secondary energetic chain-branching hydrogen atoms which also move preferentially in the direction of the original beam. The secondary energetic free electrons and hydrogen atoms will also give up their energy primarily through ionization reactions and H_2 dissociation reactions.¶

In the course of these reactions, the excitation of lattice vibrations (associated with the sensible heat content and temperature of the solid) will not be favored quantum mechanically if the temperature is maintained below 1°K during bombardment. This is because the higher frequency vibrational modes (that couple to localized energetic interactions) are frozen out of the equilibrium distribution by quantum statistics at low temperatures, and hence the rates at which the higher frequency vibrational modes can be excited are very small in a lattice below 1°K by detailed balancing considerations (Hess[9]). It is estimated that less than 0.03% of the total beam power will eventually be absorbed by lattice vibrations.** On the other hand, the vibrational excitation of H_2 molecules (by impact with primary and secondary hydrogen atoms and free electrons) will absorb a more significant fraction of the total beam power, but the vibrational excitation of an H_2 molecule in the lattice will increase the probability and lower the energy requirement for the chain-branching dissociation reactions $e + H_2 \rightarrow e + 2H$ and $H + H_2 \rightarrow 3H$ (see Ref. 32). It is estimated that between 25% and 50% of the original energy†† in the beam will be absorbed eventually by chain-branching dissociations of H_2 molecules, which generate additional fast-moving free hydrogen atoms as well as residual free hydrogen atoms. The latter free H atoms may become trapped interstitially[2] or assume lattice sites occupied previously by H_2 molecules which have been dissociated. If we take 0.375 as a tentative estimate of the energy fraction finally absorbed by chain-branching dissociation reactions, it follows that a hydrogen atom with an initial energy of 10 Mev will instigate the eventual production of about 1.66 million free hydrogen atoms in the solid. Conditions will be favorable for the trapping and stabilization of the free hydrogen atoms if a magnetic field of about 100 kG is applied through the solid. In this manner about 2.0×10^{23} free hydrogen atoms will be produced and trapped in the solid during each second of bombardment. Hence, about 15% of the H_2 molecules in the solid will undergo effective dissociation to yield trapped free hydrogen atoms during a total bombardment time of about 5.5 min. The resulting H-H_2 solid propellant wafer, 15% free hydrogen atoms by weight, will have a stored recoverable specific energy $Q \cong 7.81$ kcal/g and thus will yield a theoretical specific impulse $I_{sp} \cong 742$ sec for rocket engine conditions that make the Appendix formula (A6) applicable.

It should be noted that the over-all efficiency for energy storage in the H-H_2 solid propellant is approximately 0.28, with 250 kw cyclotron power for 5.5 min yielding 5.55×10^3 kcal of stored energy in a 0.71 kg wafer of solid hydrogen. To produce a 1000 kg amount of the propellant would require a conveyer belt operation and 129 hr of total bombardment time. The strong magnetic field must be maintained, along with the low temperature, for safe storage of the propellant, and the atomic hydrogen concentration can be monitored conveniently with electron spin resonance measurements during and after the bombardment of a wafer.

IV. Manufacture of an H-H_2 Solid Propellant by Impregnation with Radioactive Phosphorus

The radioactive isotope of phosphorus P^{32} decays solely by β-ray electron emission (to yield sulfur S^{32}) with a half-life of 14.3 days and a mean energy of 690 kev for the emitted β-ray electrons. About 300 times greater in specific activity than tritium, the radionuclide P^{32} has been extensively used in medical applications and is available commercially.

Consider a volume of liquid hydrogen impregnated uniformly with radioactive phosphorus atoms in the ratio of one P^{32} atom for every 50,000 H_2 molecules (i.e., 0.002% molar P^{32}) and cooled gradually through its freezing point and down to a temperature below 1°K, which is maintained for a two-week "curing" period. During this time about half of the P^{32} atoms will emit β-ray electrons having a mean energy of 690 kev and a mean range in the low-density solid of about 2 cm. Almost all the energy of the β-ray electrons will be absorbed by ionization processes which yield secondary electrons with energies between 15 ev and 10 kev. The secondary electrons will in turn give up their energy through further ionization reactions, vibrational and electronic excitations of H_2 molecules, dissociations of H_2 molecules, electronic excitations of H atoms, and lattice (collective molecular) vibrational excitation reactions. At least a tenth of the original energy in the β-ray electrons will be effective in producing free hydrogen atoms via secondary electron impact dissociation reactions and free hydrogen $H + H_2 \rightarrow 3H$ dissociation reactions. Since the net energy absorbed per dissociation is 4.5 ev, at least 1.53×10^4 H_2 molecules will be

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§ A hydrogen atom initially with 10 Mev energy will lose its electron and travel as a proton during about half the time it spends in motion in solid hydrogen; it is understood tacitly in our discussion that "hydrogen atom" means "hydrogen atom or proton."

¶ The dissociation energy of a ground-state H_2 molecule is about 4.5 ev, but electrons having at least 11 ev are required for the quantum mechanical threshold of the dissociation reaction $e + H_2 \rightarrow e + 2H$, which involves a transition of the molecule from the $^1\Sigma$ ground-state to a $^3\Sigma$ repulsive state. Near threshold, each free H emerges with about 3.2 ev of translational kinetic energy.

** The associated local heating throughout the solid (less than 60 w $\cong$ 14.3 cal/sec through the entire volume, giving a local heating rate of about 1.8×10^{-3} cal/cm^3-sec) is controllable by virtue of the very high thermal diffusivity of solid hydrogen, of the order 10^2 cm^2/sec for temperatures below 1°K.

†† Energy not absorbed by the dissociation of H_2 molecules and lattice vibrations must eventually be emitted as visible and ultraviolet radiation, resulting from electronic recombination of ions and the radiative decay of vibrationally excited H_2 molecules and electronically excited H atoms and H_2 molecules.

dissociated by the secondary energetic particles that are generated by a β-ray electron with 690 kev initial energy. Thus, during the two-week curing period, at least 15% of the H_2 molecules will have undergone dissociations to yield free hydrogen atoms. If a magnetic field of about 100 kG is applied to the solid, conditions will be favorable for the trapping and stabilization of the free hydrogen atoms in the H_2 matrix. The resulting H-H_2 solid propellant, at least 15% atomic hydrogen by weight, will yield a specific impulse $\gtrsim 742$ sec for rocket engine conditions that make the Appendix formula (A6) applicable.

V. Energy Release

Since the activation energy is close to zero, the recombination reaction $H + H \rightarrow H_2$ proceeds rapidly even at cryogenic temperatures if the species are mobile in the gas or liquid phase.[1,30] According to elementary collision reaction theory, the rate of such a free radical recombination reaction is given by $f \cong \bar{\sigma} n \bar{v}$ where $\bar{\sigma}$ is the velocity-averaged total cross section for the reaction, n is the concentration of the free radicals, and $\bar{v}$ is their mean velocity in the gas or liquid. The velocity-averaged total cross section $\bar{\sigma}$ for the reaction $H + H \rightarrow H_2$ is about 1.1×10^{-16} cm^2 at thermal energies ($\lesssim 0.5$ ev), with account taken of the fact that the reaction proceeds only in the total electron spin zero channel,[15] and it is required that n be greater than 10^{21} H atoms/cm^3 for a useful propellant in the stored (matrix-isolated) cryogenic solid state. Thus, if a cryogenic solid containing trapped free radicals were to melt and attain a temperature of, say, 30°K and an associated mean particle velocity $\bar{v} > 10^4$ cm/sec, then the characteristic time for the free radical recombination reaction would be $f^{-1} \cong (\bar{\sigma} n \bar{v})^{-1} < 10^{-9}$ sec. Quite clearly, in a time less than a nanosecond it would not be possible to pump and utilize the free radical mixture as a liquid propellant. Hence, it is necessary to use matrix-isolated H atoms directly without prior melting in the form of a solid propellant.

Ignition of an atomic hydrogen solid propellant can be accomplished by any means (electrical or other) that warms a surface layer of the cryogenic matrix to a temperature at which the rate of heat release from recombination of the reactive species exceeds the rate of heat loss by thermal diffusion. Generally, this will be the case if a surface layer of millimeter thickness is maintained above the critical temperature for significant escape from trapping sites (expected to be in the vicinity of 4°K for hydrogen atoms in a well-formed H_2 matrix) for a time of the order of an msec.

VI. Deflagration of an H-H_2 Solid Propellant

Under proper conditions, the deflagration that follows ignition of an atomic hydrogen propellant can be expected to be steady and stable, albeit very rapid, with the recombination reaction taking place almost exclusively in the fluid (very light liquid and gas) adjacent to the melting surface of the solid matrix. An elemental volume of the solid will be warmed to the melting point in a time much less than a μsec, a duration too brief for reactive species to absorb energy, escape from their trapping sites, diffuse through the solid and undergo reaction. Heat transport into the interiors of the matrix will be restrained because the thermal diffusivity of solid H_2 decreases rapidly with increasing temperatures above 1°K; the thermal diffusivity is given approximately by (see Ref. 6, p. 13) $D \cong 1.5 \times 10^4$ (exp $-T/0.845°\mathrm{K}$) cm^2/sec in the temperature range $4°\mathrm{K} \lesssim T \lesssim 12°\mathrm{K}$ and remains of the order 10^2 cm^2/sec (with roughly proportional decreasing thermal conductivity and specific heat) as the temperature decreases from about 4°K to below 1°K. Moreover, because solid hydrogen is generally transparent to the bulk of electromagnetic radiation in the infrared and visible wavelengths, the absorption of radiation emitted by hot gas in the chamber is not expected to produce a significant temperature rise in the depths of the propellant.

Consider an H-H_2 solid propellant, 15% atomic hydrogen by weight, at an initial temperature of 1°K and a constant pressure of 100 psia. If an elemental volume of the solid is heated, the density will remain approximately constant at $\rho_s = 0.088$ g/cm^3 until the melting point is reached at a temperature just above 14°K. The density of the fluid, equal to about 0.073 g/cm^3 at a pressure of 100 psia and a temperature near the melting point, will decrease continuously with increasing temperature according to the formula

$$\rho \cong (0.170 \text{ g-°K/cm}^3)(T - 11.67°\mathrm{K})^{-1} \tag{1}$$

for $T > 14.0°\mathrm{K}$ without significant discontinuity at the liquid-gas transition temperature $\sim 32°\mathrm{K}$ at 100 psia (because the critical point for H_2 is at 33°K and 189 psia). Continuity of mass flux in the case of steady one-dimensional deflagration yields the relation

$$\rho u = \rho_s v_s \tag{2}$$

where u is the local fluid velocity in a coordinate frame for which the melting surface is at rest and v_s is the constant burning velocity of the solid (i.e., the rate of linear regression of the melting surface with respect to the solid at rest). It follows from Eqs. (1) and (2) that

$$u \cong 0.518\, v_s(T/1°\mathrm{K} - 11.67) \tag{3}$$

for a fluid element at temperature T.

Now with the propellant mixture yielding the over-all net energy release $Q \cong 7.81$ kcal/g, the functional dependence $c_p = c_p(T)$ for H_2 gives a final (adiabatic flame) temperature of about 2090°K for the product H_2 gas. If Δt denotes the time interval following melting for a fluid element to attain the temperature of 1000°K, then the temperature of a fluid element will increase by the amount $\Delta T = 1000°\mathrm{K} - 14°\mathrm{K} = 986°\mathrm{K}$ in traveling the distance

$$\Delta x \equiv \int_0^{\Delta t} u\, dt \tag{4}$$

from the melting surface. Letting ω denote the weight fraction of H atoms at any point in the fluid, we have the recombination rate equation

$$\frac{d\omega}{dt} = -f\omega^2 \tag{5}$$

in which

$$f = 1.61 \times 10^{11} \left(\frac{\rho}{\rho_s}\right)\left(\frac{T}{14°\mathrm{K}}\right)^{1/2} \sec^{-1} \tag{6}$$

is the rate function associated with a velocity-averaged total cross section of $\bar{\sigma} \cong 1.1 \times 10^{-16}$ cm^2 for the recombination reaction. The temperature of a fluid element will increase from $T \cong 14°\mathrm{K}$ (for which $\omega \cong 0.15$, as will be seen later) to $T \cong 2090°\mathrm{K}$ (for which $\omega = 0$) with an approximately linear[‡‡] dependence on ω,

$$T \cong 2090°\mathrm{K} - (13{,}840°\mathrm{K})\omega \tag{7}$$

By putting Eq. (3) and $dt = f^{-1} d(\omega^{-1})$ into Eq. (4) and using Eqs. (6, 1, and 7), we obtain

$$\begin{aligned} \Delta x &\cong (8.65 \times 10^{-8} \sec) v_s \int_{14}^{1000} [(\theta - 11.67)/(2090 - \theta)]^2\, d\theta/\theta^{1/2} \\ &\cong (7.0 \times 10^{-7} \sec) v_s \end{aligned} \tag{8}$$

Thus, the thermal gradient for heat flux to the melting surface is given approximately by

$$\Delta T/\Delta x \cong (1.41 \times 10^9\ °\mathrm{K/sec}) v_s^{-1} \tag{9}$$

[‡‡] The effective specific heat of the fluid is bolstered at low temperatures by the heat of vaporization (~ 107 cal/g) distributed about 32°K and by the heat of conversion of para-H_2 to ortho-H_2 (~ 170 cal/g converted).

The latter quantity enters the heat flux balance at the melting surface

$$\lambda(\Delta T/\Delta x) \cong v_s \rho_s h_1 \qquad (10)$$

where $\lambda \cong 0.25$ mw/cm-°K $\cong 6.0 \times 10^{-5}$ cal/cm-sec-°K is the estimated[§§] thermal conductivity of the fluid at 14°K and $h_1 \cong 22$ cal/g is the enthalpy required to warm and melt a unit mass of the solid initially at 1°K.[¶¶] Hence, from Eqs. (9) and (10) we obtain the burning velocity

$$v_s \cong 210 \text{ cm/sec} \qquad (11)$$

The essential correctness of the deflagration model is confirmed by consistency estimates. First note that an elemental volume of the solid will be warmed to the melting point in a time given approximately by the expression $D/v_s^2 \cong 8.0 \times 10^{-9}$ sec, where $D \cong 3.5 \times 10^{-4}$ cm^2/sec is the thermal diffusivity of the solid at a temperature near the melting point, and thus a negligible fraction of the hydrogen atoms will have time to recombine while in the solid and above the critical temperature (~4°K) for significant escape from trapping sites. Next observe that the distance $\Delta x \cong 1.47 \times 10^{-4}$ cm [given by Eqs. (8) and (11)] has the same order of magnitude as the mean free path for H_2 molecules at 1000°K and 100 psia. On the other hand, the magnitude of Δx is small compared to the entire flame thickness, which can be estimated to be about 1.81×10^{-2} cm by replacing the upper limit in the integral in Eq. (8) with the value 2000. Finally note that the neglect of species and thermal diffusive transport in writing Eqs. (5) and (7) is justified, because the diffusivities in the fluid are very small compared to the mean flow velocity $u|_{T=1000°K} \cong 1.07 \times 10^5$ cm/sec multiplied by the approximate flame thickness 1.81×10^{-2} cm.

Summary

Two main supplementary technical aids are now being employed in experiments to achieve higher concentrations of atomic hydrogen with matrix-isolation, namely, the use of very low temperatures (in the range 0.1°K to 1.5°K) produced by advanced cryogenic apparatus and the use of very strong magnetic fields (in the range 50 kG to 100 kG) produced by superconducting magnets. A significant improvement in the trapping effectiveness of an H_2 matrix occurs at temperatures below 1.5°K, while very strong magnetic fields can prevent $H + H \rightarrow H_2$ recombination reactions by effecting the parallel alignment of unpaired electron spins in free hydrogen atoms. Significant concentrations of atomic hydrogen, apparently about 10% molar, have been obtained in the matrix-isolated condensate from a hydrogen glow discharge cooled very rapidly to about 1.3°K in a magnetic field of approximately 50 kG. Similar experiments in progress with magnetic fields as large as 100 kG will clarify the effectiveness of this method for atomic hydrogen propellant manufacture and storage. The use of a radioactive β-ray emitter isotope (tritium under current experimental study, P^{32} as a proposed alternative) may yield H-H_2 propellants (with $I_{sp} \cong 740$ sec estimated in the case of P^{32}) by secondary electron impact dissociations of H_2 in an impregnated matrix maintained below 1°K (prospectively at 0.1°K in the case of tritium) in a strong magnetic field. Another method for manufacturing an H-H_2 propellant (~15% atomic hydrogen by weight, $I_{sp} \cong 740$ sec) involves bombardment of H_2 with a cyclotron-produced beam of 10 Mev hydrogen atoms.

An estimate of the characteristic time for the $H + H \rightarrow H_2$ recombination reaction shows that matrix-isolated atomic hydrogen must be used directly without prior melting as a solid propellant. Under suitable conditions, the deflagration of an atomic hydrogen propellant is expected to be steady and stable, although very rapid. A burning velocity of about 2.1 m/sec is predicted for an H-H_2 propellant (~15% atomic hydrogen by weight) at a chamber pressure of 100 psia.

Appendix: Theoretical Specific Impulse Formula

Let Q denote the over-all net energy release per unit mass of propellant and η denote the over-all efficiency of the rocket engine in converting this energy release to kinetic energy of the gas at the exhaust plane of the nozzle. Assuming that the sensible enthalpy of the cold propellants is negligible[*] compared to Q, the specific impulse is given by

$$I_{sp} = (2\eta Q)^{1/2}/g \qquad (A1)$$

where $g \equiv 980$ cm/sec^2 is the acceleration of gravity at sea level. The over-all efficiency for energy conversion in Eq. (A1) can be expressed as

$$\eta = \eta_{\text{ideal}}\,\eta_{\text{losses}} \qquad (A2)$$

in which $\eta_{\text{ideal}} = 1 -$ (temperature of gas at the exhaust plane of the nozzle)/(chamber temperature of the gas) is the ideal thermodynamic efficiency of the rocket engine, and the factor $\eta_{\text{losses}} (\leq 1)$ accounts for real fluid dissipative effects. We have

$$\eta_{\text{ideal}} = [1 + 2(\gamma - 1)^{-1} M_{ex}^{-2}]^{-1} \qquad (A3)$$

according to the theory for inviscid, isentropic, one-dimensional flow of a perfect gas with γ denoting the effective constant ratio of specific heats and M_{ex} denoting the ideal Mach number of the gas at the exhaust plane of the nozzle. With optimum design the practical efficiency factor η_{losses} in Eq. (A2), associated with possible reductions in the exhaust velocity and Mach number due to unrecoverable heat losses to the chamber and nozzle walls, real gas viscous flow effects, etc., can be brought to a value close to unity.[†] From inviscid, isentropic, one-dimensional flow theory we also obtain the relation between the expansion area ratio of the nozzle, denoted here by R, and the ideal Mach number of the gas at the exhaust plane,

$$R = M_{ex}^{-1}[2(\gamma + 1)^{-1} + (\gamma - 1)(\gamma + 1)^{-1} M_{ex}^2]^{(\gamma + 1)/2(\gamma - 1)} \qquad (A4)$$

which can be inverted for $R \gg 1$ to yield

$$M_{ex}^2 = \left(\frac{\gamma + 1}{\gamma - 1}\right)^{(\gamma + 1)/2} R^{\gamma - 1} - \left(\frac{\gamma + 1}{\gamma - 1}\right) + O[R^{-(\gamma - 1)}] \qquad (A5)$$

Thus, for a spacecraft with an expansion area ratio $R = 60$ and exhaust gas with an effective constant ratio of specific heats $\gamma = 1.25$, we find that Eqs. (A5) and (A3) yield $M_{ex}^2 = 24.0$ and $\eta_{\text{ideal}} = 0.750$, while for $R = 60$ and $\gamma = 1.30$, Eqs. (A5) and (A3) yield $M_{ex}^2 = 27.9$ and $\eta_{\text{ideal}} = 0.808$, respectively. If we assume the latter values for R and γ and set the efficiency factor η_{losses} equal to unity in Eq. (A2), we obtain the theoretical specific impulse formula from Eqs. (A1) and (A2)

$$I_{sp} = 265(Q/1 \text{ kcal/g})^{1/2} \text{ sec} \qquad (A6)$$
$$[\text{for } R = 60, \gamma = 1.30, \eta_{\text{losses}} = 1]$$

For example, in the case of the conventional chemical propellant hydrogen-oxygen system with the optimum mixture ratio 4.7 of O_2 to H_2 by weight, we have $Q = 2.95$ kcal/g and Eq. (A6) gives $I_{sp} = 456$ sec.

[§§] A significant fraction of ortho-H_2 will be present in the solid as a by-product of the propellant manufacturing process, and the ortho-H_2 and atomic H fractions will suppress the thermal conductivity from the value 0.85 mw/cm-°K for liquid para-H_2 at 14°K and 100 psia.

[¶¶] We have 14 cal/g coming from the heat of fusion, 5 cal/g from the T^3 integration, and about 3 cal/g from the λ anomaly in heat capacity at about 1.6°K (with a high fraction of ortho-H_2 resulting in the solid as a by-product of the propellant manufacturing process).

[*] For example, the sensible enthalpies of H_2 and O_2 at their normal boiling points (20°K and 90°K, respectively) are both less than 0.03 kcal/g and hence negligible compared to their stoichiometric energy release $Q = 3.18$ kcal/g.

[†] Provided that thermodynamic equilibrium is maintained between the molecular (internal and translational) degrees of freedom during the expansion of the gas through the nozzle, energy partitioned into the vibrational, rotational and electronic excitations is taken into account in the value for γ. Since γ decreases toward unity as the number of effective internal degrees of freedom increases, the ideal thermodynamic efficiency is reduced by an increase in the number of internal degrees of freedom according to Eqs. (A3) and (A5) with R fixed. On the other hand, energy losses due to nonequilibrium finite-time relaxation of the internal degrees of freedom must be taken into account through the factor η_{losses}.

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