CURRENT STATUS OF FREE RADICALS AND ELECTRONICALLY EXCITED

METASTABLE SPECIES AS HIGH ENERGY PROPELLANTS

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CONTENTS

1. Introduction

Considerable interest has been attached to the research and development of free radicals and electronically excited metastable species for use in rocket propellants, because markedly superior performance is predicted theoretically for them. 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 even well above 750 sec are predicted if it is possible to employ the most promising free radicals or electronically excited metastable species (i.e., "metastables"). 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 (Carter[28], Windsor[210]).

This report provides an up-to-date survey study of free radicals and electronically excited metastable species as high energy propellants for rocket engines[†]. Included as free radicals in our study are nascent or atomic forms of diatomic gases in addition to the highly reactive diatomic and triatomic molecules that possess one or more unpaired electrons. For use as a propellant, a free radical must be a stable (ground-state) quantum mechanical structure and have a rather high energy of reaction per unit mass, which implies that the free radical must be of relatively low molecular weight. Electronically excited metastables of possible interest as propellants must have sufficient resistance to spontaneous electromagnetic decay (i.e., a sufficiently long radiative lifetime) in addition to having a high specific energy content.

[†]Metallic hydrogen and vibrationally excited molecular species, also of interest as possible high energy propellants, are not discussed in this report. A recent description of current experimental research on the production of metallic hydrogen has been given by Lubkin[119]. Noteworthy experimental and theoretical results on vibrationally excited hydrogen, oxygen, and other molecules have been obtained recently and reported in Refs. 37, 39, 54, 55, 76, 103, 109, 123, 160, 182, 195 and 207.

Free radicals and metastables that may offer possibilities as propellants are discussed in Sections 2 and 3. In section 4 it is shown that propellants composed of any of the free radicals H, N, O, CH, BH, NH, BH_2, CH_2 or the metastables $(2^3S_1)He*$, $(^2D)N*$, $(^3P_{2,0})Ne*$, $(^3P_{2,0})Ar*$, $(^1D)O*$, $(a^1\Delta_g)O_2*$ can give performance (predicted by the theoretical specific impulse formula derived in Appendix A) superior to the maximum attainable for O_2-H_2 or any other conventional oxidizer-fuel combination. In particular, extraordinary theoretical performance is predicted for atomic hydrogen, the CH free radical, and the metastable excited states of helium, nitrogen, neon, and atomic oxygen with H_2.

The essence of the manufacturing and storage problem is described in Section 5, prior to the detailed discussions of methods of production in Section 6 and matrix-isolation storage in Section 7. It is shown in Appendix B that a very small characteristic time is associated with the heat pulse produced by a chance recombination reaction of matrix-isolated free radicals, and thus neighboring free radicals cannot absorb requisite energy from such a heat pulse for escape from their trapping sites. Because the host matrix material will be vaporized along with product gases during the energy release, the matrix-isolation host species must also serve as the working fluid for a free radical or metastable propellant, and a decisive advantage is noted to accrue if the free radical or metastable can be produced in situ from one of the matrix host species H_2, N_2, O_2, He, Ne or Ar. Deductive considerations show that among the propellant condidates with this property, atomic hydrogen is an H_2 matrix is most accessible to near-term development with existing technology.

A review of current experimental work related to the manufacture of an atomic hydrogen propellant is presented in Section 8, where the two main technical aids now being employed to achieve higher concentrations of reactive

species with matrix-isolation, the use of very low temperatures and very strong magnetic fields, are discussed in detail. It is shown that important progress toward the development of an atomic hydrogen propellant appears imminent with venerable methods of production and storage being augmented by these new technical aids. In Section 9 it is observed that the manufacture of an $H-H_2$ propellant, 15% atomic hydrogen by weight, may be possible by ultra-energetic hydrogen atom bombardment of solid H_2 (theory described in Appendix C) or by impregnation of solid H_2 with radioactive phosphorus (theory sketched in Appendix D). The theoretical estimates presented in Section 10 show that matrix-isolated free radicals or metastables must be used directly without prior melting as solid propellants. Finally, the steady deflagration of an $H-H_2$ solid propellant, 15% atomic hydrogen by weight, is analyzed in Appendix E.

2. Free Radicals

Quantum mechanical analysis shows that a host of free radicals are likely to have adequate (ground-state) stability and sufficient specific energy of reaction to warrant further consideration as propellants (Schneiderman[170], Kepford[107]). The outstanding practical candidates for free radical propellants are shown in Table 1, in which the first eight entries, namely H, N, O, CH, BH, NH, BH_2 and CH_2, are free radicals that have been studied experimentally for many years (Pimentel[157], Milligan[134,137], Windsor[210], Ramsay[163]), while the last three entries are the seemingly most promising additional free radicals that have been conjectured to exist by quantum mechanical analysis.

FREE RADICAL	GROUND STATE	CHEMICAL REACTION	SPECIFIC ENERGY (kcal/gm)
H	$^2S_{1/2}$	$2H \longrightarrow H_2$	52.10
N	$^4S_{3/2}$	$2N \longrightarrow N_2$	8.03
O	^3P	$2O \longrightarrow O_2$	3.71
CH	$^4\Sigma^-$	$2CH \longrightarrow 2C(\text{solid phase}) + H_2$	10.90
BH	$^3\Pi$	$2BH \longrightarrow 2B + H_2$	6.19
NH	$^1\Delta$	$2NH \longrightarrow N_2 + H_2$	5.25
BH_2	$^2A_1$	$BH_2 \longrightarrow B + H_2$	5.18
CH_2	$^3\Sigma_g^-$	$CH_2 \longrightarrow C(\text{solid phase}) + H_2$	5.29
He_2O	$^1\Sigma_g^+$	$2He_2O \longrightarrow 4He + O_2$	4.35
H Li	$^1\Sigma^+$	$2HLi \longrightarrow H_2 + 2Li$	5.46
H_2Li	$^2\Sigma_u^+$	$H_2Li \longrightarrow H_2 + Li$	3.94

Table 1. Known and theoretically conjectured free radicals that
may offer possibilities as propellants.

There is no experimental evidence that the latter entries, namely

He_2O, HLi and H_2Li, can be produced in sufficient amounts to be useful as propellants (Kepford[107], Henneker[77]), and since there is no advantage that would accrue in greater specific energy from the use of these latter entries, it is reasonable that attention in our survey should be concentrated on the three monatomic radicals H, N and O, the three diatomic radicals CH, BH and NH, and the two triatomic radicals BH_2 and CH_2.

3. Metastables

An electronically excited state of an atom or molecule is said to be metastable if its radiative lifetime is greater than a microsecond. Assuming that it is not possible to suppress the spontaneous electro-magnetic radiative decay of a metastable state[†], propulsion applications would appear to require radiative lifetimes of the order 10^3 sec or greater. A list of known metastables that offer even remote possibilities as propellants is given in Table 2. Known metastables with radiative lifetimes less than a millisecond or with relatively smaller values for their specific energy [= (excitation energy of species)/(mass of species), expressed in column five of Table 2 by using the molecular weight values and the units conversion formula: 1 eV/particle ≅ 23.0 kcal/ mole] have been excluded from a broader tabulation (Muschlitz[144]).

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† It has been noted independently by J. Zmuidzinas and by the present writer that it may be possible to interfere destructively with the quantum mechanical probability amplitude for spontaneous electromagnetic radiative decay of an atomic metastable state, say by imposing a standing-wave electromagnetic field of critical amplitude and wavelength on metastables in a lattice. The theoretical analysis required to establish necessary critical conditions would be a fundamental extension of the quantum mechanical calculations in Refs. 17, 50, 41-45, 99, 111, 122, 214 and 215.

	STABLE STATE	STATE	(e.V.)	(kcal/g?)	(sec)	LITERATURE VALUES
H	$^2S_{1/2}$	$2^2S_{1/2}$	10.20	232	0.12	144,52,120,122,169
He	$^1S_0$	2^3S_1	19.82	114	8200	140,50,41-45,122,143,6
He	$^1S_0$	2^1S_0	20.61	118	.02	92,198,153,10,43,7
N	$^4S_{3/2}$	^2D	2.38	39.1	61,000(†)	144,208,65,152
N	$^4S_{3/2}$	^2P	3.58	58.9	13	144
O	^3P	^1D	1.97	28.3	110	144
O	^3P	^1S	4.17	60.0	1.31	102,101
Ne	$^1S_0$	$^3P_{2,0}$	16.62, 16.71	19.0, 19.1	(††) >0.8	199,168,197
Ar	$^1S_0$	$^3P_{2,0}$	11.55, 11.72	6.65,6.75	(††) >1.3	199,168,197
H_2	$^1\Sigma_g^+$	$c^3\Pi_u$	11.86	135	.0010	100,60,213
N_2	$^1\Sigma_g^+$	$A^3\Sigma_u^+$	6.22	5.07	~10	61-64,190,14,173
O_2	$^3\Sigma_g^-$	$a^1\Delta_g$	0.98	0.705	2000	66
CO	$^1\Sigma^+$	$a^3\Pi$	6.01	4.94	~.004	14,97
NO	$^2\Pi$	$a^4\Pi$	4.7	3.60	0.1	116
CH_2	$^3\Sigma_g^-$	$\tilde{a}^1A_1$	<1	<1.64	~.01	66
C_6H_6	$^1A_{1g}$	a^3B_{1u}	3.8	1.09	28	144

Table 2. Known electronically excited metastables that may offer possibilities as propellants. (†)Value for $^2D_{1/2}$ state of N with $^2D_{1/2}$ given as 1.4×10^5 sec in Ref. 208. (††) No theoretical estimate or crude experimental value exists.

6

In the absence of a conceptual scheme for preserving the shorter-lived metastables, the electronically excited metastable species of practical interest as possible propellants are 2^3S_1 helium, ^2D nitrogen, $^3P_{2,0}$ neon and argon, ^1D oxygen either with a nonreactive working fluid or with H_2 "after-burning", and finally $a^1\Delta_g$ oxygen with H_2 "after-burning" (i.e., the propellant $O_2^* - H_2$).

In addition to the basic metastables discussed above and shown in Table 2, there are hydrides and other low molecular weight metastable compounds that can be made chemically by reacting $(2^3S_1)He^*$, $(^3P_{2,0})Ne^*$, $(^3P_{2,0})Ar^*$, $(^2D)N^*$, or $(^1D)O^*$ with ordinary (ground-state) hydrogen and other low molecular weight atoms. Such electronically excited metastable compounds have less specific energy than their metastable atomic progenitors, owing to the energy lost in the formation of the chemical bond and the greater molecular weight of the compound. Nevertheless, a metastable compound might be of considerable interest as a propellant if it were to have a radiative lifetime much greater than its metastable progenitor. Although one cannot prove a quantum mechanical theorem which demonstrates that this could never be the case, it is unlikely that compound-formation effects an increase in the radiative lifetime for spontaneous electromagnetic decay[†] of <u>any</u> metastable (Freed[59], Bixon[9], Guberman[71], Segal[171],

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[†] On the other hand, collisional reaction rates and decay rates associated with external electromagnetic perturbations can be suppressed by metastable compound-formation, as exemplified by the $(2^3S_1)He^*$ states (with observed lifetimes about 1.5×10^{-5} sec) and $(a^3\Sigma_u^+)$ He_2^* states (with observed lifetimes greater than 0.1 sec) produced in electron-bombarded superfluid helium (see Refs. 40, 58, 75, 78, 81, 108, 184, 185). The radiative lifetime of a metastable for spontaneous electromagnetic decay provides a theoretical upper bound on the observed lifetime of a metastable that undergoes collisional reactions and/or induced decay.

Rosenfield[165], Nesbet[147]). In fact, the interatomic Coulomb field felt

by a metastable atom in a compound molecule usually increases the rate

of electromagnetic radiative emission by a factor typically of the order

10^4, and hence the radiative lifetime of a metastable compound would

ordinarily have a magnitude less than the radiative lifetime of its ato-

mic metastable progenitor by a factor typically of the order 10^{-4} †.

Attempts to produce metastable helium hydride He^*H and, more recently,

the metastable compounds OHe^* and ONe^* in significant amounts from

$(2^3S_1)He^*$ and $(^3P_{2,0})Ne^*$ for experimental applications have been un-

successful (Kepford[107])††. Likewise, it has not been possible to produce

and store electronically excited metastable states of free radicals in

significant amounts for detection (Linevsky[118]). Thus it appears most

practical to concentrate future theoretical and experimental studies on

the long-lived metastables of helium, nitrogen, oxygen, neon and argon

that are listed in Table 2.

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† The interatomic Coulomb field felt by a metastable atom in a compound molecule
generally has the order of magnitude of that due to a proton acting at a dis-
tance of several Bohr radii $[\sim(\alpha m)^{-1}$ in units $\hbar = c = 1$ and $\alpha \equiv e^2/4\pi \cong (137)^{-1}]$.
This leads to the formal replacement of a fine-structure constant α by a
number of the order unity in the matrix-element for the transition, when one
alters the vertex of a Feynman diagram for spontaneous radiative decay to give
a Feynman diagram associated with the interatomic Coulomb field decay (see,
e.g., Ref. 50). Since the matrix-element is thereby increased by a factor of the
order α^{-1} , the radiative decay rate is increased by a factor of the order α^{-2}
$\sim 10^4$ for the metastable atom in a compound molecule.

†† These metastables are theoretically auto-ionizing states (Russek[167],
Bhatia[6], Miller[129]), and indeed experiments indicate that auto-ionization
is concomitant with the formation of helium hydride (Neynaber[148]), the
dominant apparent process being $He^* + H_2 \longrightarrow HeH^+ + H +$ (an energetic
electron) with the resulting helium hydride ion unstable under subsequent
electronic recombination.

4. Theoretical Perfoनिance

For prescribed chamber conditions, nozzle geometry, and chemical
composition of the exhaust gas, the theoretical performance of a pro-
pellant is indicated by the associated value of the specific impulse.
An approximate theoretical specific impulse formula for conditions typi-
cal of those that would apply for an advanced propulsion system onboard
a spacecraft (vacuum environment and essentially lossless isentropic
equilibrium expansion through a nozzle with an expansion area ratio of
60:1 and an effective constant specific heat ratio of 1.30) is derived
in Appendix A with the result given by (A.6),

$$I_{sp} = 265 \, (Q/1 \; kcal/gm)^{\frac{1}{2}} \; sec,$$

where Q denotes the overall net energy release per unit mass of propel-
lant. Assuming that the free radical reactions in Table 1 go to comple-
tion and the metastable species in Table 2 are quenched completely to their
ground states, the energy release Q is given for any free radical or meta-
stable propellant by multiplying the specific energy in Table 1 or Table 2
by the weight fraction of the energized species in the propellant. Thus,
for example, in the case of H with H_2 as the working fluid, an atomic hy-
drogen weight fraction of .20 (meaning one free H atom for every two H_2
molecules) yields Q = 10.42 kcal/gm and I_{sp} = 857 sec, according to the
approximate specific impulse formula above. Table 3 displays Q and I_{sp}
values calculated in this manner for the best conventional chemical pro-
pellants and the most promising free radical and metastable propellants.
The weight fractions of the latter species are fixed at simple fractional values
that give performance at least comparable to that of conventional propellants, and
thus Table 3 shows the approximate weight fractions required for practical
competitive use of free radical and metastable propellants.

PROPELLANT		WEIGHT FRACTION OF OXIDIZER OR FREE RADICAL	Q (kcal/gm)	I_{sp} (sec)
CONVENTIONAL	$O_2 - H_2$	.825	2.95	456
	$F_2 - H_2$	.938	3.16	471
	$O_3 - H_2$	.889	3.83	520
FREE RADICAL	H	1.000	52.10	1918
	H-(inert working fluid, e.g., H_2 or He)	.500 .250 .100	26.05 13.02 5.21	1355 959 606
	CH-(")	.500	5.45	620
	N-(")	.500	4.02	531
	BH-(")	.500	3.10	467
	NH-(")	.500	2.62	430
	BH_2-(")	.500	2.59	427
	CH_2-(")	.500	2.64	431
	O-(inert,noncombustible working fluid)	.500	1.85	361
	$O - H_2$	.500	3.64	506

Table 3. Theoretical performance of the best conventional and the most promising
free radical and metastable propellants.

PROPELLANT	WEIGHT FRACTION OF METASTABLE	Q (kcal/gm)	I_{sp} (sec)
$(2^3S_1)He^* - \begin{pmatrix} \text{inert working} \\ \text{fluid, e.g.,} \\ H_2 \text{ or He} \end{pmatrix}$	.500 .100 .050	57.0 11.4 5.70	2001 895 633
$(^2D)N^* - (\quad " \quad)$	.500	5.97[†]	648
$(^3P_{2,0})Ne^* - (\quad " \quad)$	.500 .250	9.52 4.76	820 580
$(^3P_{2,0})Ar^* - (\quad " \quad)$	.500	3.35	486
$(^1D)O^* - \begin{pmatrix} \text{inert, noncombus-} \\ \text{tible working} \\ \text{fluid} \end{pmatrix}$	.500	3.26[††]	480
$(^1D)O^* - H_2$	.500	5.05	597
$(a^1\Delta_g)O_2^* - H_2$	.825	3.53	498

METASTABLES

Table 3 (continued).

[†] Includes 4.02 kcal/gm resulting from the ground-state recombination $2N \longrightarrow N_2$ reaction that follows de-excitation.

[††] Includes 1.85 kcal/gm resulting from the ground-state recombination $2O \longrightarrow O_2$ reaction but no contribution from a conventional oxidation reaction.

Since I_{sp} is proportional to $Q^{\frac{1}{2}}$ and Q is directly proportional to the weight fraction of the free radical or metastab¹ species, it is a simple matter to figure the I_{sp} value for any propellant in Table 3 with an altered weight fraction value.

An inspection of Table 3 shows the extraordinary theoretical performance predicted for atomic hydrogen, the CH free radical, and the metastable excited states of helium, nitrogen, neon and atomic oxygen with H_2. Performance superior to the best conventional propellants is also indicated for atomic nitrogen with a weight fraction of .5 (meaning one N atom for each seven H_2 molecules if hydrogen is employed as the inert working fluid), while the free radicals BH, NH, BH_2, CH_2 and O would require weight fraction values in excess of .5 in order to surpass the performance of the best conventional propellants. Because of the relatively large molecular weights of O_2, F_2 and O_3, an increase in specific impulse cannot be achieved by supplementing a free radical recombination that yields H_2 as a product with a subsequent conventional combustion reaction (Windsor[210]). On the other hand, a significant increase in specific impulse is attainable if the ground-state atomic oxygen recombination process, the ^1D metastable atomic oxygen quenching and recombination processes, or the $a^1\Delta_g$ molecular oxygen quenching process is supplemented by a conventional combustion reaction with H_2, as shown by the illustrative entries in Table 3. The paramount issue is whether free radical and metastable propellants can be manufactured, stored, and used in practice in the required concentrations and amounts for rocket propulsion.

5. Manufacture and Storage

Free radicals and metastables are produced by a large variety of physical and chemical molecular dissociation and electronic excitation reactions. Except under rather special conditions, however, such reactive species cannot be produced in high concentrations and/or in large amounts, as required for propellant manufacture. Moreover, for the storage of highly reactive free radicals and metastables 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. Free radicals and metastables 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 or excitation processes that take place exclusively within a pre-formed matrix.

In the sections which follow, the methods for production of the reactive species and storage by the technique of matrix-isolation are reviewed and considered from the standpoint of rocket propellant requirements. Despite the fact that no free radical or metastable propellant has been manufactured and stored in a practical quantity to date, the survey presented here shows that important progress appears imminent with the venerable methods of production and storage being augmented by new technical aids. Indeed, the odds appear to favor the successful manufacture, storage, and use of an atomic hydrogen propellant within the present decade.

6. Methods of Production

Table 4 provides a list of methods that have been used to produce free radicals and metastables in gases, liquids, and solids.

METHOD OF PRODUCTION	REFERENCES FOR FREE RADICALS	REFERENCES FOR METASTABLES
PHOTOLYSIS: VISIBLE OR ULTRA-VIOLET RADIATION	189, [157], [130 — 138], [93 — 96], [164], [176], 1, 47, 73, 79, 151, 158, 159, 187	149, [118], [125]
X-RAYS	[157]	[125]
γ-RAYS	[157], [21], [202], 196	————
ELECTROMAGNETIC DISCHARGES	172, 11, 12, 16, 19, 51, 56, 57, 146, 150, 26, 80, 72, 200, 211	145, 181, 118
THERMAL METHODS	189, 25, 137, 179, 51, 177, 18, 38, 205, 206	121, 82, 3, 118
CHARGE TRANSFER PROCESSES	————	145, 46, 201, 5, 53, 178
ELECTRON IMPACT	[157], 203, 15	[125], [118], 191-193, 2, 126, 115, 29-31, 183-185, 81, 83, 40, 58, 13, 203, 15, 75, 106, 108 145, 179, 209, 204, 62, 3, 34, 69
ATOM & MOLECULE BOMBARDMENT	[157]	86, 186, 82, [125]

Table 4. Methods of production of free radicals and metastables. Square brackets denote in situ production references, while all other references describe production in a gas or liquid.

Most useful for basic scientific investigations in which small quantities of the reactive species are adequate, the very controllable method of photolysis utilizes visible or ultraviolet radiation produced by a high-intensity flash, an arc light, or a laser of suitable wavelength (below the dissociation or close to the excitation wavelength of the species). In photolysis, a so-called precursor species undergoes dissociation or excitation with the absorption of quanta in the intense radiation, thereby yielding the free radical or metastable (in the gas phase or in situ through an inert solid matrix at a cryogenic temperature, in usual applications). The method of photolysis cannot be employed for the production of large amounts of free radicals or metastables, as required by propulsion applications, because of severe limitations in the amount of energy that can be communicated to a medium by devices that emit visible or ultraviolet radiation. For example, a power level of the order of 10^5W is required to energize reasonable amounts of solid H_2 to a useful $H-H_2$ propellant mixture in a reasonable time (see Appendix C); such a required power level is several orders of magnitude above what can be delivered by a laser that emits radiation having a wavelength less than .276 μm (the threshold for dissociation of H_2).

Less developed than photolysis is the use of higher energy electromagnetic quanta, x-rays and γ-rays, which must effect dissociations and electronic excitations primarily through intermediate absorption processes. Although x-rays and γ-rays allow for in situ production of the reactive species, the effective absorption cross-sections are small for light-atom solids and thus the higher energy electromagnetic quanta are not attractive energy sources for the manufacture of large amounts of free radical or metastable propellants.

Electromagnetic discharges (microwave, radiofrequency, etc.) and various
thermal methods have been used widely for the gas phase production of free
radicals and metastables. These methods are capable of producing free
radicals and metastables at sufficiently high rates in the gas phase for
possible use in the manufacture of practical amounts of propellants. In
particular, free radicals can be produced copiously with glow discharges
at low resultant temperatures which facilitate the required rapid conden-
sation and trapping of the gas discharge in a cryogenic matrix. However,
electromagnetic discharges and thermal methods are not applicable to
in situ production and the more efficient concomitant trapping of the
reactive species. Likewise, charge transfer processes, as exemplified
by the helium ion reaction $He^+ + He \longrightarrow (2^3S_1) He^* + He^+$, have been found
to produce metastables copiously under suitable conditions in the gas phase
but not in a solid matrix.

Most promising for the production of free radicals and metastables
in the amounts required for propellants are electron impact techniques.
The latter are effective for copious production in situ in a cryogenic
matrix as well as in a cryogenic liquid, in a gas, or in (transverse bom-
bardment of) atom and molecular beams. For in situ production of reactive
species propellants by electron impact, it is necessary to generate free
electrons in quantity throughout a matrix (see Sections 8,9 and Appendices
C, D), because even very energetic electrons have a very short range in a
solid (e.g., an electron with an inital kinetic energy of 1 MeV will pene-
trate a distance of only about $(0.4 \text{ gm/cm}^2)/\rho$, where ρ is the density of
the solid).

+ A high-energy beam of electrons might be employed to energize thin wafers of a
matrix in a manner similar to the hydrogen atom bombardment in Appendix C, but
power-delivery and charge-accumulation considerations favor neutral atom bom-
bardment of a wafer.

Methods for the production of reactive species in situ by atom and molecule bombardment appear to hold considerable promise in theory, but still[†] have not been investigated with appropriate experimental research programs. At high energies for the atoms or molecules in the beam, secondary electrons will be produced via ionization processes in the matrix and assist in the production of reactive species by electron impact reactions (e.g., see Appendix C).

All of the free radicals and metastables that appear in Table 3 have been produced in high concentrations by one or more of the methods in Table 4. Specific references for the efficient production of H, N and O are given in the review article by Carstens et al.[27], for the production of CH, BH, NH, BH_2 and CH_2 in the review articles by Milligan and Jacox[134,135,137] and Ramsay[163], and for the production of the metastables $(2^3S_1)He^*$, $(^2D)N^*$, $(^3P_{2,0})Ne^*$ and Ar^*, $(^1D)O^*$ and $(a^1\Delta_g)O_2^*$ in the review article by Muschlitz[145]. Moreover, the methods of production for the latter reactive species appear to be readily adaptable to scale-up and large-quantity manufacture. In fact, production efficiencies can be expected to improve with scale-up and the increase in volume-to-surface-area ratios, owing to the suppression of surface recombination and quenching reactions. Therefore, the essential problem is the stabilization and storage of the reactive species by matrix-isolation.

[†]In 1960 Pimentel wrote (Ref. 157, p. 109): "The potentialities and limitations of atom bombardment are virtually unexplored.... The technique surely deserves continued exploration".

7. Matrix-Isolation

Important technical advances with the _in situ_ and gas condensation
applications of the matrix-isolation technique have been made in recent
years by Pimentel[157-159], Weltner[205,206], Milligan[130-138], and Jacox[93-96].
Since the host matrix material will be vaporized along with reaction pro-
duct gases during the energy release (see Section 10), the host species
must also serve as the working fluid for a free radical or metastable
propellant. Substances which have been used effectively for matrix-isola-
tion of highly reactive species and have low molecular weights are H_2, N_2,
O_2 and the lighter inert gases He, Ne, Ar. The latter candidates for the
dual role of matrix host and working fluid appear in Table 5 with the
temperature values required to maintain the solids at prescribed vapor
pressures (data extracted from Ref. 125, p. 192). With the exception of
helium, all of these substances are solids that have molecular concen-
trations close to .045 moles/cm^3 at temperatures less than $4^\circ K$.

Notwithstanding intensive development and applications of the techni-
que, it has not been possible to secure a reactive species concentration
greater than about 1% molar[†] in a matrix by the now venerable _in situ_ and
gas condensation methods of trapping with temperatures of the solid as low
as $4.2^\circ K$ (Fontana[56,57], Wall[202], Brown[21], Windsor[211], Fite[51], Brackmann[16],
Linevsky[118]).

[†]The molar concentration of about 1% was obtained for the free radical NCN
in an argon matrix by Milligan[130-132] with _in situ_ flash photolysis of the
precursor species cyanogen azide, N_3CN. Also see Ref. 157, p. 106.

TEMPERATURE (°K) REQUIRED TO MAINTAIN SOLID IN
EQUILIBRIUM AT INDICATED VALUE OF VAPOR PRESSURE

SPECIES	MOLECULAR WEIGHT	FREEZING POINT AT 760 TORR	10 TORR	10^{-1} TORR	10^{-3} TORR	10^{-5} TORR	10^{-7} TORR
H_2	2.016	14.0	11.7	8.0	6.05	4.8	4.0
He (†)	4.003	—	—	—	—	—	—
Ne	20.180	24.6	18.5	13.9	11.1	9.2	7.9
N_2	28.014	63.2	54.0	41.7	34.1	29.0	25.2
O_2	32.000	54.4	62.7	48.1	39.8	34.1	29.9
Ar	39.948	83.9	62.5	48.2	39.2	33.1	28.6

Table 5. Properties of matrix host-working fluid species. (†) Extreme pressures are required to solidify helium at low temperatures (e.g., 26 atmospheres pressure at 1° K), and the helium data from Ref. 125, p. 192 erroneously pertains to liquid-gas equilibrium values.

A principal difficulty that prevents the achievement of higher free radical and/or metastable concentrations is the imperfect isolation of free radicals in the direct deposition of a gas mixture or the imperfect isolation of precursor molecules for _in situ_ production (Pimentel[161])[†] . Another reason why higher concentrations of reactive species have not been secured with direct deposition methods is that solids formed from a gas by rapid condensation at a very low temperature (i.e., less than 1/2 the freezing point of the substance) have defect-laden crystalline or amorphous structures which favor the loss of reactive species by diffusion away from trapping sites (Pimentel[157])[††] and inhibit the cooling of additional condensed layers because of relatively poor thermal conductivity (Windsor[211,212]). A decisive advantage accrues, therefore, if the free radical or metastable can be produced _in situ_ from one of the matrix host species in Table 5 after a nearly perfect lattice structure has been formed by gradual cooling to a very low temperature. Moreover, the exceptionally high thermal diffusivity of such an ultra-cold lattice makes it possible to control the thermal side-effects of _in situ_ production,

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[†] A systematic experimental investigation aimed at identifying precursors which isolate themselves _preferentially_ (prior to _in situ_ reactive species production) has not been performed to date, however.

[††] The critical temperatures for the escape of atoms from traps in a rapidly formed (imperfect) lattice generally lie in a band from about 1/7 to 1/2 of the substance's freezing point, thus from about $9^{\circ}K$ to $32^{\circ}K$ for N in N_2 and from about $2^{\circ}K$ to $7^{\circ}K$ for H in H_2 (see Ref. 157, pp.75-78). For a nearly perfect lattice formed by gradual cooling of the substance, somewhat higher values for the bands of critical temperatures are indicated.

which might otherwise nullify the trapping effectiveness of a matrix with local heating that promotes the escape of reactive species from trapping sites. Those free radical and metastable propellant candidates in Table 3 which can be produced _in situ_ from matrix host species in Table 5 are atomic ground-state hydrogen, atomic ground-state and ^2D metastable nitrogen, atomic ground-state and ^1D metastable oxygen, 2^3S_1 metastable helium, $^3P_{2,0}$ metastable neon and argon, and molecular $a^1\Delta_g$ oxygen. Since practical competitive weight fractions (see Table 3) for ground-state or ^2D metastable atomic nitrogen are unlikely to admit stabilization in an N_2 matrix under the most favorable conditions (see Section 8), ground-state and ^2D metastable atomic nitrogen might be precluded as a prime candidate. The requirement of a radiative lifetime greater than 2 hours would preclude the metastables of atomic and molecular oxygen and very probably the metastables of neon and argon as well[†]. Finally, the severe technical difficulties involved in maintaining helium as a solid (see comment in caption under Table 5), and perhaps also the limited availability and high cost of helium ($\sim$ \$35/kgm) might preclude the helium metastable. Our prime candidate for a propellant is assuredly ground-state atomic hydrogen in an H_2 matrix.

Particularly noteworthy, the very low concentrations of reactive species obtained experimentally with venerable matrix-isolation techniques are well below what is predicted to be attainable by theoretical analysis that assumes an ideal lattice and the random static isolation of free radicals, subject to the proviso that two adjacent (nearest-neighbor) trapping

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[†]The observed lifetime of a matrix-isolated metastable species can be considerably less than the (vacuum-isolated) radiative lifetime because of the perturbing influence of the lattice (see Ref. 89, pp. 329-334).

sites cannot both accommodate reactive species (Jackson[89,90], Golden[70], Chessin[32]). According to such theoretical investigations of the problem, mole fractions in the neighborhood of 15% should be attainable with a nearly perfect lattice structure, in situ production, and ideal isolation (that admits only   nearest-neighbor recombinations). However, Jackson[91] has given a dynamical stability analysis based on a phenomeno-logical continuum model which appears to indicate that local

heat   diffusion from a chance reaction of a pair of free radicals (e.g., $H + H \longrightarrow H_2$ or $N + N \longrightarrow N_2$)may limit stable matrix-isolated concentrations of reactive species to less than about 2 or 3% molar. It is shown in Appendix B that Jackson's model leads to a characteristic heating time of the order 10^{-14} sec if the matrix is maintained at $4^{\circ}K$ or at a lower (realizable) temperature. Clearly, free radicals in the vicinity of a reacting pair cannot absorb requisite energy and escape their trapping sites during the very small characteristic time associated with a heat pulse in a matrix at $4^{\circ}K$ or at a lower temperature. A quantum mechanical treat-ment of the trapping stability problem, which takes account of the discrete character of particle and energy transport processes, would be of considera-ble interest and importance.

8. Current Experimental Work

To achieve the higher concentrations of free radicals and/or metastables required for useful propellants, it appears necessary to augment the vene-rable matrix-isolation method with supplementary technical aids that assist in the stabilization of the reactive species. Two main supplementary tech-nical aids are now being employed in experiments, namely, the use of very low temperatures (in the range $0.1^{\circ}K$ to $1.5^{\circ}K$)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 $1.5^{\circ}K$,

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 radicals, thereby inhibiting radical-radical recombination reactions.

The use of strong magnetic fields to assist in the stabilization of matrix-isolated free radicals is not a new idea (see, for example, Jones[104], Windsor[210,211], Fite[51], Brackmann[16]), 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 6 shows the low temperature-strong magnetic field combinations predicted theoretically (Ref. 104, p. 25) to yield substantial saturation[†] of electron spin-alignment in atomic hydrogen and thus to inhibit the recombination reaction $2H \longrightarrow H_2$ (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 6 are neither necessary nor sufficient, for atomic

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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 non-alignment of the electron spin in a hydrogen atom, given by $e^{-2\mu B/kT}$ where $\mu/k \approx 1^{\circ}K/15$ kG is the spin-magnetic moment of an electron divided by Boltzmann's constant. The values in Table 6 obtain if the probability factor is required to equal $.25 \times 10^{-16}$, a number that makes the lifetime of the atomic hydrogen sufficiently long for practical utilization (Ref. 104).

TEMPERATURE (^{O}K)	2	1	0.5	0.1	0.05
MAGNETIC FIELD (kG)	570	285	142.5	28.5	14.25

Table 6. Combinations of low temperatures and strong magnetic fields predicted theoretically to stabilize atomic hydrogen by nearly complete alignment of electron spins.

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 (Jones[104]) and electron-spin multipole radiative transitions (Mizushima[139]) 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[80] 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^{O}K in a magnetic field of approximately 50kG[††].

[†]The required quantum mechanical calculation would have features in common with the analysis reported in Ref. 156.

[††]Hess[80] 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 estimate made by Etters[48].

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 $1.2^{\circ}K$ in a magnetic field of 100kG; 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 later this year (Brown[22]).

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 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 $0.1^{\circ}K$ and a 35kG 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 Appendix D). Measurement of the atomic hydrogen concentration is accomplished by determining the magnetic susceptibility of the solid. This experiment will also yield results presently (Brown[22]).

9. Alternative Proposals for Manufacturing H-H₂ Propellants

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 $1^\circ K$ in a very strong magnetic field. This possible method for the manufacture of an F-H$_2$ propellant (about 15% atomic hydrogen by weight) has been worked out in a preliminary theoretical fashion by the present writer and is described here in Appendix C. The second scheme involves the use of the radio-nuclide 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 .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 $1^\circ K$ 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 a H-H$_2$ propellant (at least 15% atomic hydrogen by weight) has been sketched by the present writer in Appendix D. Both of these two schemes offer promise of providing an atomic hydrogen free radical propellant that will yield a specific impulse of about 740 sec for rocket engine conditions that make formula (A.6) applicable.

10. Energy Release

For all of the highly energetic free radical recombination reactions in Table 1 the activation energies are close to zero, and these recombination reactions proceed rapidly even at cryogenic temperatures if the species are mobile in the gas or liquid phase (Sinha[174], Adrian[1]). 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. Now the cross-section $\bar{\sigma}$ is certainly greater than 10^{-18} cm^2 for the radical-radical reactions of interest at low energies,[†] and it is required that n be greater than 10^{21} free radicals/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 $f^{-1} \cong (\bar{\sigma} n \bar{v})^{-1} < 10^{-7}$ sec. Quite clearly, in a time less than a tenth of a microsecond 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 free radicals directly without prior melting as solid propellants.

The necessity of using matrix-isolated metastables as solid propellants can be established by an argument similar to the one given above for free radicals. Electronically excited metastable species can react chemically or

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[†] Two orders of magnitude larger than the conservative general lower bound evoked here, the total cross-section for the reaction $H + H \longrightarrow H_2$ is about 1.1×10^{-16} cm^2 at thermal energies ($\gtrsim 0.5$ eV), with account taken of the fact that the reaction proceeds only in the total electron spin zero channel.

undergo an inelastic collision with virtually any atom or molecule, in-
cluding the inert gases in their ground states. Three types of colli-
sional quenching or de-excitation processes are possible: (1) collisional
processes leading to thermal (increased molecular translational energy)
or radiative release of the metastable species excitation energy (see Refs.
23,24,49,68,105,110,114,124,142,144,145), (2) ionization reactions (see Refs.
4,20,35,85, 87, 98,113,128,144,154,162,180,188), and (3) excitation
transfer reactions (see Refs. 68,112,166,173). The cross-sections for all
of these reactions are large, typically of the order 10^{-15} cm^2 at low to
moderate particle velocities. Although the latter ionization and excita-
tion transfer reactions do not in themselves effect the release of exci-
tation energy in thermal or radiative form, the products of the latter
reactions quickly undergo subsequent electronic recombination and energy-
liberating collisional processes at the high species concentrations of
interest. Thus, if a cryogenic solid containing a useful concentration
of trapped metastables were to melt and attain a temperature of, say, $30^{o}K$,
the characteristic time for overall effective quenching and sensible
energy release would be of the order or less than about a nanosecond, pre-
cluding use of a cryogenic solid containing metastables except directly as
a solid propellant.

Ignition of a free radical or metastable solid propellant can be accom-
plished 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 or quenching 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 tem-
perature 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 a millisecond. Because metastable species can also be quenched efficiently by suitable static electric fields or by electromagnetic radiation of appropriate wavelength (see Refs. 17,84,99,111,117, 141,155,214,215), more controllable nonthermal ignition systems are conceivable as alternatives for metastable solid propellants.

Under proper conditions, the deflagration that follows ignition of a free radical or metastable propellant can be expected to be steady and stable, albeit very rapid, with the recombination or quench'ng 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 microsecond, 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 solids of interest have thermal diffusivities which decrease rapidly with increasing temperatures above 1°K. For example, the thermal diffusivity of solid hydrogen is given approximately by (Ref. 36, p.13) $D \doteq 1.5 \times 10^4 \times (\exp - T/.845^\circ K) cm^2/sec$ in the temperature range $4^\circ K \gtrless T \gtrless 12^\circ K$ 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 the solids of interest are 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 solids.

Straight-forward order-of-magnitude considerations show that the burning velocity of a free radical or metastable solid propellant (i.e., the rate of linear regression of the melting surface) will be determined by the heat flux from the hot fluid to the surface via the equation

$$\lambda \ \frac{\Delta T}{\Delta x} \doteq V_s \ \rho_s \ h_L$$

where λ is the thermal conductivity of the liquid at the melting point (surface temperature) of the solid, ΔT is the temperature rise in the fluid in a small distance Δx (of the order of the local mean free path for molecules in the fluid) measured from the surface, V_s is the burning velocity of the solid, ρ_s is the density of the solid, and h_L is the enthalpy required to warm and melt a unit mass of the cold solid. The deflagration of an $H-H_2$ solid propellant (15% atomic hydrogen by weight) is discussed quantitatively in Appendix E, where the steady-state burning velocity $V_s \simeq 2.1$ m/sec is predicted for the propellant at a chamber pressure of $p = 100$ psia. As shown by the analysis in Appendix E, the heat flux to the solid is moderated by the large velocity of the flow and the rapid expansion of the fluid with heat release from the recombination reaction.

In the handling of a free radical or metastable propellant, careful precautions must be taken to insure that a sufficiently low stabilizing temperature (augmented by a sufficiently strong magnetic field, in the case of a free radical propellant) is maintained uniformly throughout the matrix at all times. It is also clear that contact of the solid propellant with any material which might catalyze energy release or absorb the reactive species from the matrix must be avoided. For example, it is known that platinum, nickel and certain other metals can catalyze the recombination of atomic hydrogen at low temperatures. Moreover, atomic hydrogen is absorbed readily

by and diffuses interstitially through virtually all ferrous alloys in contact with molecular hydrogen (Smialowski[175], Interrante[88]) with the dissociation $H_2 \rightarrow 2H$ catalyzed at any hydrogen-steel interface, and it may not be possible to contain an ultra-cold $H-H_2$ solid propellant in a high-strength steel casing. Solutions to the handling problems associated with free radical and metastable solid propellants should be obtainable by performing systematic experimental research with sample quantities of the cryogenic solid propellants.

11. Recommendations for Future Work

The following problems are of prime importance and worthy of detailed theoretical analysis in the near future:

(1) A quantum mechanical treatment of the trapping stability problem which takes account of the discrete character of particle and energy transport processes in a matrix.

(2) The specialization of (1) for atomic hydrogen in an H_2 matrix, extended to include the quantum mechanical effects of a superimposed strong magnetic field on the stabilization at very low temperatures.

(3) The extension of (2) to include the effects of heat transport into a pre-stabilized $H-H_2$ propellant that undergoes surface deflagration.

It is recommended that the current atomic hydrogen experimental program at LRC be expanded to include other basic experiments which will provide data for testing the theoretical results of (2) and (3).

Summary

Propellants composed of any of the free radicals H, N, O, CH, PH, NH, BH_2, CH_2 or the metastables $(2^3S_1)He^*$, $(^2D)N^*$, $(^3P_{2,0})Ne^*$, $(^3P_{2,0})Ar^*$. $(^1D)O^*$, $(a^1\Delta_g)O_2^*$ can, in theory, give specific impulses well above the maximum attainable for O_2 - H_2 or any other conventional oxidizer-fuel combination. In particular, extraordinary theoretical performance is predicted for atomic hydrogen, the CH free radical, and the metastable excited states of helium, nitrogen, neon, and atomic oxygen with H_2.

A large variety of molecular dissociation and electronic excitation reactions can be employed to produce free radicals and metastables in gases, liquids and solids, but the reactive species cannot be produced in high concentrations and/or in large amounts except under rather special conditions. Moreover, there is only one method known to be effective for the storage of these reactive species, namely, matrix-isolation. In the latter technique, the reactive species are trapped as isolated entities in an inert solid at a cryogenic temperature, either by rapid condensation of a gas mixture or with in situ production in a pre-formed matrix by electromagnetic quanta or energetic particle bombardment. Although no free radical or metastable propellant has been manufactured and stored in a practical quantity to date, important progress appears imminent with the venerable methods of production and storage being augmented by new technical aids.

Electromagnetic discharges and various thermal methods are capable of producing free radicals and metastables at sufficiently high rates in the gas phase for possible use in the manufacture of practical amounts of propellants, but these methods are not applicable to in situ production and the more efficient concomitant trapping of the reactive species.   Particularly effective for the production of free

radicals and metastables in situ, electron impact techniques are most pro-
mising for the manufacture of reactive species propellants. The short
range of energetic electrons in a solid requires that they be generated in
quantity throughout the matrix. Methods for the production of storable
reactive species in situ by atom and molecule bombardment also hold consi-
derable promise and warrant future experimental study.

Since the host matrix material will be vaporized along with product
gases during the energy release, the host species must also serve as the
working fluid for a free radical or metastable propellant. Candidates for
the dual role of matrix host and working fluid are H_2, N_2, O_2, He, Ne and
Ar. A decisive advantage accrues if the free radical or metastable can be
produced in situ from one of the latter matrix host species. Among the
propellant candidates with this property, atomic hydrogen in an H_2 matrix
is most accessible to near-term development with existing technology.

Two main supplementary technical aids are now being employed in experi-
ments to achieve higher concentrations of reactive species with matrix-
isolation, namely, the use of very low temperatures (in the range $0.1^\circ K$ to
$1.5^\circ K$) 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 a
matrix is expected at temperatures below $1.5^\circ K$, while very strong magnetic
fields can prevent radical-radical recombination reactions by effecting
the parallel alignment of unpaired electron spins in free radicals. Signi-
ficant concentrations of atomic hydrogen, apparently about 10% molar, have
been obtained in the matrix-isolated condensate from a hydrogen glow dis-
charge cooled very rapidly to about $1.3^\circ K$ in a magnetic field of approxi-
mately 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 $1^{\circ}K$ (prospectively at $0.1^{\circ}K$ in the case of tritium) in a strong magnetic field. Another method for manufacturing an $H-H_2$ propellant ($\sim 15\%$ atomic hydrogen by weight, $I_{sp} \cong 740$ sec) involves bombardment of H_2 with a cyclotron-produced beam of 10 MeV hydrogen atoms.

Estimates of the characteristic times for generic free radical recombination reactions and generic metastable quenching reactions show that the matrix-isolated reactive species must be used directly without prior melting as solid propellants. Under suitable conditions, the deflagration of a free radical or metastable propellant is expected to be steady and stable, albeit very rapid. A burning velocity of about 2.1 m/sec is predicted for an $H-H_2$ propellant ($\sim 15\%$ atomic hydrogen by weight) at a chamber pressure of 100 psia. The handling problems associated with such solid propellants are believed to be amenable to experimental solutions.

Appendix A: Theoretical Specific Impulse Formula

Let Q denote the overall net energy release per unit mass of propellant and η denote the overall 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

$$I_{sp} = \sqrt{2 \eta Q} / g, \qquad (A.1)$$

where $g \equiv 980$ cm/sec^2 is the acceleration of gravity at sea level. The overall efficiency for energy conversion in (A.1) can be expressed as

$$\eta = \eta_{ideal} \, \eta_{losses} \qquad (A.2)$$

in which $\eta_{ideal} = 1 -$ (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 $\eta_{losses}(\leq 1)$ accounts for real fluid dissipative effects. We have

$$\eta_{ideal} = [1 + 2(\gamma - 1)^{-1} M_{ex}^{-2}]^{-1} \qquad (A.3)$$

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 (A.2), 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

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[†]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 .03 kcal/gm and hence negligible compared to their stoichiometric energy release $Q = 3.18$ kcal/gm.

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,

$$R = M_{ex}^{-1} \left[2(\gamma+1)^{-1} + (\gamma-1)(\gamma+1)^{-1} M_{ex}^{2} \right]^{(\gamma+1)/2(\gamma-1)},$$ (A.4)

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

$$M_{ex}^{2} = \left(\frac{\gamma+1}{\gamma-1} \right)^{(\gamma+1)/2} R^{\gamma-1} - \left(\frac{\gamma+1}{\gamma-1} \right) + O(R^{-(\gamma-1)}).$$ (A.5)

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 (A.5) and (A.3) yield $M_{ex}^{2} = 24.0$ and $\eta_{ideal} = .750$, while for $R = 60$ and $\gamma = 1.30$ (A.5) and (A.3) yield $M_{ex}^{2} = 27.9$ and $\eta_{ideal} = .808$ respectively. If we assume the latter values for R and γ and set the efficiency factor η_{losses} equal to unity in (A.2), we obtain the theoretical specific impulse formula from (A.1) and (A.2),

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[+]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 (A.3) and (A.5) 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}.

$$I_{sp} = 265 \ (Q/1 \ kcal/gm)^{\frac{1}{2}} \ sec,$$

$$[for \ R = 60, \ \gamma = 1.30, \ \eta_{losses} = 1].$$

(A.6)

Formula (A.6) is used to estimate the performance of propellants in the body of this report. 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/gm and (A.6) gives $I_{sp} = 456$ sec.

Appendix B: Local Heat Pulse Produced by a Chance Reaction of Free Radicals in a Matrix

Following Jackson[91], let W denote the energy transmitted to the lattice by the recombination reaction of a pair of free radicals. Since only a fraction of the total energy release from such a recombination reaction will be absorbed by the lattice, we have $W < 4.5$ eV for $H + H \rightarrow H_2$ and $W < 9.8$ eV for $N + N \rightarrow N_2$. Let T_f denote the minimum local steady-state temperature required for freeing a radical from a trapping site and T_o denote the initial uniform temperature of the solid matrix. Then trapped radicals may possibly be freed by the approximately Gaussian heat pulse that emanates from a chance reaction through a spherical region of radius

$$r_f \approx [W/nc \ (T_f - T_o)]^{1/3}$$

(B.1)

in which $n \approx .045$ moles/cm^3 is the concentration of molecules (e.g., H_2 or N_2) in the solid and $c \approx [(T_f + T_o)/20°K]^3$ cal/mole $- °K \approx 2.6 \times 10^{19} [(T_f + T_o)/20°K]^3$ eV/mole $- °K$ is a simple approximation for the mean molar specific heat of the solid (proportional to T^3 at temperatures below about 15 K) in terms of the mean temperature $\frac{1}{2}(T_f + T_o)$ over the thermal range of interest (see Ref. 91).

Letting D denote the thermal diffusivity of the solid, it follows that trapped radicals within distance r_f of the recombination reaction experience the heat pulse during a time duration given approximately by

$$t_f \cong r_f^2/D \cong \left[W/nc(T_f - T_0)\right]^{2/3}/D. \tag{B.2}$$

For the typical parameter values $W = 2$ eV, $T_f = 10^\circ K$, $D \cong 150 \ cm^2/sec$ at $T_0 \cong 4^\circ K$ and $D \cong 100 \ cm^2/sec$ at $T_0 \cong 1^\circ K$, we obtain

$$\left. \begin{array}{l} r_f \cong .95 \times 10^{-6} cm \\ \\ t_f \cong .60 \times 10^{-14} sec \end{array} \right\} \quad \text{at} \quad T_0 \cong 4^\circ K \tag{B.3}$$

$$\left. \begin{array}{l} r_f \cong 1.05 \times 10^{-6} cm \\ \\ t_f \cong 1.10 \times 10^{-14} sec \end{array} \right\} \quad \text{at} \quad T_0 \cong 1^\circ K. \tag{B.4}$$

It is evident that radicals in the vicinity of a chance recombination reaction cannot absorb requisite energy and escape their trapping sites during the small characteristic time of order 10^{-14} sec in (B.3) and (B.4), for a radical would have to acquire a velocity of the order 10^6 cm/sec to move an Ångström during the characteristic time of the heat pulse. Hence, a quantum mechanical treatment of the trapping stability problem is required.

Appendix C: 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 inch diameter and radiofrequency power supplied at about 250 kV, will deliver an external (extracted) beam of 10 MeV protons at a steady current of about .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 $3 \times 10^3 \ cm^2$ (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) state of hydrogen, $H^+ + Ce \longrightarrow H + Ce^+$, can be estimated for 10 MeV protons by extrapolation of lower energy data (Spiess[178]) 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 Hughes[86] 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 3×10^3cm^2.

Now suppose that a 10 liter volume (equivalently, .71 kgm) 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 3×10^3cm^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 (Contreras[36], Miller[127]).

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 (Brackmann[16], Fite[51]). 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 3Å) 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 $1^{\circ}K$ 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 $1^{\circ}K$ by detailed balancing considerations.

[†]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.

It is estimated that less than .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 Truhlar[194]). 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 (Bondybev[12]) or assume lattice sites occupied previously by H_2 molecules which have been dissociated. If we take .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.

[†] The associated local heating throughout the solid (less than 60 W ≈ 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.

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 v ergo effective dissociation
to yield trapped free hydrogen atoms during a total bombardment time of
about 5.5 minutes. The resulting $H-H_2$ solid propellant wafer, 15% free
hydrogen atoms by weight, will have a stored recoverable specific energy
$Q \doteq 7.81$ kcal/gm and thus will yield a theoretical specific impulse
$I_{sp} \doteq 742$ sec for rocket engine conditions that make formula (A.6) applic-
able.

It should be noted that the overall efficiency for energy storage in
the $H-H_2$ solid propellant is approximately .28, with 250 kW cyclotron
power for 5.5 minutes yielding 5.55×10^3 kcal of stored energy in a .71 kgm
wafer of solid hydrogen. To produce a 1000 kgm amount of the propellant
would require a conveyer belt operation and 129 hours 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.

Appendix D: 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 radio-active phosphorus atoms in the ratio of one P^{32} atom for every 50,000 H_2 molecules (i.e., .002% molar P^{32}) and cooled gradually through its freezing point and down to a temperature below $1^{\circ}K$, 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 $H + H_2 \longrightarrow 3H$ dissociation reactions. Since the net energy absorbed per dissociation is 4.5 eV, at least 1.53×10^4 H_2 molecules will be 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 formula (A.6) applicable.

Appendix E: Deflagration of an H - H₂ Solid Propellant

Consider an H - H_2 solid propellant, 15% atomic hydrogen by weight, at an initial temperature of $1^{\circ}K$ and a constant pressure of 100 psia. If an elemental volume of the solid is heated, the density will remain approximately constant at $\rho_s = .088 \ gm/cm^3$ until the melting point is reached at a temperautre just above $14^{\circ}K$. The density of the fluid, equal to about .073 gm/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

$$\rho \cong (.170 \quad gm-^{\circ}K/cm^3) \ (T - 11.67^{\circ}K)^{-1} \qquad (E.1)$$

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

$$\rho u = \rho_s \ v_s, \qquad (E.2)$$

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 (E.1) and (E.2) that

$$u \doteq .518 \ v_s \ \left(\frac{T}{1^{\circ}K} - 11.67 \right) \qquad (E.3)$$

for a fluid element at temperature T.

Now with the propellant mixture yielding the overall net energy release $Q \doteq 7.81$ kcal/gm, the functional dependence $c_p = c_p(T)$ for H_2 gives a final (adiabatic flame) temperature of about $2090^{\circ}K$ for the product H_2 gas. If

Δt denotes the time interval following melting for a fluid element to attain the temperature of $1000^{\circ}K$, then the temperature of a fluid element will increase by the amount $\Delta T = 1000^{\circ}K - 14^{\circ}K = 986^{\circ}K$ in travelling the distance

$$\Delta x \equiv \int_{0}^{\Delta t} u \, dt \quad . \tag{E.4}$$

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

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

in which

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

is the rate function associated with a velocity-averaged total cross-section of $\bar{\sigma} \cong 1.1 \times 10^{-16} \text{ cm}^2$ for the recombination reaction. The temperature of a fluid element will increase from $T \cong 14^{\circ}K$ (for which $\omega \cong .15$, see below) to $T \cong 2090^{\circ}K$ (for which $\omega = o$) with an approximately linear[†] dependence on ω,

$$T \cong 2090^{\circ}K - (13,840^{\circ}K)\omega \quad . \tag{E.7}$$

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

[†]The effective specific heat of the fluid is bolstered at low temperatures by the heat of vaporization ($\sim$107 cal/gm) distributed about $32^{\circ}K$ and by the heat of conversion of para$-H_2$ to ortho$-H_2$ ($\sim$170 cal/gm converted).

$$\Delta x \doteq (8.65 \times 10^{-8} \text{ sec}) \; v_s \int_{14}^{1000} \left(\frac{\theta - 11.67}{2090 - \theta} \right)^2 \frac{d\theta}{\theta^{\frac{1}{2}}} \qquad (E.8)$$

$$\doteq (7.0 \times 10^{-7} \text{ sec}) \; v_s.$$

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

$$\frac{\Delta T}{\Delta x} \doteq (1.41 \times 10^9 \; {}^{\circ}\text{K/sec}) \; v_s^{-1} \qquad (E.9)$$

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

$$\lambda \; \frac{\Delta T}{\Delta x} \doteq v_s \; \rho_s \; h_l, \qquad (E.10)$$

where $\lambda \doteq .25 \text{ mW/cm-}{}^{\circ}\text{K} \doteq 6.0 \times 10^{-5} \text{ cal/cm-sec-}{}^{\circ}\text{K}$ is the estimated[†] thermal conductivity of the fluid at 14°K and $h_l \doteq 22 \text{ cal/gm}$ is the enthalpy required to warm and melt a unit mass of the solid initially at 1°K[††]. Hence, from (E.9) and (E.10) we obtain the burning velocity

$$v_s \approx 210 \text{ cm/sec.} \qquad (E.11)$$

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

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[†]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 $.C5 \text{ mW/cm-}{}^{\circ}\text{K}$ for liquid para-H_2 at 14°K and 100 psia.

[††]We have 14 cal/gm coming from the heat of fusion, 5 cal/gm from the T^3 integration, and about 3 cal/gm 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).

expression $D/v_s^2 \doteq 8.0 \times 10^{-9}$ sec, where $D \doteq 3.5 \times 10^{-4}$ 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 ($\sim 4^{\circ}K$) for significant escape from trapping sites. Next observe that the distance $\Delta x \doteq 1.47 \times 10^{-4}$ cm [given by (E.8) and (E.11)] has the same order of magnitude as the mean free path for H_2 molecules at $1000^{\circ}K$ 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 (E.8) with the value 2000. Finally note that the neglect of species and thermal diffusive transport in writing Eqs. (E.5) and (E.7) is justified, because the diffusivities in the fluid are very small compared to the mean flow velocity $u \Big|_{T=1000^{\circ}K} \doteq 1.07 \times 10^5$ cm/sec multiplied by the approximate flame thickness 1.81×10^{-2} cm.

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