

Liquid Rocket Propellants

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- I. Desirable Liquid Propellant Characteristics
- II. Liquid Rocket Propellant Performance
- III. Liquid Rocket Propellant Selection
- IV. Handling and Storage of Liquid Rocket Propellants

GLOSSARY

Anhydrous Containing no water. In a practical sense, refers to propellants that have a moisture content below a specified limit.

Bipropellant Two separate propellants, a fuel and an oxidizer. They are fed individually to a thrust chamber where mixing and combustion occurs.

Cryogenic Liquefied gases that must be refrigerated to be kept in a liquid state at atmospheric pressure. No amount of pressure will liquefy gases that are above their critical temperature. An arbitrary temperature of -240°F (122 K) is sometimes used to define the upper limit of the critical temperature of cryogenic gases.

Hypergolic Self-igniting. In the context of rocket propulsion, pertains to fuels and oxidizers that self-ignite within about 75 milliseconds after contact with each other.

MAF Mixed amine fuel. A fuel consisting of mixed amine, usually hydrazine in order to reduce the freezing point.

MHF Mixed hydrazine fuel. A special case of MAF where only hydrazines are contained.

MON Mixed oxides of nitrogen. An oxidizer consisting of nitrogen tetroxide (N_2O_4) and nitric oxide (NO). An

associated number represents the NO percentage by weight (e.g., MON-15 contains 15% NO).

Monopropellant Single substance that may be a single compound, or a mixture of several materials that are stable under normal conditions, that will combust or decompose yielding hot gases when ignited or catalyzed.

Neat Liquid propellant composed of only one chemical. Neat hydrazine is only pure N_2H_4 within the specifications for purity.

Outage Volume of propellant that still remains in the tank after all usable amounts have been expelled. Volume is retained to assure that the engine is not fed slugs of pressurizing gas instead of pure propellant.

Passivation Process to render metal and plastic surfaces nonreactive with the propellant.

Prepackaged Rocket system that is loaded and sealed with storable propellants at the manufacturing plant, thus requiring no servicing of propellants in the field.

Propellant Fuels, oxidizers, and monopropellants used to provide energy and the working fluid for the thrust of a rocket engine.

Pyrophoric Spontaneously ignitable in air.

Space storable Ability to be used in a space environment for extended periods without boil-off, freezing,

or decomposition. Usually refers to propellants that are mildly cryogenic or have high vapor pressure on earth, but because of low ambient temperatures in space they can be kept liquid under a modest vapor pressure. Examples are ammonia, oxygen difluoride, diborane, and dinitrogen tetrafluoride.

Storable Propellants that exhibit no corrosion, decomposition, or deterioration over a specified time period, usually 5–10 years, with 20 years becoming a requirement for some satellites. A low freezing point is often required, as low as -65°F (220 K) for tactical missiles, but as high as 30°F (272 K) for the Titan II. The upper temperature range can also vary, from 90°F (305 K) for an environmentally controlled system to 160°F (344 K) for tactical missiles. The term storable is often applied to a propellant combination of fuel and oxidizer. While kerosine is storable, it is usually used with liquefied oxygen, thus the kerosine/oxygen system is not storable.

Threshold limit values (TLV) As established by the American Conference of Governmental Industrial Hygienists, the time-weighted average concentration of a toxicant to which an average healthy person may be repeatedly exposed for a normal 8-hr day and a 40-hr workweek without suffering adverse effects. TLV-C is the concentration that should never be exceeded.

Ullage Volume of a full tank of propellant that is not actually occupied by liquid propellant. The empty volume allows thermal expansion of the liquid and provides an initial volume for pressurization gas.

LIQUID ROCKET PROPELLANTS provide the energy or motive power for chemical rocket propelled systems by releasing chemical energy through a combustion process. The propellants also furnish the working fluid that is expanded by the release of the thermal energy. Besides producing thrust for prime propulsion or attitude control, propellants are often burned in gas generators to drive turbopumps, hydraulic pumps, and alternators. Propellants are also used to generate gases in underwater flotation devices, and as the energy source for gas dynamic lasers.

The term liquid rocket propellants encompasses the fuels and oxidizers used in bipropellant systems, and single fluid monopropellants. Tripropellant combinations have also been studied where one component may be a solid. Hybrids are bipropellant systems that have one liquid component, usually the oxidizer with the fuel being a solid grain. So called reverse hybrids have liquid fuel and a solid oxidizer grain. Heterogeneous propellants consist of finely powdered energetic materials suspended in a liquid medium thickened to inhibit settling of the solid particles.

Propellant selection is based on many factors. The ideal propellant does not exist: the large number of propellant

candidates results from the need to make difficult trade-offs among performance, storability, physical characteristics, handling, safety, cost, and availability. All these parameters are considerations of specific applications and the degree of importance can vary greatly. A large variety of liquid fuels, oxidizers, and monopropellants have been evaluated, some of which are in operational use and others that have fallen to the wayside for various reasons.

Synthesis programs have been undertaken to produce new compounds that, theoretically at least, appeared to have desirable characteristics. Propellant mixtures have been formulated in efforts to tailor properties to meet specific requirements. Propellants are reactive and energetic materials by nature. Through an understanding of the chemical and physical properties, proper selection of materials and components, and use of appropriate procedures and equipment, liquid rocket propellants can be used safely and effectively.

I. DESIRABLE LIQUID PROPELLANT CHARACTERISTICS

The primary consideration for propellant selection is high performance coupled with low system weight. In addition, the physical and chemical characteristics of the propellants must meet the requirements of the expected operational environment of the propulsion system. The need for instant readiness by the military imposes demands for long-term storability and ease of handling. With the greater use of rocket propulsion for civilian purposes, these considerations are less important. Following are the principle factors.

CHEMICAL ENERGY. Since propulsive energy is produced in the form of hot gases, optimized performance results from maximizing the flame temperature and volume of gases produced per unit weight of the reactants. A low molecular weight of the exit gases is desired.

LIQUID RANGE. The operational environment of the missile or spacecraft dictates the freezing and boiling point requirements. Military tactical weapons often require a temperature range of -65 – 160°F (219.3–344.4 K) for worldwide deployment. Silo-based missiles and satellites may experience a much narrower range. Low-boiling propellants require heavyweight tanks or some means to keep the propellants cold. The high vapor pressure complicates the design of pump and regeneratively cooled thrust chambers. Special handling procedures and equipment are needed for servicing cryogenic systems. The freezing and boiling points of various propellants are listed in [Tables I and II](#). Vapor pressures of selected oxidizers and fuels are plotted in [Figs. 1 and 2](#).

STABILITY. Propellants should be storable for the required time period without decomposition, gas formation,

TABLE I Physical Properties of Liquid Oxidizers

Oxidizer (formula)	Molecular weight	Freezing point		Normal boiling point ^a		Specific gravity
		°F	K	°F	K	
Bromine pentafluoride (BrF ₅)	174.9	-78.3	211.8	104.9	313.6	2.47 @ 298 K
Chlorine pentafluoride (ClF ₅)	130.4	-153.4	170.2	7.3	259.4	1.78 @ 298 K
Chlorine trifluoride (ClF ₃)	92.4	-107.1	195.9	53.2	284.9	1.81 @ 298 K
Florox (ClF ₃ O)	108.4	-86.8	207.1	84.7	302.6	1.85 @ 298 K
Fluorine (F ₂)	38.0	-362.3	54.1	-306.6	85.0	1.50 @ NBP
Fluorine/Oxygen (Flox) (70% F ₂ /30% O ₂)	36.2	—	—	-304	86.5	1.24 @ NBP
Hydrogen peroxide (90 % H ₂ O ₂ /(10% H ₂ O)	32.4	11.3	261.6	286.1	414.3	1.39 @ 293 K
Hydrogen peroxide (98% H ₂ O ₂)	34.0	31.2	272.7	302.4	423.4	1.45 @ 293 K
MON-10 (10% NO/90% N ₂ O ₄)	85.8	-9	250.4	50.8	283.6	1.47 @ 273 K
Nitric acid-type IIIA ^c	59.4	-56	224.3	140	333 ^b	1.55 @ 298 K
Nitric acid-type IV ^c	55.0	-35	235.9	76.5	297.9 ^b	1.62 @ 298 K
Nitrogen tetroxide (N ₂ O ₄)	92.0	11.8	261.9	70.1	294.3	1.43 @ 293 K
Nitrogen trifluoride (NF ₃)	71.0	-341	65.9	-201	143.7	1.54 @ NBP
Oxygen (O ₂)	32.0	-361.1	54.7	-297.3	90.2	1.15 @ NBP
Oxygen difluoride (OF ₂)	54.0	-371	49.3	-228.6	128.4	1.52 @ NBP
Ozone (O ₃)	48.0	-316	79.8	-170	160.9	1.61 @ 78 K
Perchloryl fluoride (ClO ₃ F)	102.4	-231	127	-52.3	226.3	1.39 @ 298 K
Tetrafluorohydrazine (N ₂ F ₄)	104.0	-261.4	110.2	-99.4	200.2	1.56 @ 173 K

^a NBP is normal boiling point at 1 atm.

^b Bubble point, where liquid appears to boil.

^c See Table X for nitric acid compositions.

or attack on the container material. Decomposition or residue formation at high temperatures can adversely affect regenerative cooling. Propellants should also be stable to mechanical and hydrodynamic shock and adiabatic compression.

REACTIVITY. Mild corrosion of tanks and components and deterioration of seals and gaskets can result in propellant contamination and clogging of filters and small passages. Reactivity with moisture and air invokes the need for unique transfer techniques. Spills and leaks of reactive propellants are safety hazards; benign propellants are easily and safely handled with a minimum of special equipment. A reactive fuel and oxidizer combination is needed for smooth and efficient combustion.

DENSITY. High propellant density allows the use of smaller tanks, thus minimizing the overall vehicle inert weight (improves the mass fraction). A propellant with low coefficient of expansion can be used over a larger portion of its liquid range without undue performance variation. The specific gravities of common propellants are presented in Tables I and II and as a function of temperature in Fig. 3.

VISCOSITY. Low viscosity fluids will have less pressure drop through the feed system and thrust chamber

injector, permitting a smaller pump or a lightweight pressurization system to be used.

IGNITION. Hypergolic ignition offers high reliability, a restart capability for multiburn missions and eliminates the weight of a separate ignition system. In space, secondary ignition sources are unreliable. Catalytic decomposition of monopropellants is a valuable attribute.

LOGISTICS. While low-cost propellants are desirable, they are usually a small part of the overall system cost. The costs of special handling and storage, as in the case of cryogenics, must be considered part of the total propellant cost. Propellant costs are a function of the production rate. Availability of propellant for a new or expanded program may involve construction of a new plant or expanding an existing one. The required transportation equipment is another factor.

II. LIQUID ROCKET PROPELLANT PERFORMANCE

A. General Principles

It is helpful to explore the governing equations for rocket engines in order to understand the motivation of rocket

TABLE II Physical Properties of Liquid Fuels

Fuel (formula)	Molecular weight	Freezing point		Normal boiling point		Specific gravity
		°F	K	°F	K	
Aerazine-50 (50% Hydrazine/50% UDMH ^a)	41.8	22	267.6	158	343.15	0.899 @ 298 K
Ammonia (NH ₃)	17.0	-107.9	195.4	-28.05	239.8	0.682 @ NBP
Aniline (C ₆ H ₅ -NH ₂)	93.12	207.4	266.8	363.9	457.5	0.999 @ 293 K
Diborane (B ₂ H ₆)	27.69	-264.8	108.3	-134.5	180.6	0.438 @ NBP
Diethylcyclohexane [(C ₂ H ₅) ₂ C ₆ H ₁₀]	140.3	-110.2	194.2	345	447.2	0.804 @ 293 K
Diethylenetriamine (DETA) [(NH ₂ C ₂ H ₄) ₂ NH]	103.2	-38.2	234	405	480	0.953 @ 298 K
<i>u</i> -Dimethyl hydrazine (UDMH) [CH ₃) ₂ N ₂ H ₂]	60.1	-70.9	216.0	144.2	335.5	0.791 @ 298 K
Ethane (C ₂ H ₆)	30.07	-297.9	89.95	-127.6	184.48	0.548 @ NBP
Ethanol (C ₂ H ₅ OH)	46.1	-174	158.7	172.9	351.4	0.789 @ 293 K
Ethene (C ₂ H ₄)	28.054	-273.1	103.6	154.66	169.4	0.5674 @ NBP
Ethylene dihydrazine (C ₂ H ₁₀ N ₄)	90.1	55.4	285.95	>491. ^e	>528. ^e	1.096 @ 298 K
Ethylene oxide (C ₂ H ₄ O)	44.01	-168	162	50.9	283.6	0.887 @ NBP
Furfuryl alcohol (C ₅ H ₅ OOH)	98.1	-26	240	340	444	1.13 @ 293 K
Hybaline A-5	109.2	-58	223.2	505	536	0.736 @ 293 K
Hydrazine (N ₂ H ₄)	32.04	34.75	274.7	236.3	386.6	1.008 @ 293 K
Hydrogen (H ₂)	2.016	-434.8	13.8	-423.3	20.21	0.0709 @ NBP
JP-X (40% UDMH/60% JP-4) ^a	89.3	<-71	216	211	373	0.80 @ 293 K
Kerosine (RP-1) (H/C = 2.0)	172	<-50	228	350-525 450-547	450-547	0.80-0.81 @ 293 K
Methane (CH ₄)	16.04	-296.5	90.6	-258.7	111.6	0.451 @ NBP
Methanol (CH ₃ OH)	32.04	-144	175.4	147	337	0.791 @ 293 K
MAF-1 ^b	100.0	-148	173	170	350	0.87 @ 298 K
MAF-3 ^b	90.2	<-65	219	—	—	0.917 @ 298 K
MHF-3 ^c (86% MMH/14% N ₂ H ₄) ^a	43.41	<-65	219	193.4	362.8	0.889 @ 298 K
MHF-5 ^c	45.35	-43.6	231.2	205.8	369.7	1.011 @ 298 K
Monomethyl hydrazine (CH ₃ H ₂ H ₃)	46.07	-62.3	220.8	189.8	360.8	0.879 @ 293 K
Nitromethane (CH ₃ NO ₂)	61.04	-20.2	244.1	214	374.3	1.135 @ 298 K
Pentaborane (B ₅ H ₉)	63.17	-52.2	226.4	140.1	333.2	0.623 @ 298 K
<i>n</i> -Propyl nitrate (C ₃ H ₇ NO ₃)	105.1	<-150	172	230.9	383.6	1.058 @ 298 K
Otto Fuel II ^d	186.52	-18.4	245.2	decomposes		1.232 @ 298 K
Propane (C ₃ H ₈)	44.11	-305.84	85.5	-43.7	231.1	0.5853 @ NBP
Quadricyclane (C ₇ H ₈)	92.14			226.4	381	0.982
Shelldyne-H	186.7	-101	200	460	511	1.11 @ 293 K
U-DETA (MAF-4, Hydyne) (60% UDMH/40% DETA) ^a	72.15	<-120	188.7	161	345	0.858 @ 289 K

^a Weight percent.^b See Table XII for composition.^c See Table XIII for composition.^d See Table XV for composition.^e Estimated values courtesy of GenCorp Aerojet Tech Systems.

engineers to create and use cryogenic, toxic, and explosive compounds in the pursuit of rocket-powered vehicles with minimum weight or minimum volume (or both). Liquid rockets are reaction engines derived from Newton's Laws. Saenger described the momentum principle with these words, "... all ship propellers, airplane propellers, water wheels, and oars generate their forward push at the expense of the momentum of wa-

ter or air masses which are accelerated toward the rear."

Therefore, accelerating a working fluid out the rear of a vehicle produces thrust. The working fluid can be cold gas, monopropellant decomposition products, bipropellant combustion products, or molecules that have been heated by an electrical, solar or nuclear energy source. The thrust of a liquid propellant rocket derives primarily

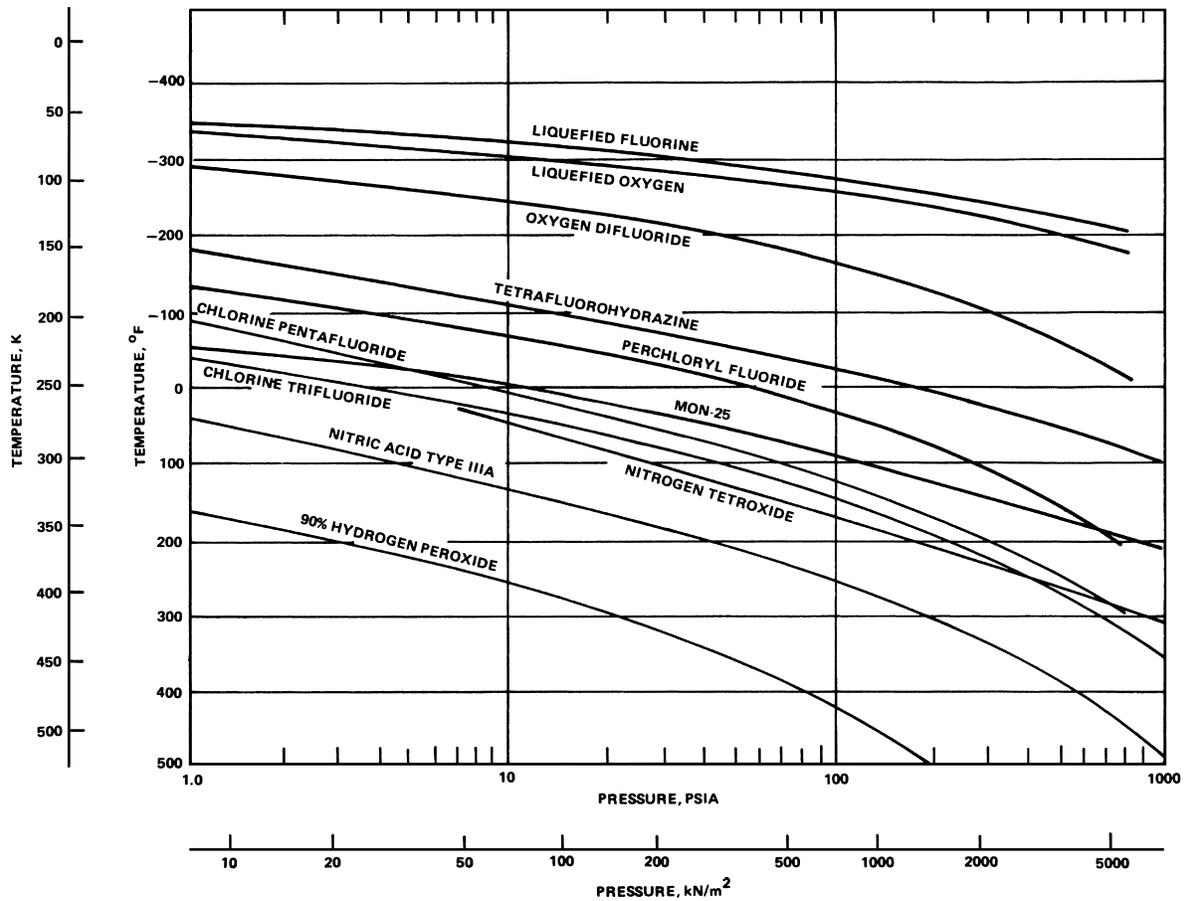


FIGURE 1 Vapor pressure of liquid oxidizers.

from a high velocity of exhaust products exiting the engine at the exit plane.

A simple party balloon inflated with air illustrates all these principles. The energy source is the elastic energy of the stretched rubber. The working fluid is the air enclosed within the inflated balloon. The exhaust nozzle is the hole where the air can escape. At the exit plane of the balloon, the air is flowing at a higher velocity than the bulk of air still remaining in the balloon. The applicable Newton's Law is that the time rate of change in momentum will be proportional to the net external force. This is the first equation, the classic equation for thrust of a rocket.

$$F = mV_e + (P_e - P_a)A_e \quad (1)$$

Where:

- m is mass flow rate of working fluid (lb/sec, Kg/s)
- V_e is velocity of the working fluid where it exits the free body (ft/sec, m/s)
- P_e is the pressure of the working fluid at the place the working fluid exits the free body (lb/ft², Pascals)

P_a is the pressure in the surroundings of the free body (lb/ft², Pascals)

A_e is the area of the exit of the nozzle (ft², m²)

From 90 to 100% of the thrust is contributed by the first term, and the term may be called velocity thrust or momentum thrust. In this term it can be seen that the higher the flow rate, the higher the thrust, and the higher the exit velocity, the higher the thrust. For a fixed flow rate of working fluid, this equation shows why rocket engineers attempt to maximize thrust per unit flow rate by maximizing exit velocity.

The second term of the thrust equation commonly contributes 0–10% to the thrust and is called "pressure thrust." Pressure thrust is greatly dependent upon the pressure environment surrounding the free body. For instance, at liftoff, the pressure thrust of the Space Shuttle Main Engine (SSME) is actually negative since P_a exceeds P_e at sea level. In space vacuum, where P_a is practically zero, the pressure thrust of the SSME contributes on the order of 10% to the thrust. For a vehicle operating at constant altitude, arranging so that $P_e = P_a$ results in what is defined

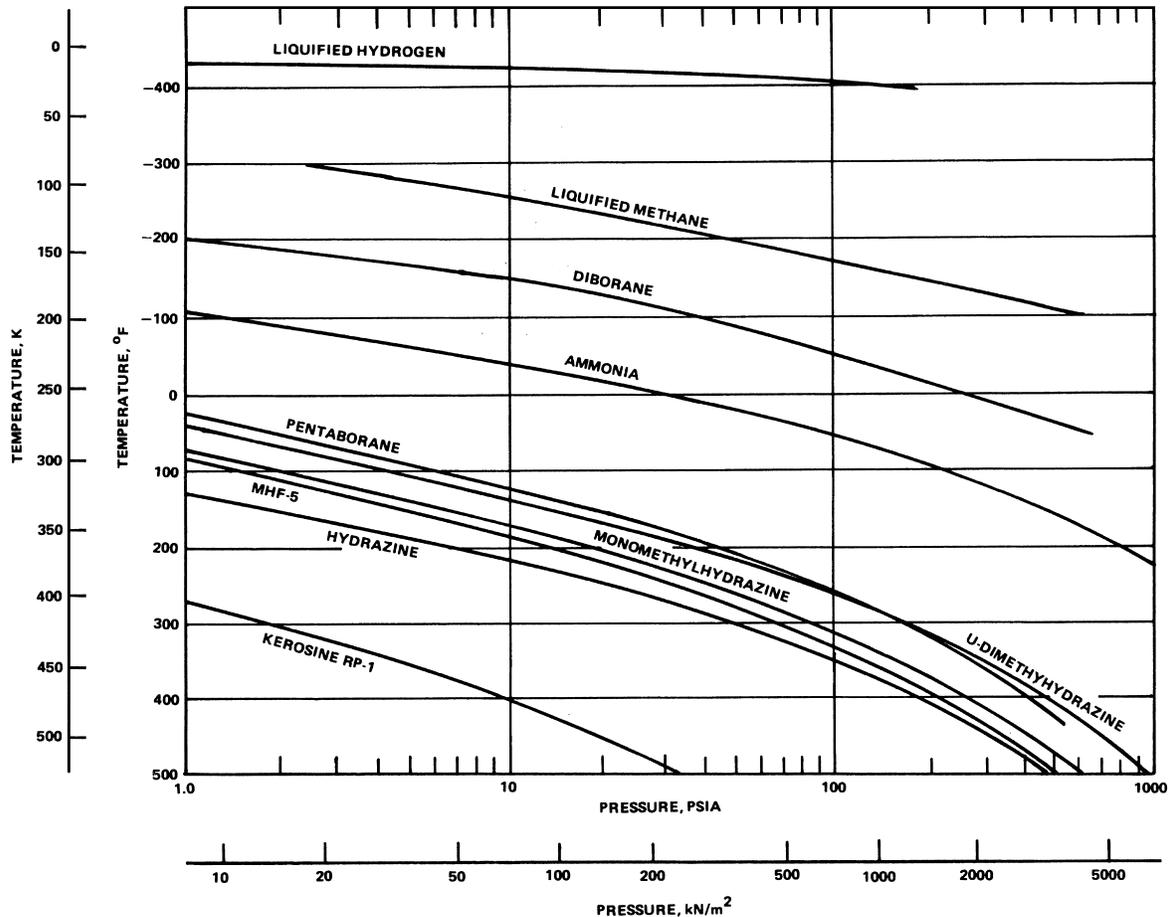


FIGURE 2 Vapor pressure of liquid fuels.

as optimum expansion ratio where pressure thrust is deliberately set to be zero. Allowing P_e to be greater than P_a may be thought of as wasted energy that could have been converted to more thrust at the same flow rate of propellant

Thrust per unit flow rate is defined as specific impulse (I_{sp})

$$I_{sp} = F/m \quad (2)$$

Specific impulse is the conventional parameter for theoretical comparison of various propellants and for assessment of the efficiency of actual delivered rocket engine performance compared the the theoretical.

In the English units, m is the weight flow rate in pounds per second. Since the thrust is in pounds, this leaves the unit of specific impulse to be seconds. For a more physical definition, specific impulse must be thought of as pounds of force per pound per second of propellant flow. In any units, the higher the value of specific impulse, the higher the specific performance of the rocket. In the MKS system of units, if thrust is in newtons and mass flow rate is in kilograms per second, the units of specific impulse will reduce to meters per second.

A propellant combination with higher specific impulse will result in either a lighter vehicle for a fixed payload or more payload for a fixed weight of vehicle. For missiles the trade might be range and payload. The lighter the vehicle, the easier and cheaper it might be to construct, transport, and handle. Furthermore, lighter may mean less raw material of construction that might translate to lower cost. Vehicle designers tend to choose the highest specific impulse propellant combination, if all other characteristics are equal or at least acceptable. Of course, all other characteristics are never equal, so for different kinds of vehicles, different propellant combinations provide the best compromise.

Returning to Eq. 1, dividing by m and arranging for optimum expansion ratio ($P_e = P_a$) the following results:

$$F/m = V = c \quad (3)$$

This velocity that remains on the right side of the equation can be interpreted as the actual physical velocity of the working fluid relative to the rocket vehicle. This velocity is defined as effective exhaust velocity and is commonly assigned the letter c . Note that effective exhaust velocity

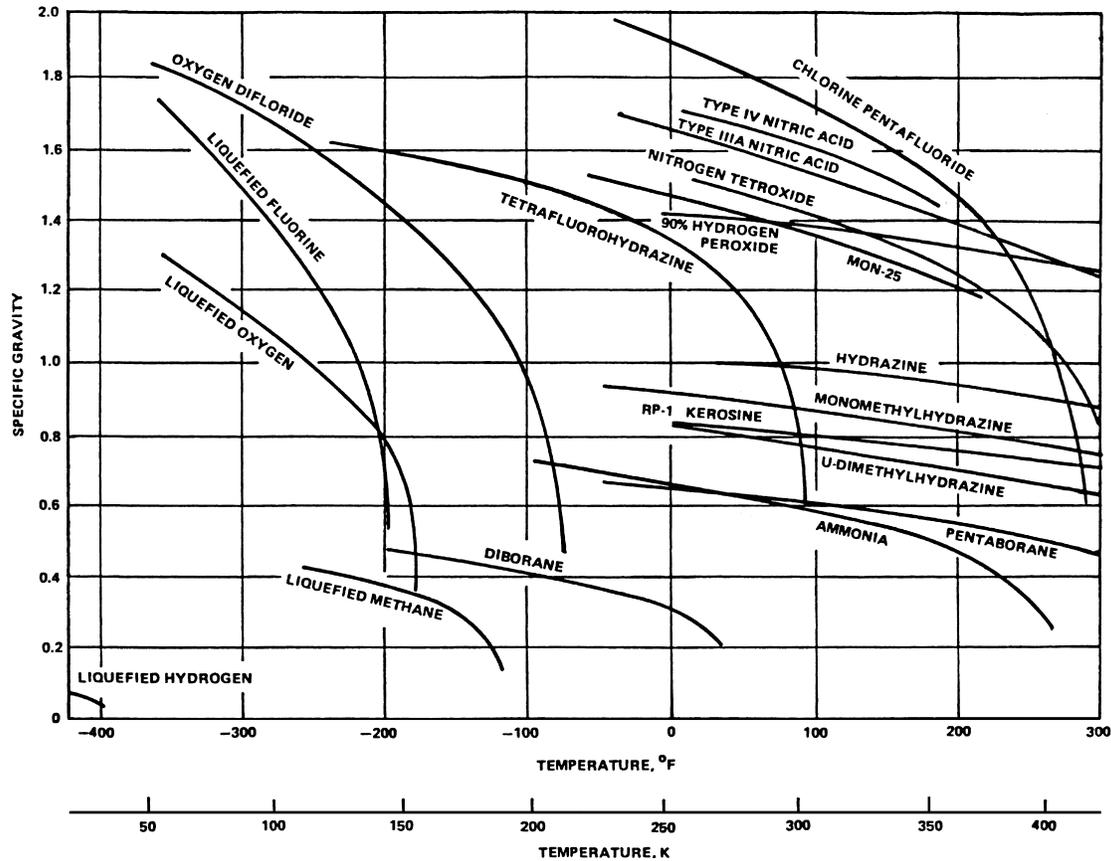


FIGURE 3 Specific gravities of liquid rocket propellants.

in the metric system is also the specific impulse value in the metric system for optimum expansion ratio. When a rocket is reported to have a specific impulse of 1000 m/sec, it means that the velocity of gases exiting the nozzle is 1000 m/sec relative to the nozzle.

In the air-filled party balloon, the air is a compressible fluid being accelerated out of an exit hole. For a rocket engine, the exit hole is the exit plane of a converging-diverging supersonic nozzle. From the principles of thermodynamics and fluid mechanics, an equation can be derived using conservation of energy, perfect gas, and a concept called a reversible adiabatic flow. Without the details of a derivation, the velocity out of the exit of a nozzle is written as:

$$V_e = \sqrt{\frac{k}{k-1} 2g \frac{R}{MW} T_c \left[1 - \left(\frac{P_e}{P_c} \right)^{\frac{k-1}{k}} \right]} \quad (4)$$

Where:

- V_e is exit velocity of the working fluid
- k is the ratio of specific heats of the working fluid
- g is the gravitational constant
- R is the universal gas constant

- MW is the molecular weight of the working fluid
- T_c is the absolute temperature of the working fluid at the entrance of the nozzle
- P_e is the pressure of the working fluid at the exit of the nozzle
- P_c is the pressure of the working fluid at the entrance of the nozzle

Approximately, P_c and T_c are the pressure and temperature of the working fluid in the combustion chamber.

From Eq. 4 several of the driving factors for propellant selection can be recognized. To maximize V_e which maximizes thrust, the desirable factors are

1. The lowest value of k
2. The lowest value of molecular weight
3. The highest value of T_c
4. The highest value of P_c

The value of k varies from 1.28 for helium to 1.66 for carbon dioxide. Air, hydrogen, oxygen, and nitrogen are 1.4. This value is not really selectable, however, the lowest molecular weight gases also tend to have the lowest k .

The lowest molecular weight is 2.02 for hydrogen. Here is the driver for the selection of liquid hydrogen, hydrides, and all other fuels packed with as many hydrogen atoms as science can achieve. Carrying along nitrogen, oxygen, and carbon compounds in the exhaust increases the mixture molecular weight and penalizes V_e . If the source of heat energy is from a solar concentrator, a nuclear reactor, or electrical energy, the working fluid can be pure hydrogen. However, when the source of energy is chemical decomposition or combustion, this increased molecular weight of the working fluid is unavoidable.

For a chemical rocket, energy released in the combustion chamber heats the working fluid to very high temperatures. Maximum combustion chamber temperature yields maximum exit velocity. Here is the driver for selection of oxidizers of legendary reactivity in an attempt to run T_c as high as possible while minimizing melting all the parts of the rocket. Some of the highest heat releases stem from the oxidation of metals. This is the driver for including metallic aluminum or even beryllium as part of the combustion process.

High chamber pressure, P_c , is a factor that could allow enormous expansion ratios that still result in P_e greater than P_a . When P_c is greater than P_a , it might be considered a loss of opportunity to convert that extra pressure to extra exhaust velocity. Throwing away the extra exit pressure means that specific impulse could have been higher.

To summarize, the vehicle designer wants the lowest molecular weight exhaust, the highest combustion temperature, and the highest chamber pressure that the mission requires or the sponsor is willing to pay for, and it is all caused by the relationship of Eq. 4.

Returning to Eq. 1, if mass flow is replaced by the continuity equation, velocity is replaced by Eq. 4, the perfect gas equation of state is applied, and variables are mathematically manipulated, the thrust equation becomes:

$$F = P_c A_t C_f \quad (5)$$

where P_c is combustion chamber pressure, A_t is the area of throat of the converging-diverging supersonic nozzle, and C_f is a complicated term involving k , P_c , and P_e and is called the thrust coefficient.

Equation 5 is an interesting way of arriving at rocket thrust because it separates the pressure thrust (pressure times area) of the rocket chamber from the contribution of the converging-diverging supersonic nozzle. All the messy mathematics is in C_f . Values of C_f vary from approximately 1.0 to a maximum theoretical value of 1.964 for infinite ratio of P_a/P_e . So the thrust of an actual rocket is somewhere between 100 and 200% of the pressure thrust, depending upon the nozzle expansion ratio.

If F is replaced by Eq. 5 in the definition of specific impulse (Eq. 2), then:

$$I_{sp} = \frac{P_c A_t C_f}{m} \quad (6)$$

A new term can be defined by collecting all the variables except thrust coefficient. That new variable is defined as the characteristic exhaust velocity, called c^* and pronounced "see star." Physically, it may be thought of as the velocity of the working fluid at the throat of the converging-diverging nozzle.

$$c^* = \frac{P_c A_t}{m} \quad (7)$$

Replacing Eq. 7 in Eq. 6 shows an interesting relationship for I_{sp} :

$$I_{sp} = c^* C_f \quad (8)$$

Again, the performance of the nozzle has been separated from the performance of the chamber. In this way, c^* is representative of the combustion properties of the propellants used in the rocket while C_f is representative of the nozzle.

Tests can be run at atmospheric pressure without the trouble of measuring thrust in order to optimize mixture ratio of a bipropellant or to evaluate the survivability of the hardware to the effects of high P_c and T_c . It is much easier and faster to accurately measure P_c of prototype, heavyweight rocket hardware than it is to measure thrust. As a result, the first measure of how well an injector performs is nearly always c^* efficiency which is measured c^* compared to theoretical c^* .

The above relationships will predict or measure the performance of rocket engines within 10%. Of course, the real world will impose the effect of real gases, three dimensions, and various other losses on the process of development, but the basic selection and evaluation parameters for propellant definition have been defined.

B. Theoretical Calculations

Specific impulse is also defined from the total enthalpy change of the propulsion system between the combustion chamber and the nozzle exit:

$$I_{sp} = \sqrt{2J(H_c - H_e)/g} \quad (9)$$

where H_c is enthalpy of combustion products before expansion, Btu/lbm (J/kg), H_e enthalpy of combustion products after expansion, Btu/lbm (J/kg), and J mechanical equivalent of heat 778 ft lbf/Btu (0.101988 kg m/J). Two sets of conditions are considered when making performance calculations, those of the combustion chamber and those of the expansion nozzle.

1. Combustion Chamber

The conditions of the propellant entering into the combustion chamber (composition, temperature, physical state,

and mixture ratio) and the chamber pressure are used to calculate the chamber temperature and hot gas reaction, product composition, and properties. This information defines the nozzle inlet conditions that allow calculation of I_{sp} and C^* and provides information needed for engine design, estimates of heat transfer, and nozzle flow and expansion parameters. The combustion process is assumed to be adiabatic and proceeds to completion.

Chamber (flame) temperature, T_c , and gas composition are calculated using mass, pressure and energy balance equations, and chemical equilibria data.

The energy equation does not provide a direct solution of the chamber temperature. When the enthalpy of the reaction products above a standard reference temperature equals the heat of reaction of the entering propellant, the adiabatic combustion temperature is defined. For machine computation, enthalpy values of the products are represented as a power series in terms of the temperature. The general energy equation is

$$\begin{aligned} & \sum_{i, \text{propellant}} n_i \{ [(H_{T_c}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ)] + (\Delta H_f^\circ)_{T_0} \}_i \\ &= \sum_{j, \text{reaction products}} n_j \{ [(H_{T_i}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ)] \\ & \quad + (\Delta H_f^\circ)_{T_0} \}_j \end{aligned} \quad (10)$$

where T_c is adiabatic flame combustion temperature, T_i propellant temperature, T_0 reference temperature (usually

298 K), $H^\circ - H_0^\circ$ molar enthalpy (from tables), ΔH_f° heat of formation, n_i moles of reactants (propellants), and n_j moles of reaction products. To obtain values for the unknowns, T_c and n_j , the equations are solved simultaneously with a digital computer using thermochemical and equilibria data from references such as the JANAF Thermochemical Tables and the National Bureau of Standards Circulars. These tabulations cover heat capacity, enthalpy, entropy, free energy function, heat and free energy of formation, and equilibrium constants of formation over the range of 0–6000 K, as appropriate. Heats of formation of selected propellants are presented in Tables III and IV.

2. Expansion Nozzle

In the nozzle, the combustion gases are expanded isentropically, converting sensible enthalpy into kinetic energy accompanied by a drop in temperature and pressure. When the gas composition does not change (no chemical dissociation, recombination, or condensation) from the chamber to the nozzle exit plane, the process is considered to be in *frozen equilibrium*. If chemical and phase equilibrium among all combustion species is maintained under the varying pressure and temperature conditions of the nozzle expansion process, the product composition will change. This is known as *shifting equilibrium*, and performance so calculated will be the higher value because

TABLE III Thermodynamic Properties of Liquid Oxidizers

Oxidizer	Heat of formation (kJ/mol) ^a	Critical temperature		Critical pressure		Heat of vaporization	
		°F	K	psia	MN/m ²	Btu/lb	kJ/mol
Bromine pentafluoride (BrF ₅)	-548.94	388	471	669	4.612	74.1	30.12
Chlorine pentafluoride (ClF ₅)	-253.13	289.4	416.2	771	5.316	73.3	22.22
Chlorine trifluoride (ClF ₃)	-185.77	355	453	961	6.626	128.0	27.53
Florox (ClF ₃ O)	-165.69	360	455	—	—	127.9	32.22
Fluorine (F ₂)	-12.96	-199.6	144.5	809.7	5.583	71.5	6.32
Fluorine/oxygen (70/30) (FLOX)	-36.04	-199.6	144.5	809.7	5.583	77	6.48
Hydrogen peroxide (H ₂ O ₂)	-187.78	855	730	3130	21.58	596	47.07
Nitric acid-Type IIIA ^b	-140.16	520	544	1286	8.867	247	34.10
Nitric acid-Type IV ^b	-181.59	512	540	1428	9.846	270	34.52
Nitrogen tetroxide (N ₂ O ₄)	-19.58	316.8	431.4	1441	9.938	178.2	38.12
Nitrogen trifluoride (NF ₃)	-131.50g	-88	206.5	729	5.026	73.0	11.59
Oxygen (O ₂)	-12.12	-181.1	154.8	730.6	5.375	91.6	6.82
Oxygen difluoride (OF ₂)	+24.52	-72	215.4	719	4.958	88.7	11.13
Ozone (O ₃)	+118.41	9.6	260.7	803	5.537	127.9	14.27
Perchloryl fluoride (ClO ₃ F)	-21.42	203	368	779	5.372	83.9	19.96
Tetrafluorohydrazine (N ₂ F ₄)	-21.8	96.8	309	1130	7.8	64.2	15.23

^a Liquid state at 298.16 K. To obtain Kcal/mol divide kJ/mol by 4.184.

^b See Table X for nitric acid compositions.

TABLE IV Thermodynamic Properties of Liquid Fuels

Fuel (formula)	Heat of formation (kJ/mol) ^a	Critical temperature		Critical pressure		Heat of vaporization	
		°F	K	psia	MN/m ²	Btu/lb	kJ/mol
Aerozine-50 (50% hydrazine/50% UDMH) ^b	+51.51	633	607	1731	11.935	346.5	33.67
Ammonia (NH ₃)	-71.71	270.1	405.4	1636	11.280	596.2	23.56
Aniline (C ₆ H ₅ -NH ₂)	+30.71	798	698.6	771	5.316	203	43.93
Diborane (B ₂ H ₆)	+20.79	62.1	289.8	581	4.006	224.3	14.43
Diethylcyclohexane [(C ₂ H ₅) ₂ C ₆ H ₁₀]	-726.18	690	638.6	367.5	2.534	119	38.79
Diethylenetriamine (DETA) [(NH ₂ C ₂ H ₄) ₂ NH]	-77.40	433.9	496	538	3.710	210.5	50.50
<i>u</i> -Dimethyl hydrazine (UDMH) [(CH ₃) ₂ N ₂ H ₂]	+51.63	482	523	867	5.978	250.6	35.02
Ethane (C ₂ H ₆)	-25.26	90.1	305.45	708.5	4.885	210.0	14.67
Ethanol (C ₂ H ₅ OH)	-277.65	469.4	516	925	6.378	362	38.79
Ethene (C ₂ H ₄)	8.1	49.82	282.7	742.35	5.118	207.5	13.55
Ethylene dihydrazine (C ₂ H ₁₀ N ₄)	137.7	901. ^f	746. ^f	838. ^f	5.8 ^f	367.7 ^f	77.0 ^f
Ethylene oxide (C ₂ H ₄ O)	+25.15	384.4	468.9	1043	7.191	249	25.48
Furfuryl alcohol (C ₅ H ₅ OOH)	-276.35	570 ^f	572 ^f	515 ^f	3.5 ^f	235.2	53.62
Hybaline A-5	+46.02	662-932	623-773	—	—	82.26	20.88
Hydrazine (N ₂ H ₄)	+50.42	716	653	2131	14.693	583	43.43
Hydrogen (H ₂)	-9.01	-399.9	33.21	188	1.296	195.3	0.915
JP-X (40% UDMH/60% JP-4) ^b	+4.90	545	558	680	4.689	169	35.06
Kerosine (RP-1) (H/C = 2.0)	-26.03	758	676.5	315	2.172	125	49.79
Methane (CH ₄)	-89.50	-115.8	191.0	673	4.64	238.9	8.91
Methanol (CH ₃ OH)	-239.03	464	513	1142	7.87	526.8	39.32
MAF-1 ^c	-77.82	—	—	—	—	246	56.90
MAF-3 ^c	-38.66	—	—	—	—	—	—
MHF-3 ^d (86% MMH/14% N ₂ H ₄) ^b	+54.00	617	598	1373	9.467	370.2	37.38
MHF-5 ^d	+28.75	685	636	1470	10.14	324.2	34.18
Monomethyl hydrazine (MMH) (CH ₃ N ₂ H ₃)	+54.84	594	585	1195	8.24	377	40.38
Nitromethane (CH ₃ NO ₂)	-139.03	598.6	587.9	916	6.314	269.8	38.28
Pentaborane (B ₅ H ₉)	+32.38	435	497	557	3.84	219	32.17
<i>n</i> -Propyl nitrate (C ₃ H ₇ NO ₃)	-214.47	584.6	580	588	4.05	142	34.68
Otto Fuel II ^e	-410.16	(decomposes)		—	—	—	—
Propane (C ₃ H ₈)	-30.372	206.2	369.93	617.4	4.257	183.2	18.78
Shellldyne-H (RJ-5)	+136.82	985	803	510	3.52	191	82.88
U-DETA (MAF-4, Hydnyne) (60% UDMH/40% DETA) ^b	+16.44	558	565.4	805	5.55	191	32.01

^a Liquid state at 298.16 K. To obtain Kcal/mol divide kJ/mol by 4.184.

^b Weight percent.

^c See Table XII for composition.

^d See Table XIII for composition.

^e See Table XV for composition.

^f Estimated values courtesy of GenCorp Aerojet TechSystems.

the dissociated species that recombine in the nozzle add to the release of chemical energy converted into kinetic energy. The frozen and shifting equilibrium represent the high and low limits of performance due to nozzle chemistry attainable from the system. In practice, actual rocket performance usually falls in between the two. Other losses, such as incomplete combustion, heat loss, noz-

zle friction, and divergence angle may play a significant role.

To perform frozen equilibrium calculations, the exit temperature, T_e , is determined by considering the conservation of entropy (an isentropic process). The gas composition throughout the nozzle is the same as in the chamber, thus the entropy in the chamber and at the nozzle exit are

equal. The difference between frozen and shifting flow values occurs because the species mole fractions are known for the former and unknown for the latter, which makes the latter an iterative process similar in complexity to the chamber solution. Usually when making a frozen flow calculation an additional simplifying assumption is made: that the heat capacity is constant with temperature. This leads to a simple expression for the effect of temperature on entropy:

$$S = C_p \ln(T_2/T_1) \quad (11)$$

This entropy change is set equal and opposite to the change due to the pressure drop:

$$S = -R \ln(T_2/T_1) \quad (12)$$

leading to the familiar isentropic relationship:

$$\ln(T_2/T_1) = R/C_p \ln(P_2/P_1) = (k-1)/k \ln(P_2/P_1) \quad (13)$$

where

$$k = C_p/C_v = C_p/(C_p - R) \quad (14)$$

Perhaps a yet more familiar form is:

$$T_2/T_1 = (P_2/P_1)^{(k-1)/k} \quad (15)$$

For a selected exit pressure, the exhaust gas temperature can now be calculated. The change in enthalpy leads to the calculation of the specific impulse by Eq. 9.

In shifting equilibrium calculations, the gas composition changes as it transverses from the chamber through the nozzle to the exit plane. As the temperature and pressure drops, many of the dissociated species recombine which change the gas composition and release additional energy. The mass balance, pressure balance, and chemical equilibrium must be satisfied as described previously for the chamber conditions, and the exit temperature, T_e , calculated. However, instead of the energy balance Eq. 10 an expression of entropy conservation is used to solve for the exit temperature and the exhaust composition:

$$\sum_{k, \text{exhaust}} n_k [S_{T_e} - R \ln p]_k = \sum_{j, \text{chamber}} n_j [S_{T_c} - R \ln p]_j \quad (16)$$

where T_e is exhaust temperature at exist plane, T_c chamber temperature, S_{T_c} absolute molar entropy of species j at chamber temperature and 1 atm, S_{T_e} absolute molar entropy of species k at exit temperature and 1 atm, R gas constant, n_k number of moles of species k at nozzle exit, n_j number of moles of species j from chamber, and $p_{j,k}$ partial pressures (atm) of components. From the temperature and product composition, one can calculate the enthalpy drop in the nozzle, I_{sp} (shifting) is then calculated from Eq. 9. Refinement of the thermochemical performance calculations can be made to correct for two-phase losses when

condensed species are present, and for friction and heat transfer losses. Also, for an equilibrium flow system in which the nozzle species and average molecular weight are changing, the optimum nozzle area ratio for a given exit pressure can be calculated.

A familiar expression of specific impulse can be derived from Eqs. 9 and 15 and $H = C_p T$:

$$I_{sp} = \sqrt{\frac{k}{k-1} \frac{2RT_c}{gm} \left[1 - \left(\frac{P_e}{P_c} \right)^{\frac{k-1}{k}} \right]} \quad (17)$$

where k is the ratio of specific heats (C_p/C_v), P_e exit pressure, P_c chamber pressure, T_c chamber temperature, R universal gas constant, and M average molecular weight of combustion products. As noted in Eq. 17 I_{sp} varies directly with the square root of the chamber temperature and inversely with the square root of the average molecular weight of the exhaust products, thus the ratio $(T_c/M)^{1/2}$ is used as a rough figure of merit to compare propellants.

The theoretical performance of selected liquid propellant systems is presented in Tables V–IX.

III. LIQUID ROCKET PROPELLANT SELECTION

The best oxidizer performance is provided by the elements O and F. Unfortunately, their molecular forms, O_2 and F_2 , are cryogenic. The elements Cl and Br will give oxidizers better physical properties, but their high molecular weight makes them less attractive from a performance standpoint. Nitrogen serves as a “back-bone” to carry O and F in a number of oxidizers, but adds little to the overall performance. Although hydrogen is a fuel, it is an excellent working fluid because of its low molecular weight; thus, it is a desirable component in some oxidizers. From these elements, the following oxidizers are obtained: O_3 , F_2 , OF_2 , NF_3 , O_2 , N_2F_4 , ClF_5 , ClO_3F , ClF_3O , ClF_3 , N_2O_4 , H_2O_2 , HNO_3 . This listing is from the highest performance to the lowest using hydrogen as the fuel. (With another fuel, some reordering may occur.) The first five oxidizers are the highest energy and are cryogens.

The number of elements that can be considered as fuels or fuel components is limited. Based on heat release, or heat of combustion, the elements H, Li, Be, B, C, Mg, and Al can be considered. As in the case with oxidizers, nitrogen will contribute little to the heat of combustion but serves as a desirable building block, especially for holding hydrogen to produce the amine group. Carbon also is a useful hydrogen carrier, leading to the hydrocarbon family. The variety of liquid compounds that can be made from these elements is a further restriction. Metals are

TABLE V Theoretical Performance of Rocket Liquid Bipropellant Combinations (Cryogenic Systems)^a

Oxidizer	Fuel	Bulk density	O/F ratio ^b	Specific impulse (sec)		Combustion temperature	
				Frozen ^c	Shifting ^c	°F	K
Oxygen	Hydrogen	0.28	4.02	387	391	4935	2997
Oxygen	Kerosine	1.02	2.06	285	300	6160	3677
Oxygen	<i>u</i> -Dimethyl hydrazine	0.98	1.65	295	310	6010	3594
Ozone	Hydrogen	0.30	4.0	413	424	5523	3323
Fluorine	Hydrazine	1.31	2.30	334	363	7955	4675
Fluorine	Hydrogen	0.45	7.60	396	410	6505	3869
Oxygen difluoride	Hydrazine	1.27	1.54	317	339	6690	3972
Oxygen difluoride	Diborane	1.00	3.73	340	365	7964	4680
Flox-30 ^d	Kerosine	1.09	3.05	298	316	6623	3935
Flox-70 ^e	Kerosine	1.20	3.80	317	344	7820	4600

^a Courtesy of Rocketdyne, Division of Rockwell International and the U.S. Air Force Rocket Propulsion Laboratory.

^b Oxidizer to fuel mixture ratio by weight.

^c $P_c = 1000$ psia expanded to 14.7 psia ($6895 \text{ kN/m}^2 \rightarrow 101.4 \text{ kN/m}^2$).

^d A mixture of 30% fluorine and 70% oxygen, by weight.

^e A mixture of 70% fluorine and 30% oxygen, by weight.

solids, of course, as are most of their hydrides. Metals do not have a heat release appreciably greater than hydrogen and, with oxygen-based oxidizers, solid oxide products form that cannot be expanded through the nozzle, causing a loss of specific impulse. From these considerations, we obtain the following fuel categories: hydrogen, ammonia and derivatives (amines, hydrazines), hydrocarbons, borohydrides, and alcohols.

A. Cryogenic Oxidizers

1. Ozone

Liquefied ozone, O₃, has stirred the interest of propellant chemists since the late 1940s. It has a serious disadvantage in that with very little stimulus it reverts back to oxygen explosively. Many impurities are known to sensitize ozone, such as hydrocarbons, nitrogen oxides, silver, and copper.

TABLE VI Theoretical Performance of Rocket Liquid Bipropellant Combinations (Storable Systems)^a

Oxidizer	Fuel	Bulk density	O/F ratio	Specific impulse (sec)		Combustion temperature	
				Frozen ^b	Shifting ^b	°F	K
Tetrafluorohydrazine	Ammonia	1.27	4.49	307	325	7284	4302
Tetrafluorohydrazine	Hydrazine	1.43	3.16	313	334	7547	4448
Chlorine trifluoride	Hydrazine	1.50	2.78	279	295	6553	3896
Hydrogen peroxide (95%)	Hydrazine	1.26	2.00	269	287	4814	2657
Hydrogen peroxide (95%)	Pentaborane	1.04	1.06	299	308	5000	3033
Hydrogen peroxide (95%)	Kerosine	1.30	7.35	265	273	4785	2914
Chlorine pentafluoride	Hydrazine	1.47	2.66	294	313	7039	4166
Chlorine pentafluoride	MHF-3	1.41	2.79	276	303	6470	3850
Chlorine pentafluoride	NOTSGEL-A	1.70	2.6	262	285	8058	4732
Nitrogen tetroxide	Monomethyl hydrazine	1.20	2.15	278	289	5653	3396
Nitrogen tetroxide	Hydrazine	1.22	1.30	284	292	5406	3259
Nitrogen tetroxide	Aerozine-50 ^c	1.21	2.00	276	289	5590	3361
Nitrogen tetroxide	Aerozine-67 ^e	1.28	1.80	273	288	6094	3368
MON-25	Monomethyl hydrazine	1.18	2.28	279	290	5705	3425
IRFNA, Type IIIA	<i>u</i> -dimethylhydrazine	1.26	2.99	267	276	5300	3200
Hydrazine	Pentaborane	0.79	1.28	325	328 ^d	4661	2845

^a Courtesy of Rocketdyne, Division of Rockwell International and the U.S. Air Force Rocket Propulsion Laboratory.

^b $P_c = 1000$ psia expanded to 14.7 psia ($6895 \text{ kN/m}^2 \rightarrow 101.4 \text{ kN/m}^2$).

^c A mixture of 50% hydrazine and 50% UDMH, by weight.

^d When kinetic limitations are considered, $I_{sp} = 315$ seconds.

^e A mixture of 67.2% ethylene dihydrazine and 32.8% hydrazine, by weight.

TABLE VII Theoretical Performance of Rocket Liquid Bipropellant Combinations (Space Conditions—Vacuum Expansion)^a

Oxidizer	Fuel	Bulk density	O/F ratio ^b	Specific impulse (sec)		Combustion temperature	
				Frozen ^c	Shifting ^c	°F	K
Oxygen	Hydrogen	0.31	4.50	446	456	5012	3040
Oxygen	Methane	0.82	3.32	339	365	5482	3301
Oxygen difluoride	Diborane	1.00	3.82	380	428	7054	4174
Chlorine pentafluoride	Hydrazine	1.47	2.72	321	363	6533	3885
Chlorine pentafluoride	MHF-3	1.41	2.8	305	354	6010	3594
Fluorine	Hydrazine	1.31	2.34	369	424	7298	4310
Fluorine	Hydrogen	0.50	9.00	450	475	6388	3804
Tetrafluorohydrazine	Hydrazine	1.43	3.24	348	387	6978	4132
Nitrogen tetroxide	Monomethyl hydrazine	1.21	2.28	317	340	5300	3200
Nitrogen tetroxide	Aerozine-67	1.28	1.85	307	338	5741	3172
Nitrogen tetroxide	Hybaline A-5	1.22	2.33	—	380	6596	3920

^a Courtesy of Rocketdyne, Division of Rockwell International, and the U.S. Air Force Rocket Propulsion Laboratory.

^b Oxidizer to fuel mixture ratio by weight.

^c $P_c = 150$ psia (1034 kN/m²) expanded to $A_e/A_t = 40$.

The U.S. Navy and Air Force funded considerable research studying ozone decomposition, effect of additives (stabilizers and impurities), and analytical techniques. Some fluorine compounds tended to improve ozone stability, but not sufficiently to make ozone a useful rocket oxidizer. Firings of a 25% O₃/75% O₂ mixture were accomplished at the 100-lb thrust (445 N) level using alcohol and kerosine as fuels.

2. Fluorine

Liquefied fluorine (F₂) has been extensively evaluated and considerable rocket engine development has been accomplished at the 15,000 and 40,000 lb_f (66.7 and 177.9 kN) level, although it has not yet been selected for

an operational system. A very reactive material, fluorine will react with most anything, thus all fluorine systems must be scrupulously cleaned and passivated. Mixtures of fluorine and oxygen (Flox) have been evaluated as a means of increasing oxygen performance. The experimental efforts have indicated that mixtures containing 30% or less fluorine behave essentially like oxygen, thus Flox30 could be substituted for liquefied oxygen with minimal changes for about a 5–10% performance gain, depending on the fuel selected.

3. Oxygen Fluorides

Liquefied oxygen difluoride (OF₂) has been of interest for its “space storability” aspect. Its boiling point,

TABLE VIII Theoretical Performance of Rocket Liquid Tripropellant Combinations^a

Oxidizer	Fuel ^b	Bulk density	O/F ratio	Specific impulse (sec)		Combustion temperature	
				Frozen	Shifting	°F	K
Oxygen	Hydrogen (50%)	0.23	0.88	453 ^c	458 ^c	4662	2845
Oxygen	Beryllium (50%)	0.24	0.92	513	539 ^d	4681	2856
	Hydrogen (49%)						
Fluorine	Beryllium (51%)	0.17	0.85	425 ^c	432 ^c	3056	1953
	Hydrogen (69%)						
Fluorine	Lithium (31%)	0.17	0.88	468	506 ^d	2905	1869
	Hydrogen (68%)						
Hydrogen peroxide	Lithium (32%)	1.24	0.55	329 ^c	334 ^c	5606	3370
	Hydrazine (71%)						
	Beryllium (29%)						

^a Courtesy of Rocketdyne, Division of Rockwell International, and the U.S. Air Force Rocket Propulsion Laboratory.

^b Percents are by weight.

^c $P_c = 1000$ psia expanded to 14.7 psia (6895 kN/m² → 101.4 kN/m²).

^d $P_c = 150$ psia expanded to $A_e/A_t = 40$.

TABLE IX Theoretical Performance of Rocket Liquid Monopropellants^a

Monopropellant	Chamber pressure (psia)	Bulk density	Specific impulse (sec)		Combustion temperature	
			Frozen ^b	Shifting	°F	K
Ethylene oxide	300	0.887	166	175	1860	1288
Hydrazine ^c	1000	1.01	155	174	1077	854
Hydrogen peroxide (90%)	300	1.44	132	165	1370	1016
MHF-5 ^c	1000	1.011	—	215	1916	1320
Nitromethane	300	1.13	218	225	3950	2450
<i>n</i> -Propyl nitrate	300	0.935	—	179	1840	1278
Otto Fuel II	1000	1.23	—	208	2042	1390

^a Courtesy of Rocketdyne, Division of Rockwell International, and the U.S. Air Force Rocket Propulsion Laboratory.

^b Expanded to sea level, 14.7 psia (101.4 kN/m²).

^c Ammonia dissociation of 40% assumed.

−228.6° F (128.4 K), is sufficiently high so with proper environmental control in appropriate spacecraft OF₂ can be maintained in the liquid state with no boil-off, excessive pressure buildup, or need for refrigeration. Experimental rocket engine firings at the 100–400 lbf (445–1779 N) level, using diborane as the fuel were concluded successfully. Oxygen difluoride delivers about 2% less performance than fluorine with hydrogen as the fuel, and a little higher with a hydrocarbon fuel. It is a powerful oxidizing agent like fluorine and the interhalogens, and the same care in material selection, cleaning, and passivation should be exercised. There is some indication that OF₂ is less aggressive than fluorine with nonmetallic materials. Thus, OF₂ might be a better choice for some applications requiring gaskets, dynamic pump seals, and so on, since there are no nonmetallics recommended for use with flowing liquefied fluorine.

Other oxygen fluorides, O₂F₂ and O₃F₂, are thermally unstable, decomposing below −71°F (216 K).

4. Nitrogen Trifluoride

NF₃ is the first of the N–F family of oxidizers. It also is a cryogen and has lower performance than that of fluorine. Since NF₃ is less reactive than fluorine, it was selected as an oxidizer for gas dynamic laser development. A wide range of metals and plastic materials are suitable for nitrogen trifluoride service. With most fuels, NF₃ is not hypergolic and offers only a marginal performance gain over the much cheaper liquefied oxygen.

5. Oxygen

Since Professor Robert H. Goddard pioneered the use of liquefied oxygen (O₂) as a rocket oxidizer in 1926, it has been the “work horse” oxidant for missiles and space launch vehicles. Called A-Stoff, it was used in the German

V-2 missile and later in the U.S. Thor, Jupiter, Titan I, and Saturn. It is currently used in the Atlas, launch vehicle Delta, and Space Shuttle. Liquefied oxygen is nontoxic, stable, noncorrosive, inexpensive, and is readily available from commercial sources. Being a cryogen, it is not desirable for missile applications and extended space missions.

B. Storable Oxidizers

Because of the inherent difficulty of maintaining cryogenic oxidizers in a state of readiness, the military has had a particular interest in storable oxidizers. Although there is no specific definition of “storable,” it is usually considered to encompass the ability of the oxidizer to remain in a ready condition within the missile or satellite for a minimum of 5 years, and in some cases longer than 10 years. During the 1960s the military services were interested in tactical weapons that required propellants with a low vapor pressure, <100 psig (689.5 kN/m²) at 160° F (344 K); a low freezing point, −20°F (244 K) to −65°F (219 K); be noncorrosive; and would not decompose. Less severe requirements are placed on silo-based strategic weapons and space vehicles.

1. Nitrogen Fluorides

Tetrafluorohydrazine, N₂F₄, is also called dinitrogen tetrafluoride. While this oxidizer can be kept liquid under its own vapor pressure, the pressure is high, 400 psia at 70°F (2.76 MN/m² at 294 K), thus N₂F₄ is often considered space storable rather than earth storable.

Tetrafluorohydrazine first became of interest to the rocket community in 1957 as an intermediate leading to a large family of postulated N–F compounds that would make improved storable oxidizers. These hypothetical materials had attractive theoretical performance, and the estimated physical properties appeared desirable.

Under Project Principia, funded by the Advanced Research Projects Agency (ARPA), and programs supported by the military services, a large synthesis effort was initiated in the quest for high-energy, storable propellants. Among those successfully synthesized and characterized were $C(NF_2)_4$, $FC(NF_3)_3$, HNF_2 , ONF , ONF_3 , O_2NF , and FNO_3 .

While many of the properties of these materials met expectations, the family as a whole was found to be very sensitive and the compounds readily decomposed, often violently. Extensive stabilization efforts were not fruitful; however, this research has led to a number of advances in solid propellant chemistry. N_2F_4 has proved to be a valuable intermediate for the synthesis of solid oxidizers and energetic binders for rocket motors.

Mixtures of N_2F_4 with other oxidizers were also investigated in an attempt to reduce its vapor pressure and yet retain its relatively high performance. N_2F_4 is a strong fluorinating agent resulting in unwanted reactions with most additives and oxidizers. Some of the mixtures were unstable and none proved to be useful. As a liquid oxidizer, the disadvantage of tetrafluorohydrazine for tactical weapons is the rapid lowering of density as its low critical temperature of $96.8^\circ F$ (309 K) is approached (Fig. 3), complicating rocket engine design. Neat N_2F_4 remains a viable liquid oxidizer candidate for space missions where the upper temperature limit is moderate. N_2F_4 is not reliably hypergolic with common rocket fuels.

2. Interhalogens

This family represents the highest energy earth-storable liquid oxidizers. They are toxic and highly reactive. Yet, in properly prepared containers these materials exhibit outstanding storability characteristics.

a. Chlorine Pentafluoride. Chlorine pentafluoride (ClF_5) is a product that resulted from the intensive fluorine chemistry research programs. It was first synthesized in 1962, and fired in a small rocket thruster in 1964. It has excellent density and the best performance of the available storable oxidizers, which makes it attractive for volume-limited systems. Because of its reactivity, it is best suited to prepackaged systems. The military has been reluctant to use ClF_5 because of its unforgiving nature; an inadvertent release of the material produces a toxicity hazard and would likely result in a fire. ClF_5 has been extensively evaluated in a variety of rocket engines and subsystems. Chlorine pentafluoride was the selected oxidizer for the Advanced Liquid Axial Stage (ALAS) built by Aerojet for a Strategic Defense Initiative space-based interceptor. The high performance and high density would serve to minimize both the weight and volume of systems that would

have to be orbited. It has been stored in mild steel containers for more than 20 years with no signs of deterioration or corrosion. The properties of chlorine pentafluoride mirror those of chlorine trifluoride, a product that has been produced and shipped commercially for more than 40 years. ClF_5 is not in current production; however, it is easily manufactured from chlorine and fluorine. The more available ClF_3 is used as a substitute for ClF_5 in test programs when actual performance measurements are not needed. A complete ClF_3 propulsion system was demonstrated for a liquid version of the Condor missile.

b. Perchloryl Fluoride. Perchloryl fluoride (ClO_3F) is a stable derivative of perchloric acid first synthesized in 1951. It is less toxic and much less reactive than ClF_3 and ClF_5 . ClO_3F has the advantage of having some oxygen that burns preferentially with carbon. Thus, ClO_3F/MMH (monomethyl hydrazine, $N_2H_3CH_3$) has an I_{sp} close to that of ClF_3 /hydrazine. The density of perchloryl fluoride is lower than that of ClF_3 , and because of its high coefficient of expansion, the density drops rapidly at the higher temperatures of interest, $160^\circ F$ (344 K). It is not reliably hypergolic with hydrazine and other fuels. With the emergence of ClF_3 , ClO_3F no longer was of interest.

c. Oxychlorine Trifluoride. Oxychlorine trifluoride (ClF_3O), called Florox, is an oxidizer that held promise. It boils at $87.1^\circ F$ (303.8 K), and has a density of 1.852. Because of its oxygen content, Florox is especially good with carbon-containing fuels (e.g., MMH). It is difficult and expensive to manufacture which has limited its availability for rocket research programs.

d. Bromine Pentafluoride. Bromine pentafluoride (BrF_5) has received attention as an oxidizer because of its very high specific gravity (2.47). Nevertheless, its performance is mediocre.

3. Nitrogen Oxides

Nitrogen tetroxide (dinitrogen tetroxide) (N_2O_4) is the "work horse" storable oxidizer. Initially considered and evaluated for the Bomarc (but not selected for the production version), it found its first major application in the Titan II intercontinental ballistic missile. It is used in the Titan III, 34D, and IV space launch vehicles, the Space Shuttle reaction control system, and in some of the newer satellite propulsion systems. The high freezing point of N_2O_4 has restricted its use in many other applications. Produced by the fertilizer industry, N_2O_4 is available in large quantities at a low price.

Stress corrosion cracking of titanium tanks by N_2O_4 is inhibited by the addition of about 1 wt% nitric oxide (NO),

the resulting formulation being called MON-1. To assure that there will always be sufficient NO for protection since some NO is lost through venting, MON-3 (containing a nominal 3 wt% NO) is used in the space shuttle and satellites.

NO depresses the freezing point of N_2O_4 without an I_{sp} loss but with an appreciable increase in vapor pressure (Fig. 1). The freezing point of MON-25 is approximately $-70^\circ F$ (216 K). Tetranitromethane will lower the freezing point to about $-22^\circ F$ (243 K). Many attempts to find other freezing depressants have failed.

4. Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) was of interest to Germany as being better suited for military purposes than liquid oxygen. A number of missiles and aircraft were developed beginning as early as 1936. Although wartime Germany was able to produce only 80% H_2O_2 (called T-Stoff), it was not as corrosive as nitric acid and did not produce toxic fumes. It also had the advantage of being a monopropellant that could be catalytically decomposed to provide hot gases (see Section III.F.5). The Messerschmidt 163A Komet interceptor, a rocket-powered aircraft, was first flown in 1937 using hydrogen peroxide monopropellant. A later version, Me-163B, powered by a bipropellant engine used H_2O_2 as the oxidizer with C-Stoff, a hydrazine hydrate-based fuel.

After World War II, the United States produced 90% H_2O_2 , and later a 98% grade. Peroxide readily found use in missile gas generators, research aircraft, and satellite attitude control systems, and as the oxidant in aircraft superperformance propulsion systems.

The U.S. Navy sponsored the development of peroxide as an oxidant for underwater propulsion, and as an oxidant in superperformance rocket systems for jet fighters. The U. S. Air Force used a hydrogen peroxide/JP-4 bipropellant propulsion system to give additional performance to modified NF-104 aircraft used by the USAF Aerospace Test Pilot School.

While NASA and the Air Force made extensive use of hydrogen peroxide, the high freezing point of $11^\circ F$ (261.5 K) and the slow thermal decomposition have limited its use for many applications. Some attempts were made to lower the freezing point with additives such as ammonium nitrite, but with limited success. With the selection of proper materials and cleaning and passivation procedures, the decomposition rate is about 0.5% per year. The 98% peroxide has a lower rate of about 0.1% per year, but a higher freezing point, $31^\circ F$ (272.6 K). The oxygen gas that results from the decomposition can be released through relief valves and porous plugs if the resulting pressure cannot be tolerated. A 90% peroxide system may be sealed and stored for one year and a 98% H_2O_2 system for

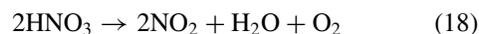
five years if proper precautions are observed. Both 90% and 98% H_2O_2 have been extensively evaluated with a variety of fuels including the hydrazines, kerosine, and pentaborane in 5000 lb_f (22 kN) engines. As can be seen from Tables V and VI, the specific impulse penalty is 25 sec for H_2O_2 /kerosine compared to LOX/kerosine and 10 sec compared to N_2O_4 /MMH. Recent thought is that the lower toxicity would make a lower cost system even with the slow decomposition problem and the lower performance.

In the 1990s, NASA and others have experimented with H_2O_2 /JP-8 engines of about 10,000 pounds thrust. The motivation is to avoid the necessity of handling and storing cryogenic liquid oxygen. The downside is a loss of about 25 sec of specific impulse which makes the vehicle heavier.

5. Fuming Nitric Acids

Various grades of nitric acid have been used extensively as storable oxidizers for many years. They have a good liquid range and are hypergolic with most amine-based fuels. Because of their corrosiveness and tendency to thermally decompose, considerable effort was expended by Germany and the United States to overcome these traits. Water enhances corrosion; therefore, early production centered on making 100% HNO_3 , known as white fuming nitric acid (WFNA), and keeping it absolutely dry. The Germans used a mixed acid, consisting of WFNA plus 10–17% sulfuric acid (a nitrating agent used in the explosives industry), which improved hypergolicity, and was believed (erroneously) to be less corrosive. They also found that the addition of 6% NO_2 to WFNA, making red fuming nitric acid (RFNA), improved stability.

After exploring the decomposition mechanisms of fuming nitric acid, several investigators found that self-dissociation of nitric acid occurs, forming water and oxygen gas:



Other studies to find freezing point depressants and means to improve thermodynamic stability lead to the obvious conclusion that one could add NO_2 and water to WFNA and force Eq. 18 to the left. An interesting development was the finding that hydrofluoric acid (HF) reduced the nitric acid corrosion rate by a factor of 10 both in aluminum and stainless steel containers. From this work a family of fuming nitric acid types was developed (Table X). Type IIIA, containing a nominal 14% NO_2 , 2% water, and 0.6% HF, became the standard nitric acid oxidizer, and is commonly called IRFNA (inhibited red fuming nitric acid). This composition was found to be the least corrosive and most stable. It was used subsequently in the prepackaged Bullpup and Lance missiles, the Bomarc, and in the Agena spacecraft. Bullpups were still functional after 18 years

TABLE X Fuming Nitric Acids—Chemical Composition Limits (Weight Percent)^a

Type	Nitrogen dioxide (NO ₂)	Water (H ₂ O)	Nitric acid (HNO ₃)	Solid as nitrates	Hydrogen fluoride (HF)
IIIA	14 ± 1.0	1.5 to 2.5	81.6 to 84.8	0.10 max.	0.7 ± 0.1
IIIB	14 ± 1.0	1.5 to 2.5	81.6 to 84.8	0.04 max.	0.7 ± 0.1
IIILS	14 ± 1.0	0.5 max.	83.7 to 86.4	0.04 max.	0.7 ± 0.1
IV ^b	44 ± 2.0	0.5 max.	52.7 to 57.4	0.04 max.	0.7 ± 0.1

^a From MIL-P-7254F Amendment 2.

^b Additional requirement for Type IV: Fe₂O₃ 0.002 wt% maximum.

of unattended storage, and the Lance had more than 15 years of successful deployment. Type I (WFNA), used in the Rascal, and Type II (RFNA with 6% NO₂ and no inhibitor), used in rocket-assisted takeoff units (RATO), are no longer used and were dropped from the specification.

The maximum amount of NO₂ that can be added to fuming nitric acid without a phase separation is 44%. This composition has the highest density, about a 3% specific impulse improvement over Type IIIA, and is more corrosive. Officially identified as Type IV, is also called High Density Acid (HDA) and Maximum Density IRFNA (MDIRFNA). It was used in some models of the Agena where the total operational period was measured in months. Phosphoric pentafluoride (PF₅) was found to be a superior corrosion inhibitor over HF but was never adopted for system use.

6. Tetranitromethane

Tetranitromethane (TNM), C(NO₂)₄, is a monopropellant that has high specific gravity (1.368) and an oxidizing potential similar to that of N₂O₄, but it freezes at 57.4°F (287.2 K). Some batches of TNM were sensitive to mechanical shock, while others readily passed safety tests, indicating the possible presence of impurities. A eutectic mixture of 64% TNM and 36%, by weight, N₂O₄ freezes at -22°F (243 K) and is less sensitive than neat TNM.

7. Other Oxidizers

Perchloric acid has received limited attention as a liquid oxidizer as perhaps being less corrosive than fuming nitric acid, yet having a low freezing point. At concentrations approaching 100%, HClO₄ is very unstable and its performance is inferior to that of nitric acid. Mixtures of amine salts of perchloric acid were studied briefly.

C. Cryogenic Fuels

1. Hydrogen

Liquefied hydrogen (H₂) has high heat release and provides very low molecular weight combustion products,

making it the fuel of choice with either oxygen or fluorine when its cryogenic nature is acceptable. Liquefied hydrogen was used in the S-II and S-IVB stages of the Saturn V launch vehicle for the Apollo program.

Liquid hydrogen is operational in Centaur, the Space Shuttle, and the upper stage of Ariane 5. Boeing is developing the RS-68 engine for the first stage of the EELV which will use LOX/LH₂.

Derived from petroleum sources, hydrogen is readily available at a reasonable cost. Liquefied hydrogen exists as a mixture of ortho- and para-hydrogen. Ortho-hydrogen reverts exothermically to the para form, increasing boil-off. This problem is avoided by catalytic ortho to para conversion by the manufacturer.

Slush hydrogen, a mixture of frozen and liquefied hydrogen, and hydrogen subcooled below its boiling point, provides increased density and storability. This is especially attractive for space vehicles to minimize structure weight and reduce the initial hydrogen boil-off rate. The density values at the triple point of hydrogen are presented in Table XI. The latent heat of fusion of solidified hydrogen at the triple point is 25.02 Btu/lb (117.32 J/mole). Solid cryogenic storage can double the in-space storage life of hydrogen.

2. Cryogenic Hydrocarbons

Liquefied methane (CH₄), ethane (C₂H₆), ethene (C₂H₄), and propane (C₃H₈), both neat and in various mixtures

TABLE XI Density Values for Slush, Liquid, and Solid Hydrogen

State	lb/ft ³	kg/m ³
At the normal boiling point ^a		
Liquid	4.425	70.889
At the triple point ^b		
Saturated liquid	4.81	77.02
50% liquid/50% solid	5.09	81.54
Solid state	5.41	86.64

^a Normal boiling point: -423.3°F (20.4 K) at 1 atm.

^b Triple point: -434.8°F (13.8 K) at 1.021 psia (7.04 kN/m²).

are excellent fuels, having better performance and combustion characteristics than kerosine, and the disadvantage of being cryogenic. The higher density of these liquefied gases offer an advantage over hydrogen in very large vehicles by keeping the tank size down, and thus overall dry weight, although there is also a reduction in specific impulse. Slush and supercooled states provide increased density and longer storability.

D. Storable Fuels

1. Storable Hydrocarbons

Much attention and effort has been devoted to develop hydrocarbon-based rocket fuels because of the low cost and widespread distribution of petroleum products. Kerosine is the most widely used fuel, generally with liquefied oxygen as the oxidizer. This combination is used in the Atlas and Thor now launch vehicles, and was used in the Titan I and the Saturn V first stage. Propellant-grade kerosine (called RP-1) is essentially JP-4 jet engine fuel with a controlled aromatic content to eliminate coke formation in regenerative cooled engine jackets. It also has a narrow density range needed for accurate volumetric loading of missile tanks.

Some hydrocarbons decompose under high temperature. If the temperature is too high in the regenerative cooling passages such decomposition will leave carbon behind to the extent that the cooling passages could become clogged. Even if not clogged a layer of carbon can reduce the heat transfer rate inside the cooling passages and result in a burn through. Reduction of heat transfer rate with a coating of carbon is actually desired in some hydrocarbon engines where a coating of carbon on the combustion chamber side of the cooling passage reduces the heat transfer rate. Where the engine is not regeneratively cooled by the fuel, it is much cheaper to use JP-8, a common military jet fuel rather than the more expensive RP-1.

Dr. Goddard used motor-grade gasoline in his experiments. Decalin, diethylcyclohexane, octane, and aviation gasoline were also used as rocket fuels in the early years of rocketry in both the United States, and Germany. During the 1950s the U.S. Air Force selected jet fuel to be used with fuming nitric acid in RATO units and super-performance propulsion systems to be used on the B-47, F-86, and other aircraft of that period. The JP-4/nitric acid system was plagued with combustion instability, hard starts, and overall unreliability. Various additives, notably amines and metal salts, were tried to reduce ignition delay and improve the combustion process, with limited success. The U.S. Navy had fared better with its JP-5/H₂O₂ engine development program. Subsequently, a hydrogen peroxide rocket system (using the onboard JP-4 fuel) was

incorporated into NF-104 aircraft used for astronaut training at the Aerospace Test Pilot School, Edwards AFB, California.

Both the U.S. Air Force and Navy funded efforts to develop petroleum-derived fuels for rocket engines using nitric acid as the oxidizer. Many different compounds were investigated including mercaptans and thiophosphates. The individual components in JP-4 were isolated and evaluated on their ability to improve or to hinder hypergolicity and combustion. Hydrazine compounds as additives were found to be the answer. Many other hydrocarbons (e.g., aromatics, aliphatics, acetylenes, terpenes, ethers) were tried in many propulsion systems. Turpentine was used in the French Diamant launch vehicle. Another fuel of interest was the German Viscol, a vinyl isobutyl ether. Most hydrocarbon fuels offer about the same specific impulse. Thus, the choices are factors of availability, physical properties, and cost. For large boosters and launch vehicles, a high propellant density is desirable to reduce overall size, and thus structure weight. Shellodyne[®]-H, hydrogenated dimer of norbornadiene, is an example of a dense fuel (1.11 kg/m³) originally developed as a thermally stable, endothermic fuel ramjets as RJ-5.

Several variations of kerosine have arisen in the 1990s:

(1) RP-2 a mixture of kerosine or heptane with quadricyclane; (2) RG-1 the Russian version of kerosine rocket fuel with higher density than RP-1; and (3) JP-8X and JP-8 + 100.

Other alternative hydrocarbons under research and development which have a 10–15 sec specific impulse advantage over RP-1 include bicyclopropylidene, spiro-pentane and tripropargyl-amine. A 10-sec increase over LOX/RP-1 is available by using LOX/UDMH as did the Juno rocket in 1957. However, the current preference is to search for something less toxic than the hydrazine family to enhance the performance of an existing kerosine fueled vehicle.

RP-2 uses quadricyclane, which releases energy from its mechanically strained molecule in addition to the energy of combustion. Quadricyclane is strained due to the cyclopropane rings. Compared to LOX/RP-1, a 50% quadricyclane/50% RP-1 mixture, the specific impulse gain is 3 sec. In a 65% quadricyclane/35% *n*-heptane, the specific impulse gain is 5 sec. For 100% quadricyclane, the specific impulse gain would be 7 sec but experiments have revealed rough combustion. Other strained ring compounds such as cubane are also being studied for performance improvement over RP-1 in existing vehicles

2. Alcohols

In Germany during the late 1930s and through World War II, methanol (CH₃OH) and ethanol (C₂H₅OH) (M-Stoff and B-Stoff) were widely used as rocket fuels, being more

available than petroleum products. The V-2 used ethanol and liquefied oxygen. Captured German technology and equipment laid the foundation for alcohol-fueled rockets in both the United States and the Soviet Union after the war. The alcohol fuels have excellent storability and combustion properties, but relatively low performance. Furfuryl alcohol ($C_4H_3CH_2OH$) improves the hypergolicity of hydrocarbon and amine fuels with nitric acid.

3. Amines

The German emphases on storability and hypergolicity led them to the amines. Tonka-250 (R-Stoff, used in the Taifun Missile) consisted of 57% xylidine and 43% triethylamine. Tonka-500 contained a number of components: toluidine, triethylamine, aniline, gasoline, and benzene. C-Stoff, used in the Me163B Komet consisted of methanol, 57%; hydrazine hydrate, 30% (reduced to 15% at the end of WW II to stretch supplies); water, 13%; and copper, 30 mg/l (as potassium cuprocyanide to improve combustion).

The U.S. Army had similar interests, plus a desiring for a low freezing point. To this end, the Jet Propulsion Laboratory investigated a large number of additives to make gasoline hypergolic. At least 50% of xylidine or amine was needed to impart hypergolicity. Furfuryl alcohol was found to be a good fuel component. The final result was MIL-P-45700, a mixture of 51% aniline and 46.5% furfuryl alcohol that froze at $-45^\circ F$ (230.4 K). This mixture was used in the Navy's Lark and in the Army's Corporal missiles. Later, 7% hydrazine was added to improve storability and low-temperature hypergolicity.

A bewildering list of amines and mixtures has been prepared as rocket fuels and evaluated by various organizations. A commercial grade of monoethyl aniline (*N*-ethyl aniline) exhibited a freezing point of $-81^\circ F$ (210 K) and excellent hypergolicity with fuming nitric acid. Diethylene triamine was of interest as a density additive. Acetonitrile improved the low-temperature viscosity of amines. None of the possible hydrocarbon/amine fuels had a performance much better than the others; thus, the application of these fuels was often based on availability, hypergolicity, freezing point, and smoothness of combustion.

4. Hydrazines

Captured stocks of World War II hydrazine hydrate opened a new era of propellant research in the United States. The technology to manufacture anhydrous hydrazine was developed, a capability not available in wartime Germany. The high freezing point of anhydrous hydrazine and its tendency for chamber explosions have restricted the use of the neat material to small space engines, where it is the mono-

propellant of choice. Unsymmetrical dimethylhydrazine (UDMH) and monomethyl hydrazine (MMH), $N_2H_3CH_3$, became the focus of considerable interest in the 1950s and are now the principal fuels used in storable liquid rocket propulsion systems. Wide acceptance of UDMH was slow because of the interest from the U.S. Navy and Air Force to use petroleum-derived fuels. Initially UDMH was used as an additive (17% UDMH) to JP-4 to stabilize combustion in the Nike Ajax. This mixture was called JP-X Type II. A 40% UDMH/60% JP-4 blend, JP-X Type I, was used in the Bomarc. JP-X is covered by MIL-P-26694.

A series of mixed amine fuels (MAF) were developed for tactical missiles and launch vehicles. (See Table XII.) MAF-1 was used in the Bullpup deployed by the U. S. Navy and Air Force. MAF-4, also known as U-DETA and Hydnye, was used in the Jupiter-C and target drones. A family of mixed hydrazine fuels (MHF) was also developed, primarily as monopropellants but also used as bipropellant fuels (Table XIII). MHF-3 was developed as the fuel for the Condor, and was used as M-86 monofuel in aircraft auxiliary power units (APUs). MHF-5 (later MHF-5B) was selected for the Condor gas generator. BA-1014 and BA-1185 were tailored for fluorine or interhalogen oxidizers. The water in these fuels was added to provide oxygen to combust preferentially with the carbon in MMH, eliminating free carbon in the exhaust.

A 50–50 wt% blend of anhydrous hydrazine and UDMH (often called Aerozine-50) is used in the Titan II, III, IV, and derivatives. A low freezing point is provided, and the stability of hydrazine is enhanced. The 50–50 mix was chosen over MMH because of lower cost and better availability. The cost difference no longer exists, and the production of MMH matches current demand. Therefore, MMH is now the preferred storable fuel for new propulsion systems. Neat UDMH was used in the Agena program and in the U. S. Army's Lance. Now MMH is used in the space shuttle reaction control system engines, the Minuteman, and Peacekeeper postboost propulsion systems, and is being selected for satellite bipropellant propulsion systems. The hydrazines have exhibited excellent storability, with no degradation for more than a 20 year period.

Symmetrical dimethyl hydrazine freezes at $16^\circ F$ (264.2 K) and has no advantages over UDMH. Ethylene dihydrazine (EDH) offers a higher density, making mixtures of EDH and hydrazine with N_2O_4 as the oxidizer attractive candidates for launch vehicle upper stages. Aerozine-67 (67.2% EDH/32.8% hydrazine, by wt.) provides a substantial payload increase over that of neat MMH or Aerozine-50, although the I_{sp} is slightly lower.

Ammonia is an excellent fuel, but its high vapor pressure has restricted its use. In 1949 JPL first evaluated ammonia with fuming nitric acid and N_2O_4 . An

TABLE XII Mixed Amine Fuel Compositions (Nominal)^a

Fuel	DETA ^b	Acetonitrile	UDMH	PRODGA ^c	DIPGA ^d	TIPRAM ^e	Water ^f
MAF-1	50.5	9.0	40.5	—	—	—	—
MAF-2	—	—	—	42.6	48.3	9.1	—
MAF-3	80.0	—	20.0	—	—	—	1.0
MAF-4 (U-DETA)	40.0	—	60.0	—	—	—	—
MAF-5	50.5	20.0	29.5	—	—	—	—

^a By weight percent.

^b Diethylenetriamine.

^c Propargyl diglycidylamine.

^d Dipropargyl glycidylamine.

^e Tripropargylamine.

^f Propellant-grade DETA and UDMH normally contain water (<1.0% by weight), thus all mixtures will have a small amount.

ammonia/liquefied oxygen engine powered the X-15 research aircraft in the XLR-99 engine.

5. Metal-Based Fuels

The known liquid metal alkyls are low in performance, but they are pyrophoric. Triethyl aluminum and triethyl boron are useful as igniters in liquefied oxygen/kerosene propulsion systems (e.g., Atlas). Of the light metal hydrides, only diborane and pentaborane are normally liquid. Diborane is especially attractive for use with Flox or OF₂ in space-storable propulsion applications. B₂H₆ decomposes above -4°F (253 K), necessitating the use of refrigeration for extended storage periods. Pentaborane is very stable as demonstrated by desert storage in mild steel cylinders

for more than 30 years. Complete combustion with liquefied oxygen and hydrogen peroxide is difficult, resulting in slow burning condensed boron particles and the formation of vitreous boron oxide solids in nozzles. Since boron fluoride is gaseous, these problems are eliminated with fluorine-based oxidizers. A unique propellant combination, pentaborane/hydrazine was also studied. In this case, the hydrazine acts as the oxidizer. The high theoretical *I*_{sp} of this system was predicated upon the formation of boron nitride (BN). Combustion inefficiencies caused by condensed products, kinetic limitations, and combustion instability made the realization of high delivered performance difficult.

Experimental fuels based on aluminum and lithium borohydride were evaluated, but were dropped when

TABLE XIII Mixed Hydrazine Fuel Compositions (Nominal)

Fuel	Freezing Point, °F(K)	Hydrazine (wt%)	MMH (wt%)	Hydrazinium nitrate (wt%)	Water ^a (wt%)
MHF-1	-65(219)	23.3	43.3	31.4	—
MHF-2	-65(219)	23.3	36.5	40.2	—
MHF-3 (M-86)	-65(219)	14.0	86.0	—	—
MHF-4	-43.6(231.2)	32.5	50.5	17.0	—
MHF-5	-44.6(230.6)	26.0	55.0	19.0	2.0 max.
MHF-5A	<-65(219)	13.0	68.0	19.0	—
MHF-5B	-45(230.4)	23.0	58.0	19.0	—
MHF-6	<-65(219)	16.5	73.0	—	10.5
MHF-7	-65(219)	14.0	81.0	—	5.0
MGGP-1	-65(219)	63.0	—	10.0	27.0
H-70 (MGGP-3)	-58(223)	70.0	30.0	—	—
TSF-1	<-65(219)	60.0	—	21.0	19.0
TSF-2	<-65(219)	58.0	—	25.0	17.0
BA-1014	-2.5(254)	66.7	24.0	—	9.3
BA-1185	-65(219)	29.8	50.5	—	19.7

^a Propellant-grade hydrazine and MMH normally contain water (<1.0 percent by weight), thus all mixtures will have a small amount.

UDMH became available. Beryllium borohydride has been tested, but its toxicity precluded further consideration.

The hybalines are a group of coordination compounds of light metal hydrides or metal borohydrides, complexed with Lewis bases such as amines or ethers. Following are some of the compositions evaluated:

- Hybaline A-3: methylamine aluminum borohydride
- Hybaline A-4: dimethylamine aluminum borohydride
- Hybaline A-5: 53 wt% A-3 and 47 wt% A-4
- Hybaline A-14: 2-ethylhexylamine aluminum borohydride

Hybaline B fuels, amine adducts of beryllium borohydride, were also prepared and studied. Hybalines may be viewed as a densified form of hydrogen bounded by energetic light metal atoms. This family of fuels are hypergolic with most rocket oxidizers. They react with water, and sometimes are pyrophoric in air. Propellant feed systems must be kept very clean since traces of moisture and air would form solid materials, causing flow problems. Hybalines are neither sufficiently stable nor storable for military applications.

Lithium has attractive theoretical performance with fluorine-based oxidizers. Experiments have been conducted using molten lithium injected into a 3000 lb_f (13.3 kN) thrust chamber with an interhalogen oxidizer. Solid lithium was used in hybrid experiments with chlorine trifluoride as the oxidizer. In this case, heat transfer to the solid metal must be controlled to prevent premature melting, yet sufficient vaporization of the fuel must occur to sustain proper combustion. Lithium alkylates, for example, butyllithium, contain insufficient lithium to enhance performance.

E. Heterogeneous and Gelled Propellants

Gelation of liquid rocket propellants is of interest for several reasons:

(1) retardation of evaporation rate of volatile or toxic liquids; (2) retardation of mixing of spilled propellants to prevent explosions; (3) suspension of energetic solid powders to improve performance; and (4) reduction of sloshing in tanks.

The above advantages come with some unique problems:

1. Difficult control of mixture ratio because of the heterogeneous flow properties
2. Slightly decreased delivered performance compared to theoretical
3. Higher pressure drops causing heavier inert weight

4. Decreased service life at temperature extremes
5. Increased unusable residual propellants further penalizing mass fraction.

Light metals have high heat release, making them attractive as fuels or fuel components. As mentioned previously, there are very few candidates that are liquids. One way to use high energy, solid materials is to suspend them in a liquid carrier. In particular, Al, AlH₃, B, Li, LiH, Be, and BeH₂ have been of most interest. Considerable research was undertaken to find techniques that would keep the solid from settling. Very fine particle size (typically 0.1–10 μm) is needed and the liquid thickened. Different hydrocarbon, hydrazine, and alcohol carriers were evaluated. Hydrazine and MMH were of most interest because of their higher energy, but were subject to gassing exacerbated by the high surface area of the metal or hydride powder. Gels, slurries, and emulsions were formulated and evaluated.

Thixotropic gels were of particular interest because of their ability to be liquefied by internal mechanical stress and to return to the gel state when the stress is removed. The consistency of thixotropic gels depends on the duration and rate of shear. Under static conditions, these gels exhibit a weak structure and are nonflowing, semi-solid substances. If, however, the yield point is exceeded and the gels are sheared at a constant rate, the structure will progressively weaken and the viscosity will decrease with time. The structure of true thixotropic materials will break down completely under the influence of high shearing action such as injection through an orifice, in which case they behave like true Newtonian liquids. As soon as the shearing action has ceased, however, the structure will reform. The rate of breakdown and reformation of the structure of a gel is a characteristic of that gel, and the time required for the transition may vary from a fraction of a second to many hours. Many gelling and thickening agents were tried, with colloidal silicon dioxide, hydroxyethyl cellulose, and polyacrylic acid being typical. Lithium and its compounds proved too reactive for a stable propellant. The toxicity of beryllium and its hydride severely restricts its usefulness. Boron gels are best suited for air-breathing engines, such as the ducted rocket. Gels containing AlH₃ evolved too much hydrogen gas to be practical. Several successful aluminum-based formulations are given in Table XIV. Alumizine, covered by MIL-P-27412 (subsequently cancelled) was fired in a modified Titan II engine. MICOM GEL was tested in an Lance engine and several organizations have evaluated NOTSGEL-A in a variety of thrust chambers with different oxidizers. These formulations meet long-term stability requirements and present no undue operational hazards.

TABLE XIV Heterogeneous Rocket Fuel Composition

Component	Alumizine-43G	NOTSGEL-A	MICOM GEL
Aluminum Powder	43.0	60.0	60.0
MMH	—	31.1	38.5
Hydrazine	56.3	5.1	—
Colloidal Silica	—	3.0	—
Modified Polyacrylic Acid	0.3	—	—
Water	0.4	—	—
Hydroxypropyl Cellulose	—	—	1.4
Hydroxyethyl Cellulose	—	0.8	—
Dimethylurea	—	—	0.1

The gelling of cryogenic propellants has also been studied. Liquified hydrogen can be gelled with light hydrocarbons (e.g. methane, ethane), which are solid at hydrogen temperatures.

Gelation of liquid hydrogen has a payoff of reducing boil-off rate and significantly reducing spill radius. A 10% density increase is possible with gelled hydrogen by the addition of 10% solid ethane or methane powder.

Current research and development activities include gelation of RP-1 in order to add aluminum powder to a LOX/RP-1 system to gain increased performance.

1. Oxidizers

Liquid rocket oxidizers are more energetic than are solid oxidizers; thus, there are no solid components that can be added to a liquid oxidizer to enhance specific impulse. However, potential for improvement in safety and operational usage is the incentive to develop gelled oxidizers. In an accidental spill, gelled oxidizers would have reduced flow characteristics and lower vaporization rates, making it easier to contain the spilled propellant and rendering it easier to clean up. Alleviation of sloshing in tanks provides greater flight stability of missiles.

Another reason to gel oxidizers is to match the flow properties of a gelled fuel. The addition of LiNO_3 to nitric acid gelled with silica, for example, increases the density, does not seriously detract from I_{sp} , and provides rheological characteristics similar to those of MICOM GEL, minimizing mixture ratio shift as propellant temperatures are varied across the operational range.

Liquefied oxygen, oxygen difluoride, fuming nitric acid, and nitrogen dioxide have been gelled. Gelation of LOX is actually possible using frozen N_2O_4 particles.

While the resulting formulations were chemically stable and found insensitive to shock, long-term storability has not been fully resolved. Syneresis, or the exuding of liquid, is a problem that may occur after several months or a few years of storage. Rheological behavior can also

change with time. The following are typical gelled oxidizer compositions:

1. Oxygen and 5 wt% alumina or titania
2. Oxygen difluoride and 4.5 wt% colloidal silica
3. RFNA and 4 wt% colloidal silica
4. IRFNA and 5 wt% carbon black
5. Nitrogen dioxide and 3.5 wt% colloidal silica
6. MON-15 and 3.5 wt% colloidal silica

The gelling of chlorine pentafluoride (ClF_5) with sub-micron particle size ferric oxide and alumina was not successful. Silica reacts with ClF_5 . Fluoride salts (e.g., CaF_2 , LiF) are chemically stable with ClF_5 , but large amounts are required for gelling.

2. Safety

Gelling of liquid propellants has been proposed as a means of reducing the consequences of an accident in which propellants are released from their container. A large-scale spill of liquid propellants will result in splashing and spreading of the liquid over a large area. Tests have shown that under similar conditions the gelled propellant will remain confined to a smaller area due to its high viscosity, making it much easier to clean up. In the case of a simultaneous spill of a hypergolic propellant combination, the propellants will ignite at the interface, but will not be involved in a violent fuel/oxidizer deflagration. The fuel will continue to burn as a normal fuel/air reaction, but because of its immobility, will not spread. Increased safety is also provided by gels when small, low pressure leaks occur at fittings or cracks since gels will not flow from the leak as would a liquid.

Tests have also shown that gelation of liquids will also reduce the rate of vaporization, thus the spread of toxic or flammable vapors is lessened. However, the vapor pressure, reactivity, and toxicity of the propellants are not altered. In other tests, tanks containing gelled propellants

subjected to bullet impact or external fire experienced pressure rupture but did not detonate as will typical high performance solid propellants.

F. Monopropellants

There are three basic types of liquid monopropellants, or monofuels:

1. Single substances (molecular compounds) that contain an oxidizing agent and combustible matter in the same molecule
2. Intimate mixtures of compounds that are stable under normal conditions
3. Thermodynamically unstable chemicals

Upon ignition, the first two types of monopropellants will undergo combustion much like a bipropellant combination. The components in the second type must be compatible at normal temperatures, but react when ignited or heated under pressure to give hot combustion gases. The third type decomposes to produce hot gases by means of a catalyst or a thermal source. These are the monopropellants, specifically hydrogen peroxide and hydrazine, that have been the most acceptable and useful in a wide variety of systems.

The challenge in developing high-energy monopropellants is finding compositions that are easy to handle and stable to a wide variety of adverse environmental influences, yet will decompose rapidly and smoothly when initiated to deliver its energy in a rocket or gas generator.

1. Molecular Monopropellants (Combustion Type)

Examples of molecular liquid monopropellants that undergo a combustion process are nitromethane (CH_3NO_2), ethylene oxide ($\text{C}_2\text{H}_4\text{O}$), *n*-propyl nitrate ($\text{C}_3\text{H}_7\text{NO}_3$), ethyl nitrate ($\text{C}_2\text{H}_5\text{NO}_3$), and tetranitromethane [$\text{C}(\text{NO}_2)_4$]. Electrical sparks and pyrotechnic squibs are used to ignite these propellants.

Ethylene oxide, a commercial chemical, was used to power decoys. It is stable under high-pressure flow conditions; however, the vapor phase is sensitive. This compound is subject to exothermic reactions when in contact with various acids, bases, salts, and catalysts. Decomposition of ethylene oxide is difficult to sustain because of its high autoignition temperature of 804°F (702 K) and carbon formation from thermal cracking.

The U. S. Navy is developing cyclodextrin nitrate with an I_{sp} of 240–280 sec and a density near 2.0 gm/cc . Dinitramine is another monopropellant candidate with an I_{sp} of 270–300 sec and a density of 1.9 gm/cc . Another monopropellant candidate in the 1990s is hydroxyl ammonium nitrate.

2. Nitroaliphatic and Nitrate Esters

These compounds have had limited application as monopropellants. Nitromethane, used by race car and model airplane enthusiasts, has the highest performance and was the most studied. It is normally sensitive to shock and thermal stimuli, and has a high flame temperature of 3950°F (2450 K). Engine tests were characterized by instability and inefficient operation. While most additives generally increase its sensitivity, a few alcohols and hydrocarbons were found to improve stability and lower the flame temperature with a modest decrease of performance. The German Myrol, consisted of 80% methyl nitrate and 20% methanol, was reasonably safe to handle.

N-propyl nitrate (NPN) was used in jet engine starters of U.S. military aircraft and for decoys. The British used the similar isopropyl nitrate for engine starters and missile gas generators. NPN was found to be sensitive to adiabatic compression. The addition of 60% ethyl nitrate resulted in an 8% specific impulse improvement, but further sensitizes NPN.

3. Composite Monopropellants

a. Amine-nitric acid. A major effort in the development of high-energy monopropellant candidates was directed at the amine nitrate-nitric acid composite-type formulations. These mixtures can be considered premixed bipropellants. This family consists principally of secondary, tertiary, ditertiary, and quaternary amines that are converted to the corresponding nitric acid salts and mixed in solution with nitric acid (WFNA or RFNA). A large variety of mixtures has been made and evaluated, sometimes with disastrous results. Examples of this class that have been studied are

1. WFNA and pyridinium nitrate (Penelope)
2. WFNA and diisopropylammonium nitrate (Isolde)
3. WFNA and [1,2,4-trimethyl-1,4-diazabicyclo(2,2,2)] octane dinitrate (Cavea)

This family of composite monopropellants has moderate theoretical performance levels ranging from ~ 220 to 260 sec (2158 to 2550 N sec/kg). The performance, sensitivity and thermal stability of these composites vary with the amine structure and oxidation ratio. As the oxidation ratio approaches stoichiometric, the performance and the sensitivity are increased and the thermal stability is decreased. As a result, these composites were found to be quite shock sensitive and of questionable thermal stability. Cavea underwent extensive characterization and engine evaluation at the $10,000\text{ lb}_f$ (44.5 kN) thrust level. After several explosions occurred, testing was discontinued.

b. Difluoroamines. Most of the difluoroamino compounds and composite monopropellants have exhibited poor thermal stability and extreme shock sensitivity. The most extensively studied of this family was 1,2-bis(difluoroamino)ethane as both a molecular monopropellant and in solution with either tetranitromethane or nitrogen tetroxide (the latter mixture known as Cyclops). The mixtures were less sensitive than the neat compound, but not sufficiently to avoid detonations.

The BN-type monopropellants are perhaps the highest energy (I_{sp} about 300 sec) (2942 N sec/kg) consisting of borane compounds dissolved in hydrazine. Dekazine (54% diamino-decaborane and 46% hydrazine) received the most attention, being fired in a 600 lb_f (2669 N) thrust chamber at 1000 psia (6:895 MN/m²). Also in this family are the Hepcats, [(CH₃)₃ NNH₂]⁺B₁₀H₁₃-type salts dissolved in hydrazine. Low-delivered performance and high sensitivity contributed to the demise of this family.

c. Otto fuel. The Otto monopropellants, a series of formulations based on desensitized aliphatic dinitroxyl esters, were originally developed for torpedo propulsion. Otto fuel II is the most successful composition, having outstanding safety characteristics while meeting stringent temperature, shock stability, and energy requirements. Under normal conditions, it is considered to be nonflammable and nonexplosive, making it a safe propellant. Its major constituent is propylene glycol dinitrate stabilized with dibutylsebacate (see Table XV). Otto Fuel II is used in the Mk 46 Mod 1 and Mk 48 torpedos, and it has been selected for several developmental programs, including a liquid-propellant gun and a rocket-propelled target drone. Ignition is accomplished with a solid squib that pressurizes the chamber to the 200 psi (1.38 MN/m³) necessary to sustain decomposition of the Otto Fuel.

4. Heterogeneous Monopropellants

Another group of composite-type monopropellants are the heterogeneous monopropellants that consist of high-energy or high-density solid ingredients suspended in various liquid vehicles as a slurry or through gelation.

TABLE XV Composition of Otto Fuel II

Component	Amount (wt%)
Propylene glycol dinitrate ^a	75.8–76.2
2-Nitrodiphenylamine	1.4–1.6
Di- <i>n</i> -butyl sebacate	22.2–22.8
Sodium ion	0.8 ppm (max.)

^a 1.2 Dinitroxypropane.

Essentially, there are three chemical types of heterogeneous monopropellants that have been studied: Arcogels, B₄C/oxidizer gels, and beryllium composites. The Arcogels are thick slurries of aluminum powder and nitrate or perchlorate salts in an uncured solid binder that do not shear thin. A typical formulation, APG-25, [63.2% NH₄ClO₄ + 20.7% Al + 14.8% (CH₂)_x + 1.3% thickener], has a density of 1.8 kg/m³ and an I_{sp} of 166 sec (1.628 kN sec/kg). Its very high viscosity greatly complicated a feed and engine system design.

Heterogeneous formulations of B₄C in various oxidizers, including nitrogen dioxide, perchloryl fluoride, and nitric acid, gelled with carbon black or SiO₂ were evaluated in small engines for prepackaged and torpedo applications. Moderate performance, about 225 sec (2,207 N sec/kg), was realized. These compositions are insensitive to shock, but appear to be unstable at 160°F (344 K).

The beryllium monopropellants consist of Be and BeH₂ in solutions of hydrazine, hydrazinium nitrate, water, or hydrogen peroxide gelled with colloidal silica, aluminum octanoate, or Kelzan-AO. One patented formulation having a theoretical performance of 310 sec (3040 N sec/kg) is:

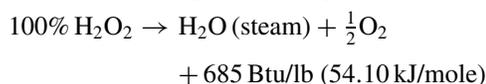


These compositions are insensitive to shock, but are subject to poor long-term storability and gassing. Because of their toxicity and inefficient combustion, beryllium-based propellants are of little current interest.

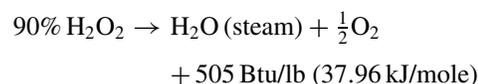
5. Molecular Monopropellants (Decomposition Type)

a. Hydrogen peroxide. Hydrogen peroxide was the first widely used monopropellant. During the late 1930s and through World War II, the Germans used 70–80% H₂O₂, and called it T-Stoff. They used it to drive the bipropellant pumps in the V-2. After the war, the technology to produce 90–99% H₂O₂ was developed. Hydrogen peroxide was also used to drive pumps in the early U.S. missiles and in satellite reaction control systems. In the X-15 high-altitude research aircraft, peroxide was used to drive the main propellant pumps and APU, and in the attitude control thrusters.

Hydrogen peroxide is decomposed catalytically to form superheated steam and gaseous oxygen:



or



Many materials act as catalysts to decompose peroxide. The following have been successfully used in operational systems:

1. Calcium, potassium, and sodium permanganate in an aqueous solution (German Z-Stoff)
2. Permanganate salts deposited on ceramic or metal balls
3. Silver and other noble metals
4. Transition metal oxides

Screens of silver or silver-plated brass are the commonly used H_2O_2 catalysts in the United States.

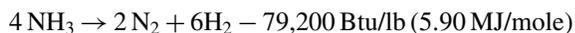
In the search for higher energy and low-freezing monopropellants, experimental compositions of hydrogen peroxide containing various amounts of ethanol, ammonia, and ammonium hydroxide, singly and in combination, were tested but with adverse effect on sensitivity and stability.

b. Hydrazine. Hydrazine's ease of decomposition and freedom from the instabilities of the other monopropellants has led to its becoming the principal fuel for low-thrust satellite propulsion. It has replaced hydrogen peroxide in almost all monopropellant applications because of its better storability and higher performance. Intelsat III and IV, Pioneer 10 and 11, Mariner 69, Landsat, FLT-SATCOM, Telestar, and Tracking and Data Relay Satellite are a few of the many systems equipped with hydrazine thrusters. Hydrazine is also used to drive the APUs in the space shuttle. H-70 (70% N_2H_4 and 30% H_2O) powers the emergency power unit (EPU) in the F-16 and F-20 fighter aircraft.

Hydrazine is decomposed by either thermal or catalytic means, producing hot gases of ammonia, hydrogen, and nitrogen:



The resultant ammonia product is also dissociated by hydrazine catalysts. Since its decomposition is an endothermic process, it must be minimized to avoid serious performance loss:



Typically, about 40% of the ammonia is dissociated, being controlled by catalyst bed design and residence time.

Hypergolic slugs were used to initiate hydrazine decomposition in the early systems. Later, catalysts composed of transition metals and their oxides were used which provided a limited restart and pulse-mode capability. These catalysts were heated electrically to about 800°F (700 K) to effect rapid hydrazine decomposition. The availability in 1964 of Shell 405 catalyst, which causes spontaneous

decomposition of hydrazine, greatly expanded the applications of monopropellant hydrazine. It opened the way for the use of hydrazine in systems requiring rapid-response multiple starts, especially the 0.2–25 lb_f (0.9–111 N) thrusters used on satellites. Shell 405 catalyst consists of a porous alumina substrate impregnated with chemically deposited iridium. The catalyst granules contain about 33 wt% Ir and are in the range of 14–30 mesh. The surface area of the catalyst is typically 70 to 120 m^2/g .

HYDRAZINE BLENDS. Various compounds have been evaluated as means of improving hydrazine monopropellant performance and to depress its freezing point without adverse effect on catalysts. The most successful of the formulations are listed in Table XIII. MHF-3 was used in auxiliary and emergency power units on many experimental and prototype aircraft. Carbon resulting from the MMH decomposition can reduce the gas generator life for some applications. The TSF series, developed as monofuels for aircraft turbine engine starters, do not have this potential carbon problem. The addition of oxygen in the form of hydrazinium nitrate (HN) helps to alleviate carbon formation. The MHF-5 series are very stable at temperatures below 140°F (333 K) in properly prepared containers. HN also provides a small I_{sp} gain over neat hydrazine. Shell 405 is the catalyst typically used with these blends. It functions at temperatures as low as –65°F (219 K).

Hydroxylamine, NH_2OH , will depress the freezing point of hydrazine, but causes excess gas evolution. Methoxyamine (*O*-methylhydroxylamine, MOA) and methoxyamine nitrate (MOAN) are also good depressants with acceptable stability and offer a small performance improvement. Hydrazoid-X consisted of 86% MOA, 12% N_2H_4 , and 2% H_2O . AMICOM propellant, 68% N_2H_4 , 20% MOAN, and 12% H_2O , has a freezing point of –58°F (223 K).

Binary, ternary, and quaternary mixtures using the following compounds have been also evaluated: ammonia, water, MMH, hydrazine azide, and monomethylamine nitrate.

G. Tripropellants

The tripropellant concept uses the high heat release from the oxidation of a light metal or metal hydride to heat hydrogen expanded to generate a very high specific impulse (see Table VIII). The hydrogen serves as an expandable, inert working fluid of low molecular weight, not unlike a thermodynamic nuclear rocket. The hydrogen can be added with the reactants, or if the hydrogen preferentially reacts with the oxidizer, it can be introduced after the combustion zone. Hydrogen can be introduced as a metal hydride, making the system appear to be a bipropellant

system; the differentiation being there is excess hydrogen (from a thermochemical standpoint) for expansion without being oxidized. Pentaborane + hydrogen peroxide is an example of such a system.

The chemical propellant systems with the highest theoretical specific impulse are beryllium/ozone/hydrogen and lithium/fluorine/hydrogen. The Be/O₂/H₂ system was experimentally evaluated with the liquefied oxygen gelled to suspend the powdered beryllium. Fluidized injection of Be powder was also attempted. The technical difficulties of incorporating the light metals and their hydrides into a liquid system has limited the development of a practical tripropellant propulsion system.

H. Hybrids

A hybrid system uses a liquid propellant (usually the oxidizer) with a solid propellant grain in the same rocket engine. The configuration of the solid fuel is similar to that of a solid propellant motor. Many different propellant combinations can be used, ranging from cryogenic oxidizers to conventional storable oxidizers, with metal-loaded fuels as well as common fuels such as rubbers or plastics. As a rule, liquid oxidizers are superior to solid in specific impulse, while solid fuels, particularly metalized, offer a performance and density improvement over liquids. Because it is possible to select dense oxidizers, such as ClF₅ with a specific gravity of 1.78 and a metal-loaded fuel with a specific gravity of 2.0, hybrid systems appear attractive for volume limited applications. Hybrids have the flexibility of being restarted and throttled in the manner of a liquid engine. Reverse hybrids, using a solid oxidizer (e.g., ammonium perchlorate) and a liquid fuel (hydrazine) have been tested. Since solid oxidizers are not as energetic as liquid oxidizers, there is little value in the reverse hybrid concept.

The Firebolt (AQM-81), a target vehicle, uses IRFNA as the oxidizer with a PBAN based solid fuel. A typical fuel composition is

1. 80 wt% polybutadiene/acrylic acid/acrylonitrile
2. 20 wt% polymethylmethacrylate (Plexiglas[®])

A 20,000 lb_f (88.96 kN) hybrid unit utilizing 90% hydrogen peroxide and an aluminum-enriched polyethylene grain was successfully tested. The oxidizer was catalytically decomposed, producing hot gases that ignited the fuel in a smooth and reliable manner.

The solid lithium/ClF₃ concept was discussed in Section III.D.5. Experimental grains consisting of powdered lithium held in a solid binder have been made and tested. Because lithium is very light, it has been difficult to get high metal loadings in a usable grain.

American Rocket Company (AMROC) attempted a launch from Vandenberg AFB with a hybrid rocket vehicle. The oxidizer was LOX and the fuel was a butadiene with the consistency of a soft automobile tire.

I. High Energy Density Materials

High-Energy Density Material (HEDM) research has been under way since the mid-1980s. Rather than presume which of the previous categories of propellants will be embellished with the development of these new technologies, the area will be discussed separately. Fundamentally, the potential for these special molecules is that they contain and will release energy far beyond what is possible with normal combustion. The strained ring hydrocarbons discussed in Section III.D.1 as kerosine additives are actually part of the HEDM activity with near-term potential.

The following are research areas with potential payoff for improved performance rocket propellants:

1. Polymeric or poly nitrogen (N₄, N₆, N₈). In 1998, AFRL announced that scientists at Edwards AFB had identified N₅ as the cation combined with the AsF₆ anion. The cation's heat of formation was calculated at 353 kcal/mol
2. Polymeric or poly oxygen (O₄, O₆, O₈)
3. Hydrides of boron (BH₂, BH₄)
4. B-N analogs of prismane (B₃N₃H₆)
5. Atomic additives to hydrogen in an O₂/H₂ system.

Adding energetic atoms to a LOX/LH₂ system has the potential to increase specific impulse by the following amounts:

1. Carbon atoms + 49 sec
2. Boron atoms + 32 sec
3. Aluminum atoms + 27 sec
4. Hydrogen atoms + 19 sec

The use of F₂/H₂ in a vehicle also has a 19-sec increase in specific impulse over LOX/LH₂, but it is hoped that the new technology will be feasible without the safety problems and complications of using liquid fluorine.

IV. HANDLING AND STORAGE OF LIQUID ROCKET PROPELLANTS

This section provides additional information on liquid propellants in current or recent use or that have been the subject of considerable evaluation and could be selected for future propulsion systems. Rocket propellants are by nature hazardous materials and must be handled

and used only in appropriate facilities by personnel who have the proper training and knowledge of their properties and approved personal protective equipment. The following outlines the type information available and the general precautions needed, but is insufficient to provide the depth of instruction required by personnel. Current regulations, operating procedures, and technical information must be consulted for the safe use of propellants.

A. Ammonia

Liquid anhydrous ammonia is a commercial chemical, used for refrigeration and as a fertilizer. It is very stable and is not shock sensitive. Being alkaline and a reducing agent, ammonia will react with most acids. It is soluble in water, alcohol, and many other solvents.

1. Specifications

Propellant-grade ammonia procured under Specification O-A-445 contains 99.8 wt% NH_3 . The major impurity is water that is limited to a maximum of 0.5 wt% to reduce corrosion. Excessive oil will deposit in engine passages and foul igniters, thus it is controlled to 5.0 ppmw (parts per million weight) maximum. The purity of ammonia produced in the United States is consistently high. In the amounts normally present in refrigeration grade ammonia, pyridine, naphthalene, and hydrogen sulfide were found not to adversely affect rocket engine performance.

2. Material Compatibility

Anhydrous ammonia will not corrode iron, steel, or aluminum. Since it is difficult to avoid some moisture in operational systems, copper, zinc, and their alloys should not be used. The use of nickel and stainless steel (300 and 400 series) is recommended.

Suitable nonmetallic materials for anhydrous ammonia service are tetrafluoroethylene polymer (Teflon[®]), chlorotrifluoroethylene (Kel-F[®]), ammonia-resistant rubber, and asbestos (free of graphite and grease).

3. Safety Considerations

Anhydrous ammonia must be handled with caution because it is a toxic, flammable compound shipped and stored under pressure. The principal hazards to personnel are inhalation of the vapor and contact of the liquid and vapor with skin and eyes. Liquid ammonia produces severe burns on contact due to its caustic action and low temperature. Gaseous ammonia is a strong irritant and can injure the eyes and respiratory tract. The TLV is 50 ppm. The flammability range of ammonia in air is 16 to

27 vol%. Its flash point is $<32^\circ\text{F}$ (273 K) and autoignition temperature is 1204°F (924.3 K).

Water fog effectively suppresses ammonia fires since it will cool the burning surface and reduce ammonia vapor pressure by absorption and dilution.

4. Storage and Handling

Anhydrous ammonia is transferred and stored as a liquefied, compressed gas and is relatively easy to handle with readily available equipment designed for ammonia service. Storage and transfer areas must be well ventilated, free from oxidizers, flammable materials, excessive heat, and sparks.

Ammonia may be stored in shipping cylinders or in non-refrigerated bulk storage tanks. Care must be taken to prevent overfilling containers. A tank is considered overfull when at any time there is insufficient vapor space above the liquid to provide adequately for the thermal expansion of the liquid as ambient temperatures fluctuate.

5. Transportation

Commercially available cylinders, rail tank cars, and cargo or portable tanks of various sizes that meet U. S. Department of Transportation (DOT) specifications are used for shipping anhydrous ammonia. DoT classifies ammonia as a nonflammable gas for shipments because the concentration range of flammability is narrow and the ignition temperature is high.

B. Chlorine Pentafluoride

Chlorine pentafluoride (ClF_5) is a colorless gas under normal conditions. It can be maintained as a liquid under its own vapor pressure, 58.8 psia (405.2 kN/m²) at 77°F (298.2 K). ClF_5 is a very strong oxidizing agent that is hypergolic with common rocket fuels and will react vigorously with water and most combustibles. It is not sensitive to heat, shock, or sparks.

The information presented in this section also applies to chlorine trifluoride (ClF_3) and similar interhalogen oxidizers.

1. Specifications

The principle impurity in ClF_5 and ClF_3 is hydrogen fluoride (HF), which causes corrosion and particulate formation. The typical assay is product: 99.8 wt% minimum and HF: 0.2 wt% maximum. The procurement specifications, MIL-P-27413 (ClF_5) and MIL-P-27411 (ClF_3), were recently canceled.

2. Material Compatibility

In a clean, dry, passivated system, ClF_5 is compatible with a wide range of metals. However, at elevated temperatures, it will react with them. It is important not to have any sources of ignition, such as contaminants, metal-to-metal friction (as in a valve), or mechanical impact sufficient to deform metal. The following metals have been successfully used: 1160, 3003, 6061, 2024, 5052, 6063 aluminum; Inconel[®], Monel[®], nickel; stainless steel, all; and copper, brass, and carbon steel.

The following metals should not be used in contact with ClF_3 or ClF_5 : titanium, tantalum, niobium, and tungsten.

There are no elastomers or plastic materials suitable for liquid flow or high pressure systems. For low gaseous flow rates where pressures are under 400 psig (2.76 MN/m²) or static liquid systems, polytetrafluoroethylene (e.g., Teflon[®], Halon, TFE) may be used. These materials must be properly cleaned and dried, and no hydrocarbon, alcohol, or halogenated solvents used. The solvents can penetrate into the plastic and are impossible to remove completely.

The use of all lubricants, including fluorocarbons, are prohibited.

3. Safety Considerations

While they do not burn or explode by themselves, ClF_3 and ClF_5 must be considered fire hazards due to their ability to ignite most materials. The TLV-C for ClF_3 is 0.1 ppm: no official value has been established for ClF_5 , but 3.0 ppm has been suggested.

4. Cleaning and Passivation

All equipment in contact with the interhalogens must be scrupulously cleaned and passivated. All grease solvents, scale, weld spatter, and moisture must be removed. All components must be completely disassembled to assure that no dead areas containing the slightest residue are overlooked. Every square inch of the system must be passivated with a tenacious fluoride coating that protects the surface against further attack by the interhalogen. Passivation is accomplished by exposing the system to a mixture of fluorine and nitrogen or helium gas. The partial pressure of fluorine is gradually increased until the system is 100% filled with gaseous fluorine at the working pressure of the system. The system may get very hot and even burn through if the pressure of fluorine is raised too quickly. Even after the system was passivated, these propellants have been known to burn through as they flow through any tight turns such as a standard elbow. Only long radius tube bends will turn the flow of these propellants.

5. Handling and Storage

ClF_5 is stored and transferred as a liquefied gas. Tanks should meet the ASME code for unfired pressure vessels. Remote-operated, packless-type valves with metal-to-metal seats should be used. Suitable diaphragm-type pumps are commercially available for the interhalogens. Soft copper and 1100 aluminum may be used for gaskets at flanged fittings; however, all-welded connections are recommended.

6. Transportation

The interhalogens are shipped in mild steel cylinders meeting DOT specifications. The largest containers presently approved have a product capacity of 2000 lb (907 kg).

C. Fluorine

Fluorine is the strongest oxidizing agent and one of the most reactive substances known. Under certain conditions, it can react with most elements and compounds, the exceptions being some of the rare gases and completely fluorinated compounds. If kept free of moisture, which reacts to form HF, fluorine is noncorrosive to clean and passivated metals. Liquefied fluorine is hypergolic with all rocket fuels. Gaseous fluorine has a yellowish color, and the liquid is amber. It has a very pungent odor. Fluorine is stable and liquid is completely miscible with liquefied oxygen and nitrogen.

1. Specifications

Fluorine procured under MIL-P-27405 has a minimum assay of 99.0 vol%. Oxygen and nitrogen are the major impurities (0.8% maximum) with some CF_4 and CO_2 (0.2% maximum) present. HF is the most troublesome impurity, causing container corrosion and forming particulate matter. HF is limited to 0.5% maximum, with 0.2% a typical value. In liquefied fluorine, HF is a solid and can be removed by filtration. Ozone and peroxides, formed during the electrolytic manufacturing process, are removed at the plant.

2. Material Compatibility

Materials selected for fluorine service must be resistant to attack by fluorine and possess appropriate strength at cryogenic temperatures.

The following metals are recommended for use in liquefied fluorine systems: nickel, aluminum, copper, brass, Monel[®], 304L, and 316 and 321 stainless steel. In addition to these, mild steel is satisfactory for gaseous fluorine from 20 to 160°F (244 to 344 K).

There are no plastic or elastomeric materials acceptable for liquefied fluorine under flow conditions or for high-pressure gaseous fluorine. Under moderate flow rates and low pressure polytetrafluoroethylene (Teflon[®]) may be used. It is very important to assure that clean, high quality Teflon[®] (no metallic impurities from the extrusion process) is used. Since it is very difficult to remove solvents that may have impregnated the plastic, solvent cleaning should not be used.

3. Safety Considerations

Fluorine is very toxic (TLV 1.0 ppm). Contact with the vapor will cause some irritation and burns. Liquefied fluorine will destroy body tissues on contact. Under spill conditions, liquefied fluorine will react with essentially all materials, usually causing a fire; thus it must be called a fire hazard. Uncontrolled mixing of liquefied fluorine and rocket fuels as in a spill situation will produce severe deflagrations.

4. Cleaning and Passivation

Proper cleaning and passivation of fluorine systems is the key to successful operation. During the passivation process, a tightly adhering film of metal fluoride is formed on the interior surfaces to protect the metal from further fluorine attack. Components should be disassembled and plastic parts removed. All contaminants, especially hydrocarbons, must be removed with solvents and detergents. Scale, slag, and weld beads are removed by sand blasting and acid pickling. Deionized or distilled water is used as a final rinse, and the equipment dried with heated nitrogen gas. The system is reassembled and purged with nitrogen.

Passivation is accomplished by slowly replacing the nitrogen with gaseous fluorine at atmospheric pressure. After this nitrogen is replaced, the pressure is increased slowly to the operational pressure and left under observation for about two hours. If there is no internal heating, the system is considered passivated.

5. Storage and Handling

Liquefied fluorine is always kept in a closed system under a low positive pressure to avoid release of its vapors to the atmosphere. Refrigeration is required that is usually supplied by the boil-off of liquefied nitrogen. Special tanks are used and constructed with three horizontal, concentric shells. The inner shell holds the product, an intermediate shell contains liquefied nitrogen, and the outer shell serves as a vacuum jacket. Monel[®] is the preferred material for the two inner shells, although stainless steel may be used if proper consideration is given

to low temperature strength. The outer vacuum jacket may contain insulation such as perlite or Santocel[®]. As long as the liquefied nitrogen is replenished, the fluorine will keep indefinitely in the liquid state.

No pressure relief devices are to be inserted in the inner fluorine tank. The liquefied nitrogen jacket will be equipped with vents and a pressure relief system typical of liquefied nitrogen systems. Remote-operated, packless-type valves designed for fluorine service should be used. All-welded connections are recommended and threaded connections should be avoided. Flanges or compression fittings require soft copper or aluminum gaskets, rings, or seals. Liquefied fluorine has been pumped satisfactorily; however, suitable pumps are not generally available. Transfer can be accomplished by using 1–5 psi (7–35 kN/m²) differential helium pressure.

6. Transportation

Liquefied fluorine is shipped in tank trucks that hold 5000 lbs (2268) kg/lbs of product. Special DOT permits are required. These truck trailers are of the three concentric shell design described in Section IV.C.4. The liquefied nitrogen volume is sufficient to last at least 10 days without replenishment, more than adequate for cross-country shipments.

D. Hydrazines

The widely used hydrazines, anhydrous hydrazine, MMH, UDMH, and the 50% hydrazine/50% UDMH blend (Aerzine-50) are clear, colorless, oily liquids with distinctively fishy ammoniacal odor. These strong reducing agents are completely miscible with water, alcohols, and most solvents. They are very hygroscopic, and tend to absorb carbon dioxide and oxygen from the atmosphere. These fuels are hypergolic with the common storable rocket oxidizers. Chemically, hydrazine is the most reactive of the family, and extra care must be exercised in handling. All are stable to friction and shock but are thermodynamically unstable. Iron, nickel, cobalt, copper, and platinum metals and their oxides will catalytically decompose hydrazine and MMH.

1. Specifications

The military specifications covering these fuels are hydrazine, MIL-P-26536; MMH, MIL-P-27404; 50–50 blend, MH-P-27402; and UDMH, MIL-P-25604. Typically the fuel assay is 98 wt% or better, with the major impurities being water and other amines. Impurities in hydrazine can adversely affect its stability and can damage catalysts when it is used as a monopropellant. Thus for the

monopropellant grade hydrazine the following contaminants are controlled: carbon dioxide, 30 ppm maximum; aniline, 0.5 wt% maximum; iron, 20 ppm maximum; chloride, 5 ppm maximum; nonvolatile residue, 50 ppm maximum; and others (MMH, alcohol), 200 ppm maximum.

2. Material Compatibility

The hydrazines are noncorrosive to most metals. Because of catalytic effects, only known materials should be used. Recommended metals and alloys include: 304, 304L, 316, 347, and 17-7PH stainless steel; 1100, 2014, 2024, 2219, 5052, and 6061 aluminum; 6Al-4V titanium. The following metals should be avoided: cadmium, cobalt, copper and alloys, iron, lead, magnesium, mild steel, and zinc. A limited number of elastomers and plastics are suitable for hydrazine family use: AF-E-332; butyl rubber; ethylene-propylene copolymer; and polytetrafluoroethylene. Viton[®] and chlorotrifluoroethylene should not be used except for short exposures.

No lubricant is completely satisfactory. The following have been used: Apiezon L, Dow Corning Silicon Compound 11, Fluorolube GR-470, Kel-F grease, Krytox PR-240AC, and Ready Lube 200.

3. Safety Considerations

The hydrazines are toxic and will irritate eyes and skin. They can be absorbed by inhalation, through the skin, and by ingestion. The TLVs are hydrazine, 0.1 ppm; MMH, 0.2 ppm; and UDMH, 0.5 ppm. They are suspected carcinogens. The hydrazines will not explode, but the vapors will make explosive mixtures with air. They are flammable in a broad range of concentrations in air: hydrazine, 4.7–100% MMH, 2.5–98%; and UDMH, 2.0–90%. Spills of these fuels on rags, dirt, rust, sawdust, and so on can result in spontaneous ignition. Because of the ease of ignition, it is common in the vicinity of an open container or a spill to have tongues of flame appear. This phenomenon is more apparent at night.

4. Storage and Handling

Storage tanks with capacities up to 20,000 gal (75.7 m³) and meeting the ASME Code for Unfired Pressure Vessels are used for the hydrazines. Type 304 stainless steel is commonly used. For small volumes, the 55-gal (0.2 m³) shipping drums may be used for storage. All containers must be thoroughly cleaned and inspected to assure that no catalytic materials are present. All air is purged from containers and piping with an inert gas, usually nitrogen, prior to filling with fuel. An inert gas blanket of a slight positive pressure is maintained at all times in systems to

keep out air and moisture. Transfer of fuels may be accomplished with pumps or differential pressure, and areas must be free of organic and oxidizing materials and rust. There must be no open fires or electrical sparks present although as noted above, spontaneous ignition is common.

Hydrazine has been observed to undergo explosive decomposition by rapid adiabatic compression of vapors when subjected to high hydrodynamic pressure (water hammer).

5. Transportation

The hydrazines are shipped in DOT-approved tank trucks, rail cars, portable tanks, and 55-gal (m³) drums. Red “Flammable Liquid” and white “Poison” labels are required.

E. Hydrogen

Liquefied hydrogen is transparent, colorless, and odorless. Because of its very low boiling point, release of liquefied hydrogen in a normal atmosphere will result in a visible, voluminous cloud of condensed moisture. Hydrogen is noncorrosive, but some metals are subject to hydrogen embrittlement, especially at higher temperatures. Hydrogen gases are combustible with air over the range of 4–75 vol% at 68°F (293 K). Mixtures of hydrogen with air from 18 to 59% by volume will detonate. Liquefied or gaseous hydrogen is hypergolic with liquefied and gaseous fluorine, chlorine trifluoride, and chlorine pentafluoride, and will form combustible mixtures with other oxidizers. All substances are essentially insoluble in liquefied hydrogen. Helium is slightly soluble, up to ~1% under pressure.

Liquefied hydrogen is chemically stable, but it is physically stable only when stored under suitable conditions. In a properly designed container, the evaporation rate can be as low as 1.5% per day in a 1000-gal (3.79 m³) container, and less in larger vessels.

1. Specifications

Liquefied hydrogen conforming to MIL-P-27201 has an assay of 99.995 vol% H₂ minimum and a minimum conversion to 95.0 vol% parahydrogen. Oxygen and hydrocarbon gases are limited to a maximum of 1.0 ppmv (parts per million volume) each. Up to 48.0 ppmv of inert gases (e.g., He, N₂) is permitted.

2. Material Compatibility

A prime consideration for materials selection for liquefied hydrogen service is the ability to retain satisfactory

physical properties at the liquefied hydrogen boiling point. Materials must be able to withstand the high thermal stresses imposed by large and rapid temperature changes. Many iron alloys, for example, lose their ductility and become brittle.

Recommended metals for liquefied hydrogen service include: 300 and other austenitic series of stainless steel; copper, brass, and bronze; aluminum; Monel[®]; and Everdur[®].

All plastics and elastomeric materials lose their flexibility at liquefied hydrogen temperatures. Some materials successfully used in applications are polyester fiber (Dacron[®]); tetrafluoroethylene (Teflon[®] or equivalent); chlorotrifluoroethylene, unplasticized (Kel-F[®]); nylon; Mylar[®]; and asbestos impregnated with TFE.

Lubricants solidify at liquefied hydrogen temperatures and are not generally used. In some special applications, vacuum grease can be used as a sealant with O-rings.

3. Safety Considerations

Hydrogen is extremely flammable. Unless carbonaceous impurities or other contaminants are present, the flame may be invisible. Explosive hazards exist when frozen air (oxygen) collects in liquefied hydrogen, and when gaseous hydrogen is mixed with air in a confined space. Skin contact with liquefied hydrogen or with equipment containing it can cause severe frostbite. Air in contact with lines and tanks can liquefy and produce an oxygen-rich environment. Hydrogen is an asphyxiant, but it is not toxic.

4. Storage and Handling

Liquefied hydrogen may be stored in stationary or mobile tanks of appropriate design and materials and tested in accordance with ASME or DOT specifications for pressure vessels. The tanks are vacuum insulated, and evacuated perlite, Santocel[®], or multilayer super insulation is usually used. Liquefied hydrogen systems are kept under positive pressure to prevent entry of air. The internal structure supporting the inner hydrogen tank within the vacuum shell is made as light as possible to reduce thermal leaks. Because the density of liquefied hydrogen is very low, this internal structure is considerably lighter than for tanks designed for other commodities. This weight restriction must be observed when liquefied nitrogen is used for pre-cooling and purging or if the container is used for another product.

Liquefied hydrogen systems must be thoroughly cleaned to remove all oils and surface films, rust, weld scale, and other particulate matter and then dried to eliminate all moisture. Prior to use, the system must be purged with warm hydrogen or helium gas to remove all traces

of air. Only vaporized gas from liquefied hydrogen should be used; the impurities present in most cylinder H₂ make it unsuitable for this purpose. All lines should be vacuum jacketed or insulated.

5. Transportation

DOT classifies liquefied hydrogen as a flammable compressed gas. Rail tank cars, tank trucks, and small cylinders holding about 200 lb (91 kg) of product are used for shipping liquefied hydrogen. These containers are vacuum jacketed and insulated and are equipped with pressure relief devices. A red "Flammable Gas" label is required.

F. Hydrogen Peroxide

Concentrated hydrogen peroxide is both a strong oxidizing agent and a monopropellant. It is a clear, colorless liquid that is slightly more viscous than water. Some gas evolution can be seen. It can be rapidly decomposed upon contact with many inorganic compounds, including iron oxide, silver, and potassium permanganate. This contact yields water (steam), oxygen, and heat. Hydrogen peroxide will not burn, but will support combustion of many organic materials. The exothermic decomposition reaction releases sufficient heat to ignite combustible materials. It is hypergolic with amine fuels, including the hydrazines, and the metal hydrides. It is considered hypergolic with hydrocarbon fuels; however, the heat release rate is insufficient to provide reliable ignition in a rocket engine without the use of some other ignition system. For this reason, a two-stage engine concept is used in which the peroxide is first catalytically decomposed and the hot gases injected into the rocket engine chamber with the fuel.

1. Specifications

Hydrogen peroxide conforming to MIL-P-16005 (recently cancelled) has an assay of 90.0–91.0 wt%. Impurities that promote decomposition must be avoided if good storage life is to be obtained; however, stabilizers or catalyst poisons cannot be tolerated if catalyst packs are not to fail prematurely. For this reason, specific impurities are closely controlled to provide reasonable storage stability and to avoid poisoning of catalysts. Dissolved metals can cause homogeneous decomposition. Hydrogen peroxide stability is determined by holding a sample at 100°C (373.15 K) for 24 hr. A maximum of 5% active oxygen loss is permitted. Aluminum content is controlled to 0.5 mg/l (g/m³). Chloride was found to cause corrosion of containers, thus it is controlled to a maximum of 1.0 mg/l (g/m³), and 3–5 mg/l (g/m³) of nitrate is added as

a corrosion inhibitor. Phosphate is a strong catalyst poison that enters during manufacture. Since it cannot be entirely eliminated at a reasonable cost, 1.0–4.0 mg/l (g/m^3) tin (as stannous chloride) is added to offset its effects. Sulfate, also a catalyst poison, is limited to 3.0 mg/l (g/m^3) maximum. Extensive studies have shown that up to 200 ppm carbonaceous materials (residuals from the principal manufacturing processes) have no detrimental effect on stability, catalysts, or engine performance.

2. Material Compatibility

In selecting materials for hydrogen peroxide equipment and systems, the effect that the hydrogen peroxide will have on the material is much less important than the effect the material may have on the peroxide. Only materials that have been found compatible by actual test should be used.

Aluminum 1060, 1260, 5254, and 5652 are suitable for long-term contact with hydrogen peroxide, as in storage tanks and related piping.

In general, 300-series stainless steel (347 preferred) and aluminum 1100, 3003, and 6061 are usable for rocket engine components and test facilities where the contact with hydrogen peroxide does not exceed four weeks at normal temperatures or a few hours at about 160°F (344 K).

Some other common aluminum alloys and stainless steels may be used when the contact is less than one hour prior to use, as in engine valves, feed lines, and injectors.

Of the nonmetals, only polytetrafluoroethylene (Teflon[®]) and chlorotrifluoroethylene (Kel-F[®]) are the only plastics suitable for extended contact with hydrogen peroxide. A number of materials, including polyethylene, selected silicone rubbers, Viton[®] A, and polyvinyl chloride, can be used for limited exposures. Caution must be exercised since the quality of these products vary greatly and not all samples are safe to use. The amount and type of plasticizers and previous exposure to solvents can have a profound effect of compatibility.

Chlorofluoro oils and greases (e.g., Halocarbon[®], Kel-F[®]) are suitable for limited use with hydrogen peroxide but should not be used with aluminum.

3. Safety Considerations

Hydrogen peroxide may ignite combustible materials on contact, including dry vegetation and ordinary clothing. Contamination, such as rust, dirt, metal filings, and so on, can cause rapid decomposition, releasing oxygen and considerable heat. The evolution of oxygen and steam may overwhelm any venting system causing the container to rupture.

Hydrogen peroxide will irritate skin, eyes, and the respiratory system. Extended contact will cause burns. While

it has a TLV of 1 ppm, toxicity is generally not a problem due to its low vapor pressure.

4. Cleaning Procedures

All containers, components, and surfaces that are subject to exposure to hydrogen peroxide must be clean and passivated. All equipment must be disassembled and aluminum, stainless steel, and plastic parts separated. Metal components are degreased with trichloroethylene (or other approved solvents or detergents) and then rinsed with alcohol and then with distilled or deionized water. Stainless parts are pickled with 70% nitric acid, and aluminum parts are treated with a 25% sodium hydroxide solution followed by a 45% solution of nitric acid. After a thorough rinse with deionized water, the components are passivated by filling large equipment and immersing small parts in 70–90% hydrogen peroxide for 4 hr and the decomposition rate of the hydrogen peroxide noted. If extensive decomposition is observed, the part is recleaned or discarded. Plastic materials are cleaned and passivated in a similar manner; however, it is best to degrease with detergents rather than solvents.

5. Handling and Storage

Horizontal-type aluminum storage tanks are normally used for hydrogen peroxide. All storage tanks must be vented and a vent filter used to prevent dirt from entering the tank. The 30-gal (0.11 m^3) aluminum shipping drums are suitable for storage containers when small quantities are involved. Shielding of the containers from the rays of the sun is desirable. Good housekeeping is essential to minimize fire hazards and to provide a safe work area. All storage and transfer areas, as well as surrounding areas that may be reached by leakage or spills, should be cleared of organic matter and combustibles. All containers, piping, and equipment that will be in contact with hydrogen peroxide must be of appropriate materials and thoroughly cleaned and passivated before use. A wide variety of valves, pumps, gauges, and transfer equipment are commercially available, but care must be exercised in their selection. Transfer of hydrogen peroxide may be accomplished by pumping, by vacuuming, or by pressuring with clean, dry nitrogen.

6. Transportation

DOT classifies hydrogen peroxide as a corrosive liquid and requires a white label during shipment. Rail tank cars, up to 8000 gal (30.28 m^3); tank motor vehicles, 4000 gal (15.14 m^3); and 30-gal (0.11 m^3) drums that meet DOT specifications are used for hydrogen peroxide shipments.

Two types of drums are available: a double-head drum suitable for all freight shipments and a single-head drum approved only for full carload and full truckload shipments.

Hydrogen peroxide is commonly shipped at 70% concentration as a feed stock for manufacture of semiconductors. Uses as a rocket oxidizer are above 90%. X-L Space Systems offers on-site concentrators to avoid shipment of the higher concentrations. Degussa-Hus Inc. will ship concentrations up to 87.5%.

G. Kerosine

Propellant-grade kerosine, formerly called RP-1, is a high-boiling hydrocarbon fraction. It is a clear liquid, with a slight red color from an added dye. It is very similar to JP-4 turbine engine fuel but with a controlled aromatic content. It is chemically stable and is insensitive to shock. Kerosine, like gasoline and diesel and jet fuel, reacts only with strong oxidizers or under high temperatures and pressures. High temperatures, especially in the presence of air can accelerate the formation of gum and sediment. Like other hydrocarbons, kerosine is flammable, and its vapor will form explosive mixtures with air. It has a fairly low vapor pressure. It is insoluble in water, and it is an excellent solvent and is soluble in many organic solvents.

1. Specifications

The major characteristics of kerosine defined by MIL-P-25576 are distillation, 10% point, 365–410°F (458.2–483.2 K); end point, 535°F (552.6 K) maximum; residue, 1.5 vol% maximum; gravity, 42.0–45.0° API; aromatics: 5.0 vol% maximum; olefins, 1.0 vol% maximum; and particulate: 1.5 mg/1 (g/m³) maximum.

2. Material Compatibility

A wide range of ferrous and nonferrous alloys is suitable for storage and shipping containers and associated components.

Only petroleum-resistant plastics and elastomers are to be used with kerosine. Some suitable nonmetals are cork, fluorocarbons, asbestos, polyvinylchloride, nitrile rubber, Buna[®]-N, Neoprene[®], and polyethylene.

Graphite-based, molybdenum disulfide, some silicon, and fluorocarbon lubricants may be used. Kerosine will dissolve petroleum-type lubricants.

3. Safety Considerations

Kerosine vapors will form ignitable mixtures with air, as does gasoline and diesel fuel. While it will ignite upon

contact with fluorine and chlorine trifluoride, it is not hypergolic with most rocket oxidizers. Kerosine will react with nitric acid, hydrogen peroxide, and strong oxidizers with evolution of heat and may ignite. Such mixtures of kerosine and oxidizers are likely to be sensitive to shock, heat, and sparks. The flash point is 110°F (316.5 K). Kerosine is a moderate skin irritant; scaling and fissuring of skin can result from frequent contact. Inhalation of vapors can cause narcosis. The toxicity of kerosine (TLV) is a function of the aromatic content, e.g., benzene.

4. Storage and Handling

Huge quantities of hydrocarbon fuels are used throughout the world. The same equipment and procedures may be used for propellant-grade kerosine, with due precautions taken to minimize corrosion and contamination. Fire protection is the major concern in facility design. All stationary and mobile tanks should be grounded, electrical devices must be explosion proof, and all vents protected with flame arresters. Buildings are to be constructed of fire-resistant materials, and the area kept free of all vegetation and combustible debris.

5. Transportation

Kerosine is classified by DOT as a “Flammable Liquid.” Standard petroleum rail cars and tank trucks are commonly used for shipping.

H. Nitric Acid

Although fuming nitric acid is a commercial chemical, special formulations are used as rocket oxidizers. White fuming nitric acid (100% HNO₃) is unstable, dissociating to NO₂ and water [Eq. (14)], and very corrosive, attacking most metals. The addition of NO₂, HF, and water greatly improves nitric acid storability, making it a valuable propellant. White fuming nitric acid is colorless, but becomes deep yellow to reddish brown as NO₂ forms. The current rocket propellant grades are a dense reddish brown. Fuming nitric acid is hypergolic with the hydrazines and most amine fuels. It will react with water and many organic materials with evolution of heat and NO₂ gas.

1. Specifications

Current propellant-grade nitric acid formulations, presented in Table X, are procured under specification MIL-P-7254. The composition of Type IIIA was selected to provide the greatest stability and minimum corrosion. Type IIIB has a lower aluminum salt content otherwise it is identical to Type IIIA. The lower water content of Type

IIIS (for limited storability) trades storability for a little higher performance, again for a special application where long storage life is not important. Type IV has the highest specific impulse and density, but is more corrosive.

2. Material Compatibility

Aluminum is the material of choice for fuming nitric acid when maximum storability and minimum metal attack is needed. The following aluminum alloys are recommended: 1060, 1100, 3003, 3004, 6061, 5052, and 5154.

Fabrication of tanks and equipment from stainless steel requires care. Crevices that are hard to clean should be avoided. To avoid loss of corrosion resistance, weld areas in unstabilized grades must be annealed to redissolve the chromium carbides and rapidly quenched. These stainless steel alloys have been found satisfactory: 303, 304ELC, 316, 347, 321, 19-9DL, and Durimet[®] 20.

Fuming nitric acid severely corrodes copper and its alloys and reacts violently with titanium.

Polytetrafluoroethylene and polychlorotrifluoroethylene are the only nonmetals resistant to fuming nitric acid. The perfluorocarbon type lubricants are also satisfactory.

3. Safety Considerations

Fuming nitric acid will not burn and is stable to impact, sparks, and shock, but it may form explosive mixtures with kerosene, other hydrocarbons, and alcohols. It will react with many organic materials and may ignite them. In an improperly prepared container or at elevated temperatures, internal pressure buildup may occur. The TLV for nitric acid is 2 ppm. Nitric acid fires and spills can be controlled with copious amounts of water. The residues then should be neutralized with sodium carbonate. Water will cause an exothermic reaction with nitric acid, causing the evolution of large amounts of NO₂; however, high-pressure water fog will contain the fumes. A special water-based foam consisting of acrylic surfactants and pectin is also available for fume suppression.

4. Storage and Handling

Aluminum and stainless steel tanks meeting ASTM Boiler and Pressure Vessel Codes, equipped with pressure relief devices, are used for fuming nitric acid storage, with aluminum 11,000 gal (41.64 m³) tanks being the most desirable. The 55-gal (0.2 m³) shipping drums may also be used for storage if in a covered area. Storage areas must be free of all vegetation and combustible material and be surrounded by a dike. Tanks and components in contact with acid must be thoroughly cleaned, degreased, detergent cleaned, and all scale and weld slag removed. Stain-

less steel components are also pickled with a dilute nitric acid/HF solution. Precautions must be taken to avoid galvanic corrosion when dissimilar metals are used in a system. Chemical type pumps are used for nitric acid transfer. Pressure transfers are not recommended.

5. Transportation

Only aluminum containers are used for cargo truck, rail car, and drum shipments of fuming nitric acid. An "Oxidizer" and a "Poison" label are required by DOT.

I. Nitrogen Tetroxide

Nitrogen tetroxide is the most widely used storable liquid oxidizer. N₂O₄ is in temperature equilibrium with NO₂. It is the NO₂ that produces the dense reddish-brown color associated with this oxidizer in both the liquid and gaseous forms. As the temperature is lowered, the equilibrium shifts toward N₂O₄ and the color changes from reddish to straw tan to a very pale yellow. At the normal boiling point (70.1°F; 294.3 K), the mixture contains about 15% NO₂ and essentially 100% at 302°F (423.2 K). Near the freezing point, the liquid becomes colorless. The MONs, mixed oxides of nitrogen, contain NO with the numerical designation representing the nominal NO content. Compositions MON-1 and MON-3 contain NO as a stress corrosion inhibitor, and composition MON-10 and higher as a freezing point depressant. The nitric oxide complexes with the NO₂ to form N₂O₃, a blue substance, which imparts a greenish color to the nitrogen tetroxide; hence the terms "green" N₂O₄ (for the MONs) and "red-brown" N₂O₄ (no nitric oxide) are frequently used. MON-1 is the commonly used composition. MON-3 is specified for the Space Shuttle to assure that throughout handling, servicing, and flight operations, the NO content remains above the 0.4% needed for stress corrosion protection. Neat N₂O₄ (NTO) was used in the Titan II missile.

MONs with the higher levels of NO will have higher vapor pressure. Otherwise, the safety, material compatibility, and handling characteristics for all of the MONs are similar and are treated alike in this section.

1. Specifications

MIL-P-26539 covers the procurement of N₂O₄ (grade NTO), MON-1, and MON-3. The requirements are presented in [Table XVI](#). MON-15 and MON-25 are also procured under this specification.

2. Material Compatibility

Moisture-free N₂O₄ and MONs are noncorrosive. The following metals are suitable for most purposes: aluminum,

TABLE XVI Nitrogen Tetroxide Specification Requirements (Chemical Composition Limits)^a

Requirement	NTO	MON-1	MON-3
N ₂ O ₄ assay (wt%)	99.5–100.0	—	—
Nitric content (wt%)	—	0.6–1.0	2.5–3.0
Water equivalent (wt%)	0.17	0.17	0.17
Chloride (wt% max.)	0.040	0.040	0.040
Particulate (mg/l max.)	10	10	10
Iron (ppm max.)	—	—	0.5

^a From National Aerospace Standard 3620.

carbon steel, Inconel[®], nickel, stainless steels, and titanium. N₂O₄ and the MONs react readily with moisture to form acids. For this reason the use of titanium or 300-series CRES are highly recommended for long-term storage and propellant-feed systems. Of the non-metals, the following have been found satisfactory: asbestos, cotton and oil-free; AFE-124R elastomer; ceramic, acid-resistant; polytetrafluoroethylene; and polychlorotrifluoroethylene. Fluorocarbon lubricants and Teflon[®] tape may also be used.

3. Safety Considerations

N₂O₄(NO₂) is a toxic gas, with a TLV of 3 ppm. It reacts exothermically with water to form nitric and nitrous acids, with an evolution of NO₂ gas. The MONs are hypergolic with the hydrazines and most amine fuels. They will react with many organic materials and may form explosive mixtures with hydrocarbon fuels and partially halogenated solvents. While these oxidizers will not burn, they will support combustion. The MONs are thermally stable and are not sensitive to mechanical impact. They will not explode.

Because of the volatility of the MONs, most leaks and spills will result in the formation of vapors. Water added to a pool of N₂O₄ will greatly increase vapor evolution; however, high-pressure water fog will suppress the fuming, but must be applied until the N₂O₄ liquid is sufficiently diluted. Special foams have been developed that are effective in suppressing the vapors for about 10 min.

4. Storage and Handling

The nitrogen oxides may be stored in mild steel tanks conforming to the ASME Boiler and Pressure Vessel Code. Shipping cylinders are also used for storage containers. Pressure relief devices are required. Because small amounts of water will form nitric acid and cause corrosion, the trend is to use stainless steel tanks and transfer equipment. Iron corrosion products are very insoluble in

the MONs and will rapidly clog filters. The small amount of iron that does dissolve complexes with the N₂O₄ to form [N₂O₃⁺][Fe(NO₃)₄⁻]. This adduct can precipitate in valves and small orifices to cause a phenomenon called “flow decay.” Users often condition the oxidizer by cooling to 40°F (278 K) and filtering through a 2 μm filter. Subsequent storage in stainless steel will slow down the formation of the “flow decay” adduct, but not eliminate it. Propellant-feed systems of titanium or aluminum are used in missiles and satellites where mission life approaches 20 years.

Pump transfer is recommended for nitrogen tetroxide and the MONs. Storage and transfer areas must be kept free of oils, fuels, and combustibles.

5. Transportation

N₂O₄ and the MONs are transported in specially constructed semitrailers, rail cars, and in high-pressure, seamless steel cylinders. Carbon steel equipment can be used, but the trend is to use stainless steel. The DOT classification is Class A Poison Gas and a white label is required.

J. Otto Fuel II

Otto Fuel II is a very stable monopropellant, developed to provide a safe fuel for use in undersea weapons. It is a bright red, oily liquid, insoluble in water but is soluble in most common solvents. Otto Fuel is thermally stable at 122°F (323 K). Very slow decomposition may occur above 150°F (339 K), and above 290°F (416 K) rapid exothermic decomposition leading to container rupture and fire will occur.

1. Specifications

Otto Fuel II is composed of a desensitized nitrate ester. The composition of Otto Fuel II is given in Table XV, and is covered by Specification MIL-O-82672(OS).

2. Material Compatibility

Most common metals, except those containing copper, are suitable for Otto Fuel service. The following nonmetals are satisfactory for contact with Otto Fuel: Butyl rubber; ethylenepropylene rubber; glass; polyethylene; polytetrafluoroethylene; polychlorotrifluoroethylene; and natural rubber. Buna-N, Neopren[®], and Viton[®] will swell in contact with Otto Fuel. Polysulfide rubber is incompatible. Most fluorocarbon and silicon-based oils and greases are acceptable. Petroleum-based lubricants are not recommended.

3. Safety Considerations

This propellant offers outstanding safety characteristics. Under atmospheric conditions, it is considered to be non-flammable and nonexplosive, making it safe to handle with proper precautions. The propellant has a high flash point of 265°F (403 K), permitting it to be classified as a low fire hazard material. It is noncorrosive. The vapors are toxic, with a TLV of 0.2 ppm; however, because of the extremely low vapor pressure it normally does not present a toxicity problem. Toxic effects may occur from ingestion and skin contact.

4. Storage and Handling

Typically 6000-gal (22.7 m³) tanks are used for bulk storage of Otto Fuel. The 55-gal (0.2 m³) shipping drums may be used for storage of small quantities. The containers must be equipped with pressure relief devices to prevent internal pressure buildup over 60 psi (414 kN/m²).

5. Transportation

Otto Fuel is shipped by 5000 gal (19 m³) tank trucks, preferably made of stainless steel. Polyethylene 55-gal (0.2 m³) drums overpacked with a steel drum are used for small shipments. An ullage of 5% is required. All containers must be provided with a means to vent excess pressure.

K. Oxygen

Oxygen is a strong oxidizer. Liquefied, highpurity oxygen is a light-blue transparent liquid that boils vigorously at normal conditions and has no odor. It is not shock sensitive, does not decompose, and is chemically stable. Liquefied oxygen is a widely used commercial product.

1. Specifications

Propellant-grade liquefied oxygen contains a minimum of 99.5 wt% O₂ with the major impurity being argon. The prime requirement for oxygen purity is based on safety. Hydrocarbons in oxygen produce a very hazardous condition. Hydrocarbon impurities that have low solubilities are especially undesirable since they are usually frozen solid and can act as ignition sources. Acetylene is limited to 0.5 ppm maximum for this reason. The military specification is MIL-P-25508.

2. Material Compatibility

When selecting materials for liquefied oxygen, consideration should be given to low temperature properties. The

ability to withstand stress resulting from rapid temperature changes is especially important. The following metals are suitable for liquefied oxygen service: stainless steel—304, 304L, 304ELC, 310, 316, 321; aluminum alloys—1000, 2014, 2024, 3000, 5050, 5052, 5083, 5154, 6061, 6063, 7075; copper and copper alloys—copper, naval and admiralty brass, aluminum bronze, cupro-nickel; and nickel and nickel alloys—nickel, 9% nickel steel alloy, Inconel[™], Hastelloy[™] B, Rene 41, K-Monel[™]. Titanium 6A14V can be used in some flight systems, but it is best avoided in storage or test facilities because of its low ignition temperature in oxygen. In fact, metals will ignite in pure oxygen at high enough pressure or high enough flow velocity.

Most nonmetal materials lose their elastomeric properties or flexibility at low temperatures, thus limiting the number of materials suitable for liquefied oxygen service. The following have been used successfully: tetrafluoroethylene polymer (Teflon[™]); polychlorotrifluoroethylene, unplasticized (Kel-F[™]); asbestos, oil and grease free; and special low-temperature silicon rubber.

Specialized lubricants such as KRYTOX[™] and thread sealants are available. The fluorolubes and perfluorocarbon based products must not contain hydrocarbons, and should not be used in aluminum equipment.

3. Safety Considerations

The principal hazards associated with the use of liquefied oxygen are

1. Frostbite when the liquid, or uninsulated piping containing it, contacts the skin
2. Fire supported by oxygen
3. Formation of shock-sensitive mixtures, especially with liquid fuels

There are no toxic effects. Oxygen does not burn, but vigorously supports combustion. It is hypergolic with pyrophoric materials, such as triethylaluminum, but not with common rocket fuels. Gaseous oxygen resulting from liquid vaporization adsorbs readily in clothing, and any source of ignition may cause flare burning.

4. Handling and Storage

Liquefied oxygen should be stored in stationary, portable, or mobile tanks designed specifically for oxygen service. Both storage and transportable containers should be vacuum jacketed; the vacuum may contain reflective insulation or noncombustible powders. Either an open vent or a pressure-relieving device to permit the escape of vapor is required. A warm vessel should be filled slowly until

the system reaches an equilibrium temperature to reduce thermal shock. Considerable boil-off of oxygen will occur during an initial fill and must be vented away from flames, combustibles, and heated surfaces.

5. Transportation

Rail tank cars and tank trucks are used for shipping liquefied oxygen. Shipments at atmospheric pressure, or under 25 psig (172.4 kN/m²) are not regulated; however, pressures over 25 psig (172.4 kN/m²) are defined by DOT as a nonflammable compressed gas.

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