The Nature of an Advanced Propellant

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Although propellant chemistry research concerns itself with everything from the synthesis and characterization of new molecules to their formulation and combustion in a rocket motor or engine, advanced propellant chemistry is primarily directed towards the search for new oxidizers. This intense effort is dictated by the greater contribution to energy which can be made by a small improvement here since the oxidizer normally comprises 70–80% by weight of the propellant combination. A semitheoretical approach to the ultimate energy achievable in propellants is presented.

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 overall efficiency of the rocket system, in turn, depends on the combined efficiencies of the combustion chamber (where the propellants are burned) and the nozzle (where the thermal energy is converted to kinetic energy). As a rough approximation in screening potential propellant combinations, it is frequently considered that specific impulse is proportional to:

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

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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 necessarily must be less safe owing to the explosion hazard. They are confusing 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. Consequently, advanced propellant chemistry 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 oxidizers primarily by studying important physical and combustion characteristics in propellants. Two papers follow on binders which act as fuels as well as conferring desirable physical properties on solid propellants. At this point there is no coverage of the light metal hydride fuels.

The next five papers 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 70–80% 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.

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 modifying polymers, and hence mechanical and burning properties of solids, have other forums. The actual firing of solid motors and 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 and converts this to translational kinetic energy in the nozzle while generating low molecular weight "perfect" gases. This latter requirement is rarely satisfied owing to the presence of HF, CO, CO_2 and H_2O 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 5% efficiency loss. Therefore, although the metals have an extremely attractive heat release, a penalty of 5% is imposed from the start, even presuming perfect combustion efficiency. Everything considered, a performance of 92% is close to maximum efficiency. The metal-free liquid bipropellant systems, however, are capable of achieving 97–98% 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 lightweight gas. Although methane and ammonia 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, molecular hydrogen will dissociate into 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.

Barrère (1) has published the performance calculations shown in Tables I and II.

It can be seen that future storable liquid propellant systems are in the 300–315 sec. range while future solid systems are around 290 sec.

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–UDMH	276	348
		HNO_3–N_2H_4	283	362
		N_2O_4–UDMH	285	336
		N_2O_4–N_2H_4	292	356
		H_2O_2–UDMH	278	345
		H_2O_2–N_2H_4	282	355
	Future	ClO_3F–N_2H_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–UDMH	345	398
	F_2–LiH	363	476
Hybrid	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

Table III

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

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, as Table III shows.

The performance of F_2, OF_2, and NF_3 or N_2F_4 shows 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 1). Inherent then in any calculation of this type is the nature of the group to which the oxidizing group of interest is bonded. 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.
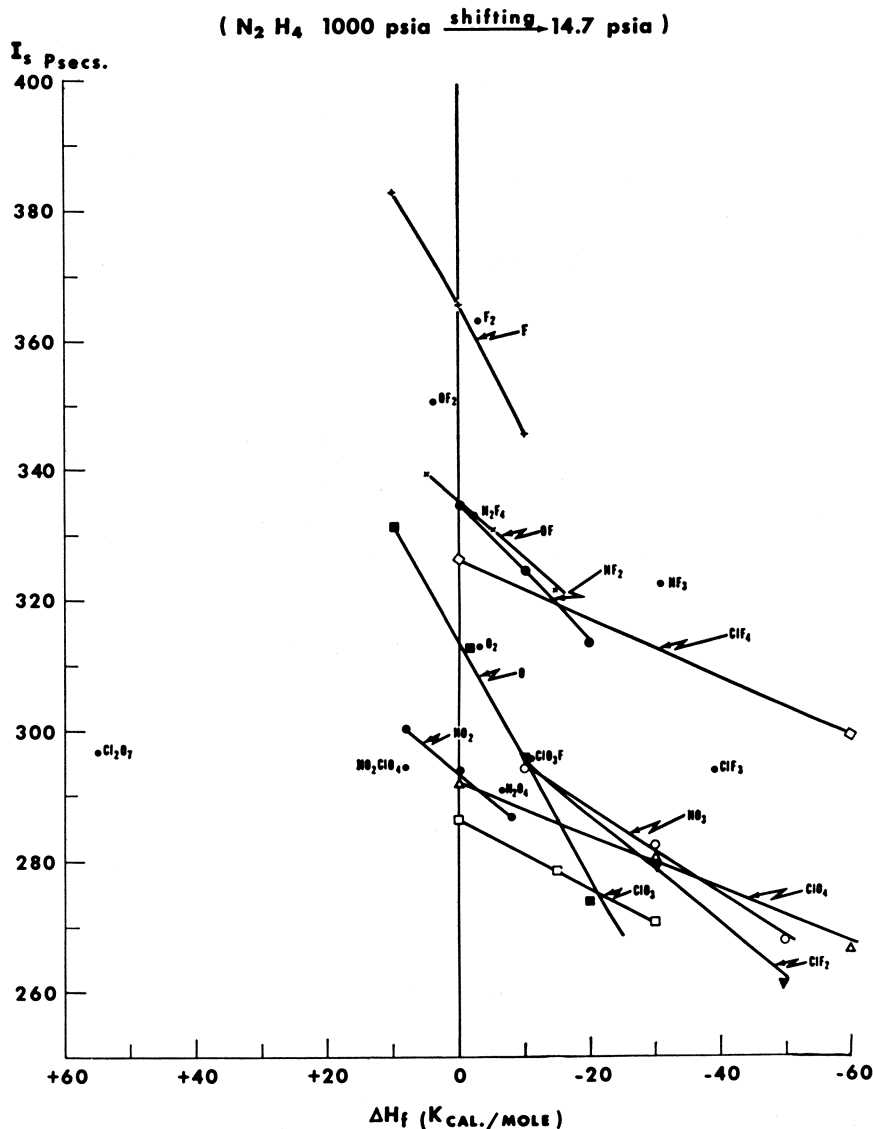

Figure 1. Oxidizer group contributions

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 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.

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. If 310 sec. 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.

The value of such a curve (*see* Table VI) may be tested by locating the known oxidizers relative to the group contribution curves.

Table VI. Correlation of Known Oxidizers with Group Contributions

Oxidizer	Location	Correlation
F$_2$	on F	excellent
OF$_2$	midway between OF and F	excellent
N$_2$F$_4$	on NF$_2$	excellent
O$_2$	on O	excellent
NF$_3$	...	poor
ClF$_3$	midway between ClF$_4$ and ClF$_2$	good
ClO$_3$F	above ClF$_2$, much above ClO$_3$	poor
N$_2$O$_4$	close to NO$_2$	good
NO$_2$ClO$_4$	between NO$_2$ and extrapolated ClO$_4$	good
Cl$_2$O$_7$	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 this is the primary limitation. Having the curve, would one have chosen ΔH_f Cl$_2$O$_7$ = +55 kcal./mole or ΔH_f NF$_3$ = −29 kcal./mole?

In conclusion, it appears that the most desirable oxidizer is one which packs in the maximum 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.

Literature Cited

(1) Barrère, M., Office Nationale d'Etudes et de Recherche Aerospatiales, *Missiles Rockets* **15**, 32 (1964).