

Introduction - The Nature of an Advanced Propellant

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The propellant chemist knows what is needed to make a truly advanced propellant - the energy of the cryogenics (fluorine/hydrogen); the density of solids and the ability to tailor properties to the mission at hand. The energetics are a direct consequence of the simplified specific impulse relationship:

$$I_s = \frac{F}{\dot{w}} = \frac{\text{thrust}}{\text{weight rate of flow}}$$

which is a major aspect of propellant performance expressed in units of pound per pound per second, or more commonly, just seconds. The over-all efficiency of the rocket system is, in turn, dependent on the combined efficiencies of the combustion chamber (where the propellants are burned) and the nozzle (where the thermal energy is to kinetic energy). As a rough approximation in screening potential propellant combinations, it is frequently considered that specific impulse is proportional to

$$\sqrt{\frac{\Delta H}{M}}$$

Thus, simply stated, a high heat release yielding low molecular weight products is most desirable.

The total figure of merit of propellant system performance is usually taken to be specific impulse multiplied by propellant bulk density to some exponent which may range from 0.05 to 1.0. The actual value of the exponent depends upon a complex relationship among the propellant, its properties, the mission, and design criteria. Thus, the high density of the propellant in a volume-limited application such as an air-launched missile is extremely important whereas for an upper-stage it is not nearly so critical.

The mission similarly influences the essential properties of the propellant ingredients. The military require rocket motors or engines which will withstand operational thermal cycling and handling. In addition, they must be safe under combat conditions in that they will not detonate in a fire or when struck by bullets for example. They must be capable of storage for years - ideally under hermetically sealed conditions. There are many who presume that a more energetic advanced propellant must necessarily be less safe due to the explosion hazard. This confuses the thermodynamic and kinetic parameters. On the other hand, rockets for space applications do not have the serious restrictions inherent in a military mission, and thus cryogenics find a notable use. Advanced propellant chemistry, as a consequence, is not generally concerned with cryogenics but rather with conferring the energetics of the cryogenics on earth-storable liquids and solids. With some levity then, one may strive to make hydrogen and fluorine, liquid or solid at room temperature! This leads directly to the context of this Symposium.

The first several papers concern themselves with a theoretical approach to extremely advanced oxidizers; the next group examine oxygen oxidizers primarily by the study of physical and combustion characteristics of importance in propellants. Following are two papers on binders which act as fuels as well as conferring desirable physical properties on solid propellants. It will be noticed at this point that there is no coverage of the light metal hydride fuels. This is a result of the vast synthetic efforts over the past ten years, which resulted in production capabilities for the boranes - diborane, pentaborane, decaborane and their derivatives. The tenacity with which the desirable hydrides of aluminum and beryllium hold on to their Lewis bases, ethers and amines, has prevented their isolation in a sufficient purity to make them useful as propellant fuels. The impure beryllium hydride prepared at Los Alamos ten years ago, just as the aluminum hydride prepared at Tufts shortly thereafter, offers little or no performance advantage over the use of the respective metals.

After the binder papers are five presentations which explore the physical, combustion and detonation properties of liquid systems. The balance of the Symposium is concerned primarily with the more energetic oxidizers based upon nitrogen-fluorine and oxygen-fluorine bonding. It is from this area that the most significant improvements will one day come. For with the oxidizer comprising 70 to 80 percent of the propellant combination, a relatively small improvement here is magnified as compared with the fuel. The use of metals, mentioned above, in both solid propellants and in liquid slurries, has been widely publicized and will not be discussed here. Their use, incidentally, originated in explosives technology and is commonplace at the present time.

It must be clearly indicated here, that as broad as the coverage of this Symposium appears, there is much propellant chemistry which has not been included. The experimental determination of thermodynamic properties such as heats of formation and equilibrium constants, as well as the calculations of theoretical performance have been presented at other symposia. The applied chemistry related to the modification of polymers, and hence mechanical and burning properties of solids, have other forums. The actual firing of solid motors and the determination of thrust and efficiency have been omitted, while the research into combustion instability and the transition from deflagration to detonation are only alluded to.

The Advanced Propellant

The ideal advanced propellant is then one which yields a high heat release in the chamber, converts this to translational kinetic energy in the nozzle while generating low molecular weight "perfect" gases. This latter requirement is rarely satisfied due to the presence of HF, CO, CO₂ and H₂O in the metal-free systems and to condensed metal oxides in the metal systems. This two-phase flow problem with a metallized propellant can easily result in a five percent efficiency loss. Therefore, although the metals have an extremely attractive heat release, a penalty of this five percent is imposed from the start even presuming perfect combustion efficiency. Everything considered, a performance of 92 percent of theoretical is close to maximum efficiency. The metal-free liquid bipropellant systems however are capable of achieving 97 to 98 percent of theoretical performance.

Low molecular weight "perfect" gases clearly point the way to hydrogen which accounts for the extreme performance of a nuclear propulsion unit. In this system, the reactor merely heats the light-weight gas. Although CH₄ and NH₃ have also been considered for nuclear applications, decomposed methane has a molecular weight of 5.4, ammonia of 7, while hydrogen has a molecular weight of 2. If too high temperatures are employed, the molecular hydrogen will dissociate into the atoms, and absorb additional

energy. In a chemical propulsion system the hydrogen will come, in the case of solids, from the binder and NH_4ClO_4 and, in liquids, from N_2H_4 and its derivatives or pentaborane or diborane - the latter being space-storable, but not earth-storable. Much of the simple theoretical comparisons of oxidizers are therefore based on combustion with N_2H_4 or B_5H_9 for liquids and on more complex systems for solids.

M. Barrère has published the following performance calculations.

Table I - Storables

Propellant	Composition	I_s	I_{sd}	
SOLID	Present Ammonium perchlorate Al + plastic	267	455	
	Future Ammonium perchlorate LiBe + plastic	290	377	
LIQUID	Present	HNO_3 -DMH	276	348
		HNO_3 - N_2H_4	283	362
		N_2O_4 -DMH	285	336
		N_2O_4 - N_2H_4	292	356
		H_2O_2 -DMH	278	345
		H_2O_2 - N_2H_4	282	355
	Future	ClO_3F - N_2O_4	295	360
		N_2O_4 - B_5H_9	306	337
		H_2O_2 - B_5H_9	312	311
		ClF_3 - N_2H_4	294	444
HYBRID	Present	H_2O_2 -Al + plastic	289	435
		HNO_3 -Al + plastic	273	414
		NO_2ClO_4 - N_2H_4	295	428
	Future	ClF_3 -LiH	293	445
		ClF_3 -Li	318	369
		N_2O_4 -BeH ₂	351	530
H_2O_2 -BeH ₂	375	566		

Table II - Cryogenics

Propellant	Composition	I_s	I_{sd}
LIQUID	O_2-H_2	391	109
	$O_2-N_2H_4$	335	365
	F_2-H_2	410	185
	$F_2-N_2H_4$	363	476
	O_2-F_2-DMH	345	398
HYBRID	F_2-LiH	363	476
	F_2-O_2 -plastic	343	412
	F_2-BeH_2	395	604
	O_2-BeH_2	371	486
	F_2-AlH_3	353	551

It can be seen that future storable liquid propellant systems are in the 300 to 315 sec. range, while future solid systems are around 290 secs. By the use of an "idealized" hybrid composed of H_2O_2/BeH_2 , 375 secs. is possible in a storable propellant. Not only is the pure hydride unavailable, but hybrid technology leaves much to be desired.

Barrère's analysis did not mention N_2F_4 or OF_2 since these are "soft" cryogenics in that their boiling points are low. Their performance is excellent, however.

Table III

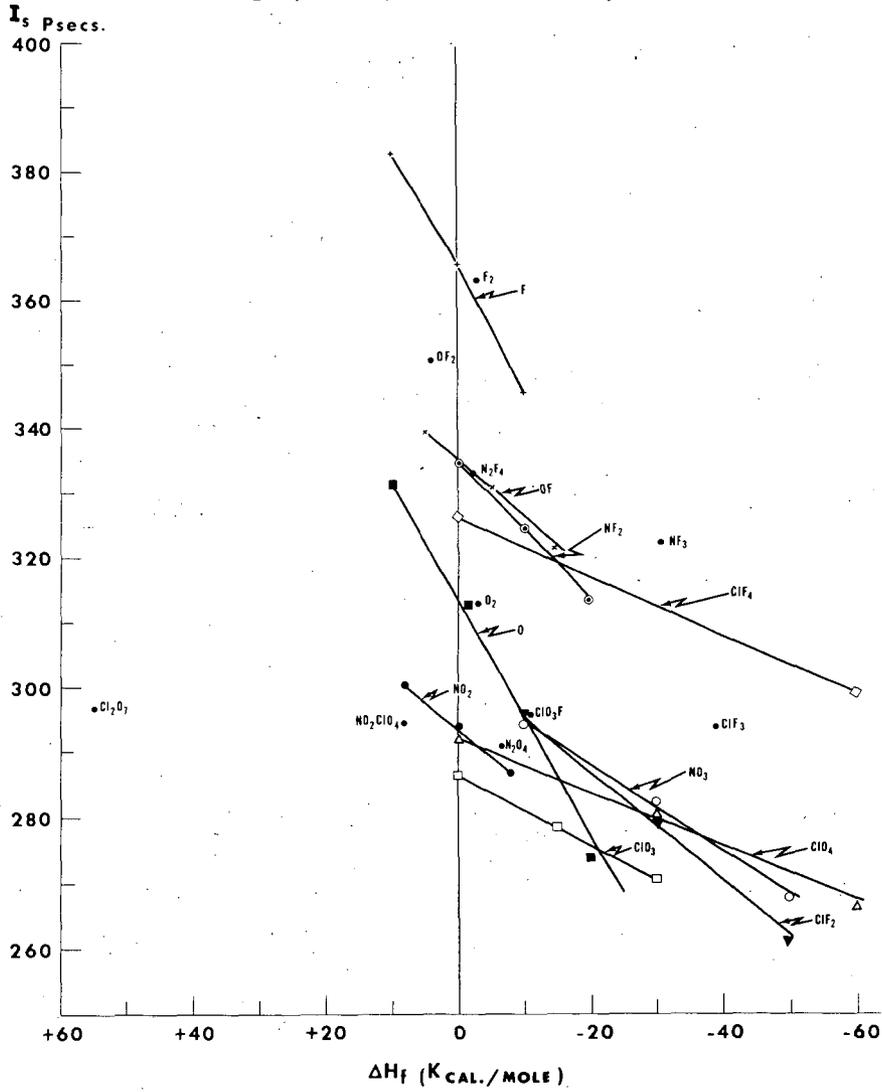
	b. p. °C	I_{sp}	
		N_2H_4	B_5H_9
N_2F_4	-74	333	333
OF_2	-145	345	359

The performance of F_2 , OF_2 and NF_3 or N_2F_4 gives the insight into where the synthesis potential of rocket oxidizers is.

An attempt has been made here to determine the relative value of an oxidizing group as a propellant with a model fuel, N_2H_4 . Hydrazine was chosen for simplicity and availability of calculations. The ΔH_f has been chosen in most cases by analogy. For example, to obtain one point for an -O, one may use one-third of +30 kcal/mole, the ΔH_f of O_3 . For another point, one-half of -3.48 kcal/mole, the ΔH_f of $O_2(1)$. In this manner a series of curves were generated (Figure I). Inherent then in any calculation of this type is the nature of the group to which the oxidizing group of interest is bonded.

Figure I

OXIDIZER GROUP CONTRIBUTIONS
 ($N_2 H_4$ 1000 psia $\xrightarrow{\text{shifting}}$ 14.7 psia)



Several conclusions which can be drawn from such a curve would have been approximated "intuitively" by the synthesis chemist by reason of his background knowledge.

If one chooses a constant ΔH_f an index of oxidizing power may be obtained. For a $\Delta H_f = -10$ kcal/mole the order in Table IV is observed.

Table IV - Relative Order of Oxidizing Power

-F	-ClF ₂
-OF	-NO ₃
-NF ₂	-ClO ₄
-ClF ₄	-NO ₂
-O	-ClO ₃

If one chooses a target I_{sp} there appear to be certain groups which, if embodied in an oxidizer, would have difficulty in attaining the objective. Consider, if 310 secs. is chosen as the target, the groups in Table V would not be expected to reach the objective unless combined with the highly energetic groups above them in Table IV.

Table V - Oxidizer Groups Not Expected to Yield 310 Secs

-ClF ₂
-NO ₃
-ClO ₄
-NO ₂
-ClO ₃

The steepest slopes observed are those for -F and -O indicating the dramatic contribution to impulse by a slight increase in ΔH_f . In general, then, -N compounds have a more positive slope than -Cl compounds, demonstrating the relatively better performance of N as a carrier atom over Cl.

A test of the value of such a curve (see Table VI) may be made by locating the known oxidizers relative to the group contribution curves.

Table VI - Correlation of Known Oxidizers with Group Contributions

<u>Oxidizer</u>	<u>Location</u>	<u>Correlation</u>
F_2	on F	excellent
OF_2	midway between OF and F	excellent
N_2F_4	on NF_2	excellent
O_2	on O	excellent
NF_3	---	poor
ClF_3	midway between ClF_4 and ClF_2	good
ClO_3F	above ClF_2 , much above ClO_3	poor
N_2O_4	close to NO_2	good
NO_2ClO_4	between NO_2 and extrapolated ClO_4	good
Cl_2O_7	far removed from extrapolated ClO_4 and ClO_3	poor

Hypothetical oxidizers may be tested in the same way. However, the question arises as to what ΔH_f to choose, and here lies the primary limitation. Having the curve, would one have chosen $\Delta H_f Cl_2O_7 = +55$ kcal/mole or $\Delta H_f NF_3 = -29$ kcal/mole?

In conclusion then, it appears that the most desirable oxidizer is one which packs in the maximum of fluorine bonded to itself (F_2), bonded to oxygen (OF_2 , O_2F_2 , O_3F_2 , O_4F_2), or bonded to nitrogen (NF_3 , N_2F_4 , N_2F_2) in decreasing order of energy. The fuel must pack in the working fluid hydrogen while both should have high heats of formation and yield products with low heats of formation. With the covalent liquids and gases, our ability to predict heats of formation is quite good - with ionic solids, the unknown contributions from lattice energy preclude this.