

## CHAPTER 7

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# LIQUID PROPELLANTS

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The classification of liquid propellants has been given in Section 6.1 of the preceding chapter. In this chapter we discuss properties, performance, and characteristics of selected common liquid propellants. These characteristics affect the engine design, test facilities, propellant storage and handling. Today we commonly use three liquid bipropellant combinations. Each of their propellants will be described further in this chapter. They are: (1) the cryogenic *oxygen–hydrogen propellant system*, used in upper stages and sometimes booster stages of space launch vehicles; it gives the highest specific impulse for a non-toxic combination, which makes it best for high vehicle velocity missions; (2) the *liquid oxygen–hydrocarbon propellant combination*, used for booster stages (and a few second stages) of space launch vehicles; its higher average density allows a more compact booster stage, when compared to the first combination; also, historically, it was developed before the first combination and was originally used for ballistic missiles; (3) several *storable propellant combinations*, used in large rocket engines for first and second stages of ballistic missiles and in almost all bipropellant low-thrust, auxiliary or reaction control rocket engines (this term is defined below); they allow long-term storage and almost instant readiness to start without the delays and precautions that come with cryogenic propellants. In Russia the nitric acid–hydrocarbon combination was used in ballistic missiles many years ago. Today Russia and China favor nitrogen tetroxide–unsymmetrical dimethylhydrazine or UDMH for ballistic missiles and auxiliary engines. The USA started with nitrogen tetroxide and a fuel mixture of 50% UDMH with 50% hydrazine in the Titan missile. For auxiliary engines in many satellites and upper stages the USA has used the bipropellant of nitrogen tetroxide with

monomethylhydrazine. The orbit maneuvering system of the Space Shuttle uses it. Alternatively, many US satellites have used monopropellant hydrazine for auxiliary engines.

A comparative listing of various performance quantities for a number of propellant combinations is given in Table 5-5 and in Ref. 7-1. Some important physical properties of various propellants are given in Table 7-1. For comparison water is also listed. Specific gravities and vapor pressures are shown in Figs. 7-1 and 7-2.

## 7.1. PROPELLANT PROPERTIES

It is important to distinguish between the characteristics and properties of the *liquid propellants* (the fuel and oxidizer liquids in their unreacted condition) and those of the *hot gas mixture*, which result from the reaction in the combustion chamber. The chemical nature of the liquid propellants determines the properties and characteristics of both of these types. Unfortunately, none of the practical, known propellants have all the desirable properties, and the selection of the propellant combination is a compromise of various factors, such as those listed below.

### Economic Factors

*Availability* in large quantity and a *low cost* are very important considerations in the selection of a propellant. In military applications, consideration has to be given to *logistics* of production, supply, and other possible military uses. The production process should be simple, requiring only ordinary chemical equipment and available raw materials. It is usually more expensive to use a toxic or cryogenic propellant than a storable, non-toxic one, because it requires additional steps in the operation, more safety provisions, additional design features, longer check-out procedures, and often more trained personnel.

### Performance of Propellants

The performance can be compared on the basis of the *specific impulse*, the *effective exhaust velocity*, the *characteristic velocity*, the *specific propellant consumption*, the *ideal exhaust velocity*, or other engine parameters. They have been explained in Chapter 3, 5 and 6. The specific impulse and exhaust velocity are functions of pressure ratio, specific heat ratio, combustion temperature, mixture ratio, and molecular mass. Values of performance parameters for various propellant combinations can be calculated with a high degree of accuracy and several are listed in Table 5-5. Very often the performance is expressed in terms of *flight performance parameters* for a given rocket application, as explained in Chapter 4. Here the average density, the

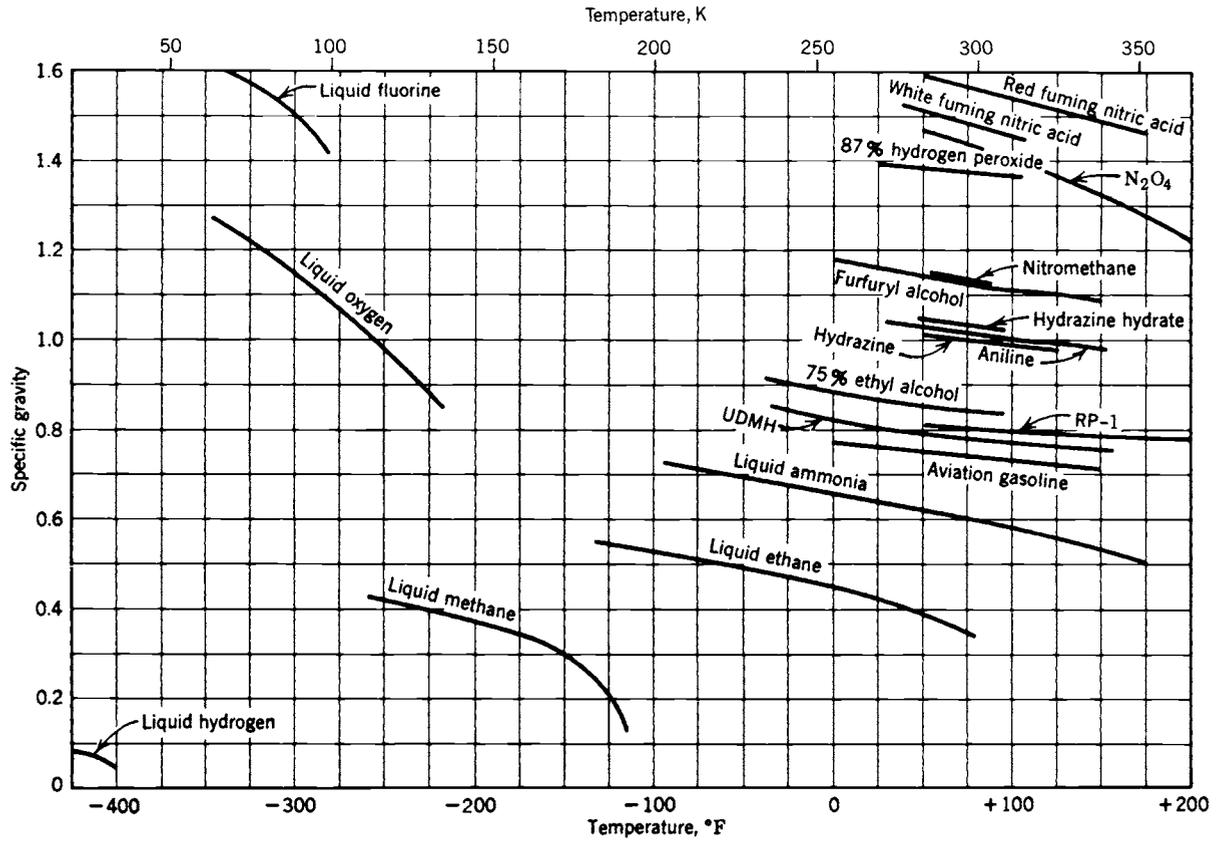


FIGURE 7-1. Specific gravities of several liquid propellants as a function of temperature.

TABLE 7-1. Some Physical Properties of Several Common Liquid Propellants

Propellant	Liquid Fluorine	Hydrazine	Liquid Hydrogen	Methane	Monomethylhydrazine
Chemical formula	F <sub>2</sub>	N <sub>2</sub> H <sub>4</sub>	H <sub>2</sub>	CH <sub>4</sub>	CH <sub>3</sub> NHNH <sub>2</sub>
Molecular mass	38.0	32.05	2.016	16.03	46.072
Melting or freezing point (K)	53.54	274.69	14.0	90.5	220.7
Boiling point (K)	85.02	386.66	20.4	111.6	360.6
Heat of vaporization (kJ/kg)	166.26 <sup>b</sup>	44.7 <sup>b</sup> (298.15 K)	446	510 <sup>b</sup>	875
Specific heat (kcal/kg-K)	0.368 (85 K)	0.736 (293 K)	1.75 <sup>b</sup> (20.4 K)	0.835 <sup>b</sup>	0.698 (293 K)
	0.357 (69.3 K)	0.758 (338 K)	—		0.735 (393 K)
Specific gravity <sup>c</sup>	1.636 (66 K)	1.005 (293 K)	0.071 (20.4 K)	0.424 (111.5 K)	0.8788 (293 K)
	1.440 (93 K)	0.952 (350 K)	0.076 (14 K)		0.857 (311 K)
Viscosity (centipoise)	0.305 (77.6 K)	0.97 (298 K)	0.024 (14.3 K)	0.12 (111.6 K)	0.855 (293 K)
	0.397 (70 K)	0.913 (330 K)	0.013 (20.4 K)	0.22 (90.5 K)	0.40 (344 K)
Vapor pressure (MPa)	0.0087 (100 K)	0.0014 (293 K)	0.2026 (23 K)	0.033 (100 K)	0.0073 (300 K)
	0.00012 (66.5 K)	0.016 (340 K)	0.87 (30 K)	0.101 (117 K)	0.638 (428 K)

<sup>a</sup>Red fuming nitric acid (RFNA) has 5 to 20% dissolved NO<sub>2</sub> with an average molecular weight of about 60, and a density and vapor pressure somewhat higher than those of pure nitric acid.

<sup>b</sup>At boiling point.

<sup>c</sup>Reference for specific gravity ratio: 10<sup>3</sup> kg/m<sup>3</sup> or 62.42 lbm/ft<sup>3</sup>.

specific impulse, and the engine mass ratio usually enter into a complex flight relation equation.

For high performance a *high content of chemical energy* per unit of propellant mixture is desirable because it permits a high chamber temperature. A *low molecular mass* of the product gases of the propellant combination is also desirable. It can be accomplished by using fuels rich in combined hydrogen, which is liberated during the reaction. A low molecular mass is obtained if a large portion of the hydrogen gas produced does not combine with oxygen. In general, therefore, the best mixture ratio for many bipropellants is not necessarily the stoichiometric one (which results in complete oxidation and yields a

Nitric Acid <sup>a</sup> (99% pure)	Nitrogen Tetroxide	Liquid Oxygen	Rocket Fuel RP-1	Unsymmetrical Dimethyl- hydrazine (UDMH)	Water
HNO <sub>3</sub>	N <sub>2</sub> O <sub>4</sub>	O <sub>2</sub>	Hydrocarbon CH <sub>1.97</sub>	(CH <sub>3</sub> ) <sub>2</sub> NNH <sub>2</sub>	H <sub>2</sub> O
63.016	92.016	32.00	~ 175	60.10	18.02
231.6	261.95	54.4	225	216	273.15
355.7	294.3	90.0	460–540	336	373.15
480	413 <sup>b</sup>	213	246 <sup>b</sup>	542	2253 <sup>b</sup>
				(298 K)	
0.042	0.374	0.4	0.45	0.672	1.008
(311 K)	(290 K)	(65 K)	(298 K)	(298 K)	(273.15 K)
0.163	0.447			0.71	
(373 K)	(360 K)			(340 K)	
1.549	1.447	1.14	0.58	0.856	1.002
(273.15 K)	(293 K)	(90.4 K)	(422 K)	(228 K)	(373.15 K)
1.476	1.38	1.23	0.807	0.784	1.00
(313.15 K)	(322 K)	(77.6 K)	(289 K)	(244 K)	(293.4 K)
1.45	0.47	0.87	0.75	4.4	0.284
(273 K)	(293 K)	(53.7 K)	(289 K)	(220 K)	(373.15 K)
	0.33	0.19	0.21	0.48	1.000
	(315 K)	(90.4 K)	(366 K)	(300 K)	(277 K)
0.0027	0.01014	0.0052	0.002	0.0384	0.00689
(273.15 K)	(293 K)	(88.7 K)	(344 K)	(289 K)	(312 K)
0.605	0.2013		0.023	0.1093	0.03447
(343 K)	(328 K)		(422 K)	(339 K)	(345 K)

high flame temperature) but usually a fuel-rich mixture containing a large portion of low-molecular-mass reaction products, as shown in Chapter 5.

If very small metallic fuel particles of beryllium or aluminum are suspended in the liquid fuel, it is theoretically possible to increase the specific impulse by between 9 and 18%, depending on the particular propellant combination, its mixture ratio and the metal powder additive. Gelled propellants with suspended solid particles have been tested successfully with storable fuels. For gelled propellants, see Section 7.5.

The chemical propellant combination that has the highest potential specific impulse (approximately 480 sec at 1000 psia chamber pressure and expansion to sea level atmosphere, and 565 sec in a vacuum with a nozzle area ratio of 50) uses a toxic liquid fluorine oxidizer with hydrogen fuel plus suspended toxic solid particles of beryllium; as yet a practical means for storing these propellants and a practical rocket engine have not been developed.

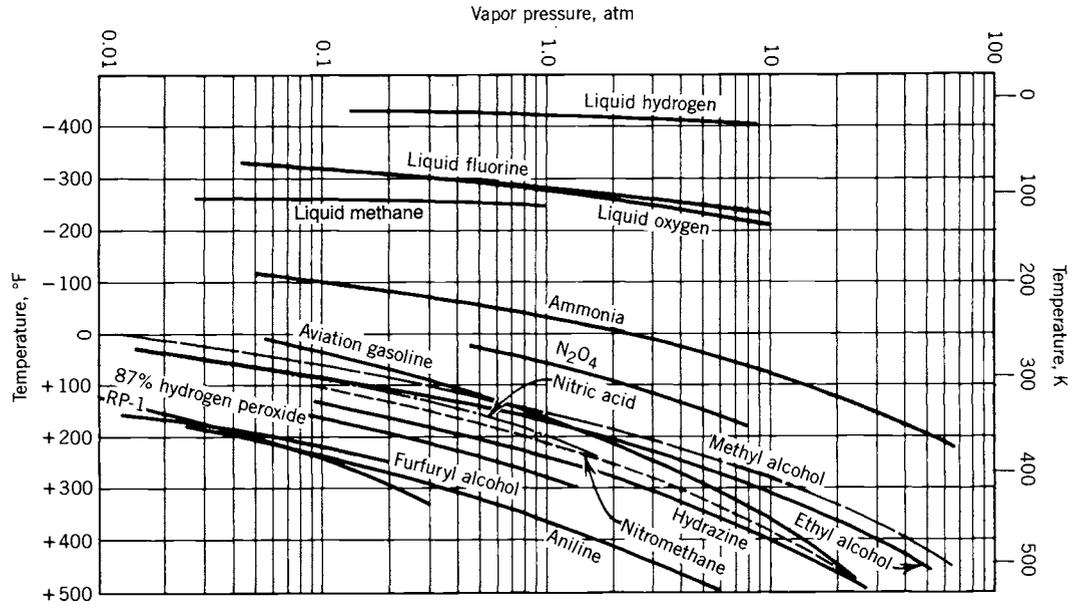


FIGURE 7-2. Vapor pressures of several liquid propellants as a function of temperature.

## Common Physical Hazards

Although the several categories of hazards are described below, they do not all apply to every propellant. The hazards are different for each specific propellant and must be carefully understood before working with that propellant. The consequences of unsafe operation or unsafe design are usually also unique to several propellants.

**Corrosion.** Various propellants, such as nitrogen tetroxide or hydrogen peroxide, have to be handled in containers and pipelines of special materials. If the propellant were permitted to become contaminated with corrosion products, its physical and chemical properties could change sufficiently to make it unsuitable for rocket operation. The corrosion of the gaseous reaction products is important in applications in which the reaction products are likely to damage structure and parts of the vehicle or affect communities and housing near a test facility or launch site.

**Explosion Hazard.** Some propellants, such as hydrogen peroxide and nitromethane, are unstable and tend to detonate under certain conditions of impurities, temperature, and shock. If liquid oxidizers (e.g., liquid oxygen) and fuels are mixed together they can be detonated. Unusual, rare flight vehicle launch or transport accidents have caused such mixing to occur (see Refs. 7-2 and 7-3).

**Fire Hazard.** Many oxidizers will start chemical reactions with a large variety of organic compounds. Nitric acid, nitrogen tetroxide, fluorine, or hydrogen peroxide react spontaneously with many organic substances. Most of the fuels are readily ignitable when exposed to air and heat.

**Accidental Spills.** Unforeseen mishaps during engine operation and traffic accidents on highways or railroads while transporting hazardous materials, including propellants, have on occasion caused spills, which expose people to unexpected fires, or potential health hazards. The U.S. Department of Transportation has rules for marking and containing hazardous materials during transport and also guidelines for emergency action (see Ref. 7-4).

**Health Hazards.** Many propellants are toxic or poisonous, and special precautions have to be taken to protect personnel. Fluorine, for example, is very poisonous. Toxic propellant chemicals or poisonous exhaust species can enter the human body in several ways. The resulting health disorders are propellant specific. Nitric acid can cause severe skin burn and tissue disintegration. Skin contact with aniline or hydrazine can cause nausea and other adverse health effects. Hydrazine and its derivatives, such as dimethylhydrazine or hydrazine hydrate, are known carcinogens (cancer-causing substances). Many propellant

vapors cause eye irritation, even in very small concentration. Inadvertent swallowing of many propellants can also cause severe health degradation.

The inhalation of certain toxic exhaust gases or gaseous or vaporized propellants is perhaps the most common health hazard. It can cause severe damage if the exposure is for long duration or in concentrations that exceed established maximum threshold values. In the United States the Occupational Safety and Health Administration (OSHA) has established limits or thresholds on the allowable exposure and concentration for most propellant chemicals. Several of these propellant gas threshold limits are mentioned later in this chapter. Toxic gases in the exhaust could include hydrofluoric acid (HF) gas; its OSHA 8-hr personnel exposure limit is 3 ppm (volumetric parts per million) and its short-term (typically, 15 min) exposure limit is 6 ppm. A concentration of 3000 ppm or 0.3% can be fatal within a few seconds. Pentaborane, which is very toxic and has been used in experimental engines, has an 8-hr personnel exposure limit at a threshold of 0.005 ppm. References 7-2 and 7-5 give more information on toxic effects.

The corrosion, explosion, and fire hazards of many propellants put severe limitations on the materials, the handling, and the design of rocket-propelled vehicles and their engine compartments. Not only is the rocket system itself exposed to the hazardous propellant, but adjacent personnel, structural parts, electrical and other vehicle equipment, and test and launch facilities have to be properly protected against the effects of possible leaks, fumes, and fires or explosions from propellant accumulations.

**Material Compatibility.** Many liquid propellants have only a limited number of truly compatible materials, both metals and nonmetals, such as gaskets or O-rings. There have been unfortunate failures (causing fires, leakage, corrosion, or malfunctions) when an improper or incompatible material was used in the hardware of a rocket engine. Depending on the specific component and loading conditions, these structural materials have to withstand high stresses, stress corrosion, high temperatures, or abrasion. Several specific material limitations are mentioned in the next section. Certain materials catalyze a self-decomposition of stored hydrogen peroxide into water and oxygen, making long-term storage difficult and, if confined, causing its container to explode. Many structural materials, when exposed to cold, cryogenic propellants, can become very brittle.

### **Desirable Physical Properties**

**Low Freezing Point.** This permits operation of rockets in cold weather. The addition of small amounts of special chemicals has been found to help depress the freezing point of some liquid propellants which solidify readily at relatively high temperature.

**High Specific Gravity.** In order to accommodate a large mass of propellants in a given vehicle tank space, a dense propellant is required. It permits a small vehicle construction and, consequently, a relatively low structural vehicle mass and low aerodynamic drag. Specific gravity, therefore, has an important effect on the maximum flight velocity and range of any rocket-powered vehicle or missile flying within the earth's atmosphere, as explained in Chapter 4. Specific gravities for various propellants are plotted in Fig. 7-1. A variation of the temperature of stored propellant will cause change in liquid level in the tank.

For any given mixture ratio  $r$ , the average specific gravity of a propellant combination  $\delta_{av}$  can be determined from the specific gravities of the fuel  $\delta_f$  and of the oxidizer  $\delta_o$ . The average specific gravity is defined as the mass of the fuel and oxidizer, divided by the sum of their volumes. Here the mixture ratio is defined as the oxidizer mass flow rate divided by the fuel mass flow rate.

$$\delta_{av} = \frac{\delta_o \delta_f (1 + r)}{r \delta_f + \delta_o} \quad (7-1)$$

Values of  $\delta_{av}$  for various propellant combinations are listed in Table 5-5. The value of  $\delta_{av}$  can be increased by adding heavy materials to the propellants, either by solution or colloidal suspension. The identical type of equation can be written for the average density  $\rho_{av}$  in terms of the fuel density and the oxidizer density.

$$\rho_{av} = \frac{\rho_o \rho_f (1 + r)}{\rho_f r + \rho_o} \quad (7-2)$$

In the SI system of units the specific gravity has the same numerical value as the density expressed in units of grams per cubic centimeter or kg/liter. In some performance comparisons the parameter *density specific impulse*  $I_d$  is used. It is defined as the product of the average specific gravity  $\delta$  and the specific impulse  $I_s$ :

$$I_d = \delta_{av} I_s \quad (7-3)$$

**Stability.** No *deterioration* and no *decomposition* with long-term (over 15 years) storage and minimal *reaction with the atmosphere* have been attained with many propellants. Good *chemical stability* means no decomposition of the liquid propellant during operation or storage, even at elevated temperature. A good liquid propellant should also have no *chemical deterioration* when in contact with piping, tank walls, valve seats, and gasket materials, even at relatively high ambient temperatures. No appreciable *absorption of moisture* and no adverse effects of small amounts of *impurities* are desirable properties. There should be no chemical deterioration when liquid flows through the hot cooling jacket passages. Some hydrocarbons (e.g., olefins) decompose and

form carbonaceous deposits on the hot inside surfaces of the cooling passage. These deposits can be hard, reduce the heat flow, increase the local metal temperatures, and thus can cause the metal to weaken and fail. About 1% per year of stored concentrated hydrogen peroxide decomposes in clean storage tanks. Between 1 and 20% of a cryogenic propellant (stored in a vehicle) evaporates every day in an insulated tank.

**Heat Transfer Properties.** *High specific heat, high thermal conductivity, and a high boiling or decomposition temperature* are desirable for propellants that are used for thrust chamber cooling (see Section 8.3).

**Pumping Properties.** A low *vapor pressure* permits not only easier handling of the propellants, but also a more effective pump design in applications where the propellant is pumped. This reduces the potential for cavitation, as explained in Chapter 10. If the *viscosity* of the propellant is too high, then pumping and engine-system calibration become difficult. Propellants with high vapor pressure, such as liquid oxygen, liquid hydrogen, and other liquefied gases, require special design provisions, unusual handling techniques, and special low-temperature materials.

**Temperature Variation.** The *temperature variation* of the physical properties of the liquid propellant should be small. For example, a wide temperature variation in vapor pressure and density (*thermal coefficient of expansion*) or an unduly high change in viscosity with temperature makes it very difficult to accurately calibrate a rocket engine flow system or predict its performance over any reasonable range of operating temperatures.

## Ignition, Combustion, and Flame Properties

If the propellant combination is *spontaneously ignitable*, it does not require an ignition system. This means that burning is initiated as the oxidizer and the fuel come in contact with each other. Spontaneously ignitable propellants are often termed *hypergolic* propellants. Although an ignition system is not a very objectionable feature, its elimination is usually desirable because it simplifies the propulsion system. All rocket propellants should be readily ignitable and have a small ignition time delay in order to reduce the potential explosion hazard during starting. Starting and ignition problems are discussed further in Section 8.4.

*Nonspontaneously ignitable propellants* have to be heated by external means before ignition can begin. Igniters are devices that accomplish an initial slight pressurization of the chamber and the initial heating of the propellant mixture to the point where steady flow combustion can be self-sustained. The amount of energy added by the igniter to activate the propellants should be small so that low-power ignition systems can be used. The energy required for satisfac-

tory ignition usually diminishes for increasing ambient temperature of the propellant.

Certain propellant combinations burn very smoothly without combustion vibration. Other propellant combinations do not demonstrate this *combustion stability* and, therefore, are less desirable. Combustion is treated in Chapter 9.

*Smoke* formation is objectionable in many applications because of the smoke deposits on the surrounding equipment and parts. *Smoke* and brilliantly *luminous exhaust flames* are objectionable in certain military applications, because they can be easily detected. In some applications the condensed species in the exhaust gas can cause *surface contamination* on spacecraft windows or optical lenses and the electrons in the flame can cause undesirable *interference* or *attenuation of communications radio signals*. See Chapter 18 for information on exhaust plumes.

### Property Variations and Specifications

The propellant properties and quality must not vary, because this can affect engine performance, combustion, and physical or chemical properties. The same propellant must have the same composition, properties, and storage or rocket operating characteristics if manufactured at different times or if made by different manufacturers. For these reasons propellants are purchased against specifications which define ingredients, maximum allowable impurities, packaging methods or compatible materials, allowable tolerances on physical properties (such as density, boiling point, freezing point, viscosity, or vapor pressure), quality control requirements, cleaning procedures for containers, documentation of inspections, laboratory analyses, or test results. A careful chemical analysis of the composition and impurities is necessary. Reference 7-6 describes some of these methods of analysis.

### Additive

Altering and tailoring propellant properties can be achieved with additives. For example, to make a non-hypergolic fuel become hypergolic (readily ignited), a reactive ingredient has been added. To desensitize concentrated hydrogen peroxide and reduce self-decomposition, it is diluted with 3 to 15% water. To increase density or to alleviate certain combustion instabilities, a fine powder of a heavy solid material can be suspended in the propellant.

## 7.2. LIQUID OXIDIZERS

Many different types of storable and cryogenic liquid oxidizer propellants have been used, synthesized, or proposed. For high specific impulse this includes boron-oxygen-fluorine compounds, oxygen-fluorine compounds, nitrogen-fluorine formulations, and fluorinated hydrocarbons; however, they all have

some undesirable characteristics and these synthetic oxidizers have not been proven to be practical. Oxidizer liquids that have been used in experimental liquid rocket engines include mixtures of liquid oxygen and liquid fluorine, oxygen difluoride ( $\text{OF}_2$ ), chlorine trifluoride ( $\text{ClF}_3$ ), or chlorine pentafluoride ( $\text{ClF}_5$ ). All of these are highly toxic and very corrosive. Several commonly used oxidizers are listed below.

### Liquid Oxygen ( $\text{O}_2$ )

Liquid oxygen, often abbreviated as LOX, boils at 90 K at atmospheric pressure; at these conditions it has a specific gravity of 1.14 and a heat of vaporization of 213 kJ/kg. It is widely used as an oxidizer and burns with a bright white-yellow flame with most hydrocarbon fuels. It has been used in combination with alcohols, jet fuels (kerosene-type), gasoline, and hydrogen. As shown in Table 5-5, the attainable performance is relatively high, and liquid oxygen is therefore a desirable and commonly used propellant in large rocket engines. The following missiles and space launch vehicles use oxygen: (1) with jet fuel—Atlas, Thor, Jupiter, Titan I, Saturn booster; (2) with hydrogen—Space Shuttle and Centaur upper stage; (3) with alcohol—V-2 and Redstone. Figures 1-4 and 6-1 show units that use oxygen. Figures 5-1 to 5-6 give theoretical performance data for liquid oxygen with a kerosene-type fuel.

Although it usually does not burn spontaneously with organic materials at ambient pressures, combustion or explosions can occur when a confined mixture of oxygen and organic matter is suddenly pressurized. Impact tests show that mixtures of liquid oxygen with many commercial oils or organic materials will detonate. Liquid oxygen supports and accelerates the combustion of other materials. Handling and storage are safe when contact materials are clean. Liquid oxygen is a noncorrosive and nontoxic liquid and will not cause the deterioration of clean container walls. When in prolonged contact with human skin, the cryogenic propellant causes severe burns. Because liquid oxygen evaporates rapidly, it cannot be stored readily for any great length of time. If liquid oxygen is used in large quantities, it is often produced very close to its geographical point of application. Liquid oxygen can be obtained in several ways, such as by boiling liquid nitrogen out of liquid air.

It is necessary to insulate all lines, tanks, valves, and so on, that contain liquid oxygen in order to reduce the evaporation loss. Rocket propulsion systems which remain filled with liquid oxygen for several hours and liquid oxygen storage systems have to be well insulated against absorbing heat from the surroundings. External drainage provisions have to be made on all liquid oxygen tanks and lines to eliminate the water that condenses on the walls.

**Example 7-1.** Estimate the approximate temperature and volume change of liquid oxygen if an oxygen tank is pressurized to 8.0 atmospheres for a long time before engine start. Assume the tank is 60% full and the evaporated oxygen is refrigerated and recondensed (constant mass).

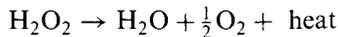
**SOLUTION.** Using Table 7-1 and Figs. 7-1 and 7-2, the vapor pressure goes from 1.0 atm (0.1 MPa) to 8 atm (about 0.8 MPa) and the equilibrium temperature goes from the boiling point of 90 K at 1.0 atm to about 133 K. The corresponding specific gravities are 1.14 and 0.88 respectively. This is an increase of  $1.14/0.88 = 1.29$  or about 77% full (29% more volume).

In tanks with turbopump feed systems the actual tank pressures are lower (typically 2 to 4 atm) and the evaporated oxygen is vented, causing a cooling effect on the liquid surface. So the numbers calculated above are too large (8 atm was selected to clearly show the effect). The warming occurs when there is a long hold period of a pressurized cryogenic propellant tank and is most pronounced when the final portion of the propellant is being emptied. Nevertheless the higher temperature, higher vapor pressure, and lower density can cause changes in mixture ratio, required tank volume, and pump suction condition (see Section 10.1). Therefore tanks with cryogenic propellant are insulated (to minimize heat transfer and density changes) and are pressurized only shortly before engine start, so as to keep the propellant at its lowest possible temperature.

### Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>)

In rocket application, hydrogen peroxide has been used in a highly concentrated form of 70 to 99%; the remainder is mostly water. Commercial peroxide is approximately 30% concentrated. Concentrated hydrogen peroxide was used in gas generator and rocket applications between 1938 and 1965 (X-1 and X-15 research aircraft).

In the combustion chamber, the propellant decomposes according to the following chemical reaction, forming superheated steam and gaseous oxygen:



This decomposition is brought about by the action of catalysts such as various liquid permanganates, solid manganese dioxide, platinum, and iron oxide. In fact, most impurities act as a catalyst. H<sub>2</sub>O<sub>2</sub> is hypergolic with hydrazine and will burn well with kerosene. The theoretical specific impulse of 90% hydrogen peroxide is 154 sec, when used as a monopropellant with a solid catalyst bed.

Even under favorable conditions H<sub>2</sub>O<sub>2</sub> will often decompose at a slow rate during storage, about one percent per year for 95%, and gas will bubble out of the liquid. Contaminated liquid peroxide must be disposed of before it reaches a danger point of about 448 K, when an explosion usually occurs. Concentrated peroxide causes severe burns when in contact with human skin and may ignite and cause fires when in contact with wood, oils, and many other organic materials. In the past rocket engines with hydrogen peroxide oxidizer have been used for aircraft boost (German Me 163, and U.S. F 104) and a missile (Britain: Black Knight). It has not been used for a long time, partly because of its long-term storage stability. However, there has been some improvement and some renewed interest in this dense oxidizer, which produces a nontoxic exhaust.

### Nitric Acid ( $\text{HNO}_3$ )

There are several types of nitric acid mixtures that have been used as oxidizers between 1940 and 1965; they are not used extensively today in the United States. The most common type, *red fuming nitric acid* (RFNA), consists of concentrated nitric acid ( $\text{HNO}_3$ ) that contains between 5 and 20% dissolved nitrogen dioxide. The evaporating red-brown fumes are exceedingly annoying and poisonous. Compared to concentrated nitric acid (also called *white fuming nitric acid*), RFNA is more energetic, more stable in storage, and less corrosive to many tank materials.

Nitric acid is highly corrosive. Only certain types of stainless steel, gold, and a few other materials are satisfactory as storage containers or pipeline materials. A small addition of fluoride ion (less than 1% of HF) inhibits the nitric acid, causes a fluoride layer to form on the wall, and greatly reduces the corrosion with many metals. It is called *inhibited red fuming nitric acid* (IRFNA). In case of accident of spilling, the acid should be diluted with water or chemically deactivated. Lime and alkali metal hydroxides and carbonates are common neutralizing agents. However, nitrates formed by the neutralization are also oxidizing agents and must be handled accordingly.

Nitric acid has been used with gasoline, various amines, hydrazine, dimethylhydrazine, and alcohols. It ignites spontaneously with hydrazine, furfuryl alcohol, aniline, and other amines. The specific gravity of nitric acid varies from 1.5 to 1.6, depending on the percentages of nitric oxide, water, and impurities. This high density permits compact vehicle construction.

Vapors from nitric acid or red fuming nitric acid have an OSHA 8-hr personnel exposure limit or a threshold work allowance of 2 ppm (parts per million or about  $5 \text{ mg/m}^3$ ) and a short-term exposure limit of 10 ppm. Droplets on the skin cause burns and sores which do not heal readily.

### Nitrogen Tetroxide ( $\text{N}_2\text{O}_4$ )

This is a high-density yellow-brown liquid (specific gravity of 1.44). Although it is the most common storable oxidizer used in the United States today, its liquid temperature range is narrow and it is easily frozen or vaporized. It is only mildly corrosive when pure, but forms strong acids when moist or allowed to mix with water. It readily absorbs moisture from the air. It can be stored indefinitely in sealed containers made of compatible material. It is hypergolic with many fuels and can cause spontaneous ignition with many common materials, such as paper, leather, and wood. The fumes are reddish brown and are extremely toxic. Because of its high vapor pressure it must be kept in relatively heavy tanks. The freezing point of  $\text{N}_2\text{O}_4$  can be lowered (by adding a small amount of nitric oxide or NO) but at the penalty of a higher vapor pressure. This mixture of NO and  $\text{N}_2\text{O}_4$  is called mixed oxides of nitrogen (MON) and different grades have been 2 and 30% NO content.

Nitrogen tetroxide is a storable propellant oxidizer and is used in the Titan missile together with a fuel mixture consisting of hydrazine and unsymmetrical dimethylhydrazine. It is also used with monomethylhydrazine fuel in the Space Shuttle orbital maneuver system and reaction control system and in many spacecraft propulsion systems. In many of these applications care must be taken to avoid freezing this propellant. The OSHA 8-hr personnel exposure limit is 5 ppm or 9 mg/m<sup>3</sup>.

### 7.3. LIQUID FUELS

Again, many different chemicals have been proposed, investigated, and tested. Only a few have been used in production rocket engines. Liquid fuels other than those listed below have been used in experimental rocket engines, in older experimental designs, and in some older production engines. These include aniline, furfuryl alcohol, xylydine, gasoline, hydrazine hydrate, borohydrides, methyl and/or ethyl alcohol, ammonia, and mixtures of some of these with one or more other fuels.

#### Hydrocarbon Fuels

Petroleum derivatives encompass a large variety of different hydrocarbon chemicals, most of which can be used as a rocket fuel. Most common are those types that are in use with other applications and engines, such as gasoline, kerosene, diesel oil, and turbojet fuel. Their physical properties and chemical composition vary widely with the type of crude oil from which they were refined, with the chemical process used in their production, and with the accuracy of control exercised in their manufacture. Typical values are listed in Table 7-2.

In general, these petroleum fuels form yellow-white, brilliantly radiating flames and give good performance. They are relatively easy to handle, and there is an ample supply of these fuels available at low cost. A specifically refined petroleum product particularly suitable as a rocket propellant has been designated RP-1. It is basically a kerosene-like mixture of saturated and unsaturated hydrocarbons with a somewhat narrow range of densities and vapor pressure. Several hydrocarbon fuels can form carbon deposits on the inside of cooling passages, impeding the heat transfer and raising wall temperatures. Ref. 7-7 indicates that this carbon formation depends on fuel temperature in the cooling jacket, the particular fuel, the heat transfer, and the chamber wall material. RP-1 is low in olefins and aromatics, which can cause carbonaceous deposits inside fuel cooling passages. RP-1 has been used with liquid oxygen in the Atlas, Thor, Delta, Titan I, and Saturn rocket engines (see Figs. 5-1 to 5-6).

*Methane* (CH<sub>4</sub>) is a cryogenic hydrocarbon fuel. It is denser than liquid hydrogen and relatively low in cost. Compared to petroleum refined hydro-

TABLE 7-2. Properties of Some Typical Hydrocarbon Fuels Made from Petroleum

	Jet Fuel	Kerosene	Aviation Gasoline 100/130	Diesel Fuel	RP-1
Specific gravity at 289 K	0.78	0.81	0.73	0.85	0.80-0.815
Freezing point (K)	213 (max.)	230	213	250	239 (max.)
Viscosity at 289 K (cP)	1.4	1.6	0.5	2.0	16.5 (at 239 K)
Flash point (K) (TCC)	269	331	244	333	316
ASTM distillation (K)					
10% evaporated	347	—	337	—	458-483
50% evaporated	444	—	363	—	—
90% evaporated	511	—	391	617	—
Reid vapor pressure (psia)	2 to 3	Below 1	7	0.1	—
Specific heat (cal/kg-K)	0.50	0.49	0.53	0.47	0.50
Average molecular mass (kg/mol)	130	175	90	—	—

carbons it has highly reproducible properties. With liquid oxygen it is a candidate propellant combination for launch vehicle booster rocket engines and also reaction engines control when oxygen is available from the main engines). Experimental oxygen-methane engines have been tested, but they have not yet flown.

### Liquid Hydrogen (H<sub>2</sub>)

Liquid hydrogen, when burned with liquid fluorine or liquid oxygen, gives a high performance, as shown in Table 5-5. It also is an excellent regenerative coolant. With oxygen it burns with a colorless flame; however, the shock waves in the plume may be visible. Of all known fuels, liquid hydrogen is the lightest and the coldest, having a specific gravity of 0.07 and a boiling point of about 20 K. The very low fuel density requires bulky fuel tanks, which necessitate very large vehicle volumes. The extremely low temperature makes the problem of choosing suitable tank and piping materials difficult, because many metals become brittle at low temperatures.

Because of its low temperature, liquid hydrogen tanks and lines have to be well insulated to minimize the evaporation of hydrogen or the condensation of moisture or air on the outside with the subsequent formation of liquid or solid air or ice. A vacuum jacket often has been used in addition to insulating materials. All common liquids and gases solidify in liquid hydrogen. These solid particles in turn plug orifices and valves. Therefore, care must be taken to scavenge all lines and tanks of air and moisture (flush with helium or pull

vacuum) before introducing the propellant. Mixture of liquid hydrogen and solid oxygen or solid air can be explosive.

Liquid hydrogen has two species, namely, orthohydrogen and parahydrogen, which differ in their nuclear spin state. As hydrogen is liquefied, the relative equilibrium composition of ortho- and parahydrogen changes. The transformation from one species to another is accompanied by a transfer of energy. Liquid hydrogen is manufactured from gaseous hydrogen by successive compression, cooling, and expansion processes.

Hydrogen gas, when mixed with air, is highly flammable and explosive over a wide range of mixture ratios. To avoid this danger, hydrogen gas leakage (a tank vent line) is often intentionally ignited and burned in the air. Liquid hydrogen is used with liquid oxygen in the Centaur upper stage, the Space Shuttle main engine, and upper stage space engines developed in Japan, Russia, Europe, and China.

Hydrogen burning with oxygen forms a nontoxic exhaust gas. This propellant combination has been applied successfully to space launch vehicles because of its high specific impulse. Here the payload capability usually increases greatly for relatively small increases in specific impulse. However, the low density of hydrogen makes for a large vehicle and a relatively high drag.

One method to increase the density of hydrogen is to use a subcooled mixture of liquid hydrogen and suspended frozen small particles of solid hydrogen, which is denser than the liquid. Experiments and studies on this "slush" hydrogen have been performed; it is difficult to produce and maintain a uniform mixture. It has not yet been used in a flight vehicle.

Some studies have shown that, when burned with liquid oxygen, a hydrocarbon (such as methane or RP-1) can give a small advantage in space launch vehicle first stages. Here the higher average propellant density allows a smaller vehicle with lower drag, which compensates for the lower specific impulse of the hydrocarbon when compared to a hydrogen fuel. Also, there are some concepts for operating the booster-stage rocket engine initially with hydrocarbon fuel and then switching during flight to hydrogen fuel. As yet, engines using two fuels, namely methane (or hydrocarbon) and hydrogen, have not yet been fully developed or flown. Some work on an experimental engine was done in Russia.

### **Hydrazine ( $N_2H_4$ )**

Reference 7–8 gives a good discussion of this propellant, which is used as a bipropellant fuel as well as a monopropellant. Hydrazine and its related liquid organic compounds, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), all have similar physical and thermochemical properties. Hydrazine is a toxic, colorless liquid with a high freezing point (274.3 K). Hydrazine has a short ignition delay and is spontaneously ignitable with nitric acid and nitrogen tetroxide.

Its vapors may form explosive mixtures with air. If hydrazine is spilled on a surface or a cloth, a spontaneous ignition with air can occur.

Pure anhydrous hydrazine is a stable liquid; it has been safely heated above 530 K. It has been stored in sealed tanks for over 15 years. With impurities or at higher temperatures it decomposes and releases energy. Under pressure shock (blast wave) it decomposes at temperatures as low as 367 K. Under some conditions this decomposition can be a violent detonation, and this has caused problems in cooling passages of experimental injectors and thrust chambers. Harmful effects to personnel may result from ingestion, inhalation of vapors, or prolonged contact with skin. The OSHA 8-hr personnel exposure limit is 0.1 ppm or 0.13 mg/m<sup>3</sup>. Hydrazine is a known carcinogen.

Hydrazine reacts with many materials, and care must be exercised to avoid storage contact with materials that cause a decomposition (see Ref 7–9). Tanks, pipes, or valves must be cleaned and free of impurities. Compatible materials include stainless steels (303, 304, 321, or 347), nickel, and 1100 and 3003 series of aluminum. Iron, copper and its alloys (such as brass or bronze), monel, magnesium, zinc, and some types of aluminum alloy must be avoided.

### Unsymmetrical Dimethylhydrazine [(CH<sub>3</sub>)<sub>2</sub>NNH<sub>2</sub>]

A derivative of hydrazine, namely, unsymmetrical dimethylhydrazine (UDMH), is often used instead of or in mixtures with hydrazine because it forms a more stable liquid, particularly at higher temperatures. Furthermore, it has a lower freezing point (215.9 K) and a higher boiling point (336.5 K) than a hydrazine. When UDMH is burned with an oxidizer it gives only slightly lower values of  $I_s$  than pure hydrazine. UDMH is often used when mixed with 30 to 50% hydrazine. This fuel is used in the Titan missile and launch vehicle and spacecraft engines in 50% mixtures and has been used in the lunar landing and take-off engines. UDMH is used in Russian and Chinese rocket engines.

Freezing does not affect UDMH, MMH, or hydrazine, but freezing of a 50:50 mixture of UDMH and hydrazine causes a separation into two distinct layers; a special remixing operation is necessary for reblending if freezing occurs in a space vehicle. The OSHA 8-hr personnel exposure limit for vapor is 0.5 ppm, and UDMH is a carcinogen.

### Monomethylhydrazine (CH<sub>3</sub>NHNH<sub>2</sub>)

Monomethylhydrazine (MMH) has been used extensively as a fuel in spacecraft rocket engines, particularly in small attitude control engines, usually with N<sub>2</sub>O<sub>4</sub> as the oxidizer. It has a better shock resistance to blast waves, better heat transfer properties, and a better liquid temperature range than pure hydrazine. Like hydrazine, its vapors are easily ignited in air; the flammability limits are from 2.5 to 98% by volume at atmospheric sea level pressure and ambient temperature. The materials compatible with hydrazine are also compatible

with MMH. The specific impulse with storable oxidizers usually is 1 or 2% lower with MMH than with  $N_2H_4$ .

Both MMH and UDMH are soluble in many hydrocarbons; hydrazine is not. All hydrazines are toxic materials, but MMH is the most toxic when inhaled, and UDMH the least toxic. Atmospheric concentrations of all hydrazines should be kept below 0.1 ppm for long periods of exposure.

Monomethylhydrazine, when added in relatively small quantities of 3 to 15% to hydrazine, has a substantial quenching effect on the explosive decomposition of hydrazine. Monomethylhydrazine decomposes at 491 K, whereas hydrazine explodes at 369 K when subjected to pressure shocks of identical intensity. MMH is a suspected carcinogen and the OSHA personnel 8-hour exposure limit is 0.2 ppm.

## 7.4. LIQUID MONOPROPELLANTS

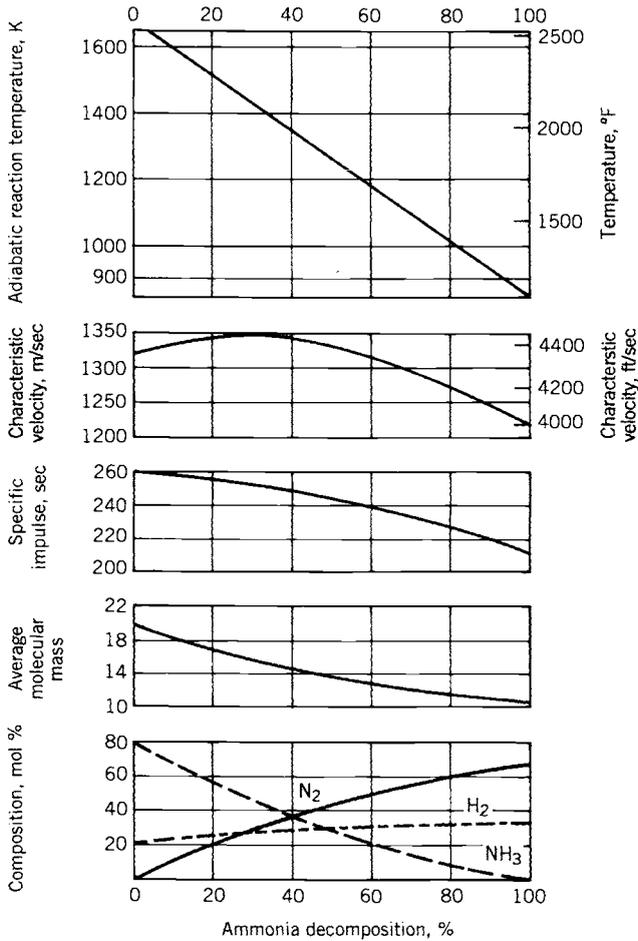
The propellant-feed and control-system simplicity associated with a monopropellant makes this type of propellant attractive for certain applications. Hydrazine is being used extensively as a monopropellant in small attitude and trajectory control rockets for the control of satellites and other spacecraft and also as a hot gas generator. (It is discussed in the preceding section.) Other monopropellants (ethylene oxide or nitromethane) were tried experimentally, but are no longer used today. Concentrated hydrogen peroxide was used for monopropellant gas generation in the USA, Russia, and Germany in engines designed before 1955.

Ignition of monopropellants can be produced thermally (electrical or flame heat) or by a catalytic material. A monopropellant must be chemically and thermally stable to insure good liquid storage properties, and yet it must be easily decomposed and reactive to give good combustion properties.

### Hydrazine as a Monopropellant

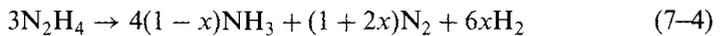
Hydrazine is not only an excellent storable fuel, but also an excellent monopropellant when decomposed by a suitable solid or liquid catalyst; this catalyst often needs to be preheated for fast startup. Iridium is an effective catalyst at room temperature. At elevated temperature (about 450 K) many materials decompose hydrazine, including iron, nickel, and cobalt. See Ref. 7–8. Different catalysts and different reaction volumes make the decomposition reaction go to different products, resulting in gases varying in composition or temperature. As a monopropellant, it is used in gas generators or in space engine attitude control rockets.

Hydrazine has been stored in sealed tanks for over 15 years. A typical hydrazine monopropellant thrust chamber, its injection pattern, and its decomposition reaction are described in Chapter 10 and typical design parameters are shown in Fig. 7–3 and a monopropellant structure in Fig. 8–16.



**FIGURE 7-3.** Operating parameters for decomposed hydrazine at the exit of a catalytic reactor as a function of the ammonia dissociation fraction. Adapted with permission from Ref. 7-8.

The catalytic decomposition of hydrazine can be described ideally as a two-step process; this ignores other steps and intermediate products. First, hydrazine ( $N_2H_4$ ) decomposes into gaseous ammonia ( $NH_3$ ) and nitrogen ( $N_2$ ); this reaction is highly exothermic, i.e., it releases heat. Secondly, the ammonia decomposes further into nitrogen and hydrogen gases, but this reaction is endothermic and absorbs heat. These simplified reactions can be written as



Here  $x$  is the degree of ammonia dissociation; it is a function of the catalyst type, size, and geometry, the chamber pressure, and the dwell time within the

catalyst bed. Figure 7-3 shows several ideal rocket engine parameters for hydrazine monopropellant as a function of  $x$ , the fraction of ammonia that is decomposed. The values are for an ideal thruster at 1000 psia chamber pressure with an area ratio of 50 expanding at high altitude. The best specific impulse is attained when little ammonia is allowed to dissociate.

Hydrazine is manufactured in several grades of purity. The standard commercial hydrazine has about 1.5% maximum by weight of water, less than 1.0% aniline, and no more than 10 mg/l of particulates, including carbon. Monopropellant-grade hydrazine has less than 1% water, less than 0.5% aniline (which is a material commonly used in the manufacture of hydrazine), and traces of ammonia, carbon dioxide, chlorides, and iron- or carbon-containing materials such as UDMH or MMH. Aniline and other organic impurities can poison the catalyst used to decompose monopropellant hydrazine; as mentioned in Chapter 10, this can cause operating problems. There is also a highly purified grade of hydrazine that has less water, less than 0.005% aniline, and less than 0.003% carbon materials; it does not contaminate the catalyst and is used now in many monopropellant applications.

### Hydroxyl Ammonium Nitrate ( $\text{NH}_2\text{OH}^+\text{NO}_3^-$ )

This is a relatively new, synthetic, propellant material rich in oxygen, but with combined hydrogen and nitrogen (fuel ingredients), it is abbreviated as HAN. It is an opaque hygroscopic solid when pure, and a clear colorless odorless liquid in aqueous solutions. The solid HAN (specific gravity of 1.84) is a potential solid propellant ingredient and the liquid HAN solution is a potential monopropellant (a 13 molar solution has a specific gravity of 1.523). Both can be made to burn smoothly and several catalysts have been effective in obtaining controlled decomposition. The boiling point (110 to 145°C) and the freezing point (-15 to -44°C) vary with the water content. HAN becomes more viscous as the percentage of water is reduced. The liquid is corrosive, toxic, denser than hydrazine monopropellant, and does not seem to be carcinogenic. The liquid is incompatible with alkali materials, many metals, and other materials. Even with relatively very compatible materials HAN solutions decompose slowly in storage; a satisfactory stabilizer has yet to be found. The monopropellant's specific impulse is between 200 and 265 sec, depending on the water content and the mixing of the aqueous HAN with one of several possible compatible organic fuel liquids. The HAN propellant formulation, its rocket engines, and solid motors are still in their research and development phase, as shown in Refs. 7-9 and 7-10.

## 7.5. GELLED PROPELLANTS

Gelled propellants have additives that make them thixotropic materials. They have the consistency of thick paint or jelly when at rest, but they liquify and

flow through pipes, valves, pumps, or injectors when an adequate shear stress is applied. They offer these *advantages*.

Small aluminum particles can be suspended in the fuels where smoky exhaust is not objectionable. Inert solid particles can be suspended in oxidizer liquids. This increases propellant density, density impulse, and thus reduces the size of tanks and vehicles. Smaller vehicles have reduced drag and thus can allow an increase in the range or speed of tactical missiles.

There is no plugging of injector orifices or valve passages and good flow control has been demonstrated.

Individual gelled fuel propellants will be essentially nonflammable and will not usually sustain an open fire.

There is reduced susceptibility of leakage or spill, reduced sloshing of liquids in the tanks, and the boil-off rate is reduced.

Long-term storage without settling or separation is possible; more than 10 years has been demonstrated.

Explosions or detonations, which happen when a vehicle accident causes liquid propellants to become inadvertently premixed, are much less likely with gelled propellants, which are difficult to mix.

Many spilled gelled propellants can be diluted with water and disposed of safely.

Short-duration pulsing is possible.

Most storable oxidizers, a few cryogenic propellants, and most liquid storable fuels can be gelled.

Explosions are much less likely when a propellant tank is penetrated by a bullet or when a missile is exposed to an external fire or a nearby detonation.

These are some of the *disadvantages*:

There is a small decrease in specific impulse due to dilution with a gelling agent, and less efficient atomization or combustion. For example, the characteristic velocity  $c^*$  of oxygen-kerosene propellant is decreased by 4 to 6% when the kerosene is gelled and aluminum is suspended in the fuel. When both the fuel and a nitric acid oxidizer are gelled, the performance loss ( $c^*$ ) can be as high as 8%. Clever injector design and the selection of good gelling agents can reduce this loss.

Loading or unloading of propellants is somewhat more complex.

Residual propellant quantity may be slightly higher, because the thixotropic fluid layer on the walls of the tanks and pipes may be slightly thicker.

Changes in ambient temperature will cause slight changes in propellant density and viscosity and therefore also in mixture ratio; this can result in more leftover or residual propellant and thus in a slight reduction of

available total impulse. This can be minimized by careful selection of gelling agents so as to match the rheological property changes of oxidizer and fuel over a particular temperature range.

Suspended metals can make the plume smoky and visible.

Some gelling agents have resulted in unstable gelled propellants; that is, they separated or underwent chemical reactions.

Experimental rocket engines have shown these gelled propellants to be generally safer than ordinary liquid propellants and to have good performance and operational characteristics (see Refs 7-11 and 7-12). This makes them less susceptible to field accidents. A variety of different organic and inorganic gelling agents have been explored with a number of different liquid propellants.

Experimental thrust chambers and rocket engine systems have been satisfactorily demonstrated with several gelled propellant combinations. One experimental engine is shown in Fig. 6-8. As far as is known, no such rocket engine has yet been put into production or flight operation. An effort is underway to demonstrate this technology clearly and to qualify a rocket engine with gelled propellants for an actual flight application.

## 7.6. GASEOUS PROPELLANTS

*Cold gas propellants* have been used successfully for reaction control systems (RCS) for perhaps 50 years. The engine system is simple, consisting of one or more high-pressure gas tanks, multiple simple metal nozzles (often aluminum or plastic), an electrical control valve with each nozzle, a pressure regulator, and provisions for filling and venting the gas. The tank size will be smaller if the tank pressures are high. Pressures are typically between 300 and 1000 MPa (about 300 to 10,000 psi). The mass of spherical storage tanks is essentially independent of pressure if they contain the same mass of gas.

Typical cold gas propellants and some of their properties and characteristics are listed in Table 7-3. Nitrogen, argon, dry air, krypton and Freon 14 have been employed in spacecraft RCSs. With high-pressure hydrogen or helium as cold gas, the specific impulse is much higher, but the densities of these gases are much lower. This requires a much larger gas storage volume and heavier high-pressure tanks. In most applications the extra inert mass outweighs the advantage of better performance. In a few applications the gas (and its storage tank) are heated electrically or chemically. This improves the specific impulse and allows a smaller tank, but it also introduces complexity.

The selection of the gas propellant, the storage tanks, and RCS design depend on many factors, such as volume and mass of the storage tanks, the maximum thrust and total impulse, the gas density, required maneuvers, duty cycle, and flight duration. Cold gas systems are used for total impulses of perhaps 1200 N-sec or 5000 lbf-sec. Higher values usually employ liquid propellants.

**TABLE 7-3.** Properties of Gaseous Propellants Used for Auxiliary Propulsion

Propellant	Molecular Mass	Density <sup>a</sup> (lb/ft <sup>3</sup> )	<i>k</i>	Theoretical Specific Impulse <sup>b</sup> (sec)
Hydrogen	2.0	1.77	1.40	284
Helium	4.0	3.54	1.67	179
Methane	16.0	14.1	1.30	114
Nitrogen	28.0	24.7	1.40	76
Air	28.9	25.5	1.40	74
Argon	39.9	35.3	1.67	57
Krypton	83.8	74.1	1.63	50

<sup>a</sup>At 5000 psia and 20°C.

<sup>b</sup>In vacuum with nozzle area ratio of 50:1 and initial temperature of 20°C.

If the operation is short (only a few minutes, while the main engine is running), the gas expansion will be adiabatic (no heat absorption by gas) and often is analyzed as isentropic (constant stagnation pressure). The temperature of the gas will drop (the pressure and specific impulse will also drop) as the gas is consumed. For long intermittent operations (months or years in space) the heat from the spacecraft is transferred to the gas and the tank temperature stays essentially constant; the expansion will be nearly isothermal. An analysis of gas expansion is given in Section 6.5.

The advantages and disadvantages of cold gas systems are described on pages 303 and 304.

## 7.7. SAFETY AND ENVIRONMENTAL CONCERNS

To minimize the hazards and potential damage inherent in reactive propellant materials, it is necessary to be very conscientious about the likely risks and hazards (see Ref. 7-4). This concerns toxicity, explosiveness, fire or spill danger, and others mentioned in Section 7.1. Before an operator, assembler, maintenance mechanic, supervisor, or engineer is allowed to transfer or use a particular propellant, he or she should receive safety training in the particular propellant, its characteristics, its safe handling or transfer, potential damage to equipment or the environment, and the countermeasures for limiting the consequences in case of an accident. They must also understand the potential hazards to the health of personnel, first aid, remedies in case of contact exposure of the skin, ingestion, or inhaling, and the use of safety equipment. Examples of safety equipment are protective clothing, detectors for toxic vapors, remote controls, warning signals, or emergency water deluge. The personnel working with or being close to highly toxic materials usually have to undergo frequent health monitoring. Also rocket engines need to be

designed for safety to minimize the occurrence of a leak, an accidental spill, an unexpected fire, or other potentially unsafe conditions. Most organizations have one or more safety specialists who review the safety of the test plans, manufacturing operations, design, procedures, or safety equipment. With the proper training, equipment, precautions, and design safety features, all propellants can be handled safely.

If a safety violation occurs or if an operation, design, procedure, or practice is found to be (or appears to be) unsafe, then a thorough investigation of the particular item or issue should be undertaken, the cause of the lack of safety should be investigated and identified, and an appropriate remedial action should be selected and initiated as soon as possible.

The discharge of toxic exhaust gases to the environment and their dispersion by the wind can cause exposure of operating personnel as well as the people in nearby areas. This is discussed in Section 20.2. The dumping or spilling of toxic liquids can contaminate subterranean aquifers and surface waters, and their vapors can pollute the air. Today the type and amount of gaseous and liquid discharges are regulated and monitored by government authorities. These discharges must be controlled or penalties will be assessed against violators. Obtaining a permit to discharge can be a lengthy and involved procedure.

## PROBLEMS

1. Plot the variation of the *density specific impulse* (product of average specific gravity and specific impulse) with mixture ratio and explain the meaning of the curve. Use the theoretical shifting specific impulse values of Figure 5-1 and the specific gravities from Figure 7-1 or Table 7-1 for the liquid oxygen–RP-1 propellant combination.  
*Answers:* Check point at  $r = 2.0$ ;  $I_s = 290$ ;  $I_d = 303$ ;  $\delta_{av} = 1.01$ .
2. Prepare a table comparing the relative merits of liquid oxygen and nitric acid as rocket oxidizers.
3. Derive Eq. 7-1 for the average specific gravity.
4. A rocket engine uses liquid oxygen and RP-1 as propellants at a design mass mixture ratio of 2.40. The pumps used in the feed system are basically constant-volume flow devices. The RP-1 hydrocarbon fuel has a nominal temperature of 298 K and it can vary at about  $\pm 25^\circ\text{C}$ . The liquid oxygen is nominally at its boiling point (90 K), but, after the tank is pressurized, this temperature can increase by 30 K. What are the extreme mixture ratios under unfavorable temperature conditions? If this engine has a nominal mass flow rate of 100 kg/sec and a duration of 100 sec, what is the maximum residual propellant mass when the other propellant is fully consumed? Use the curve slopes of Fig. 7-1 to estimate changes in density. Assume that the specific impulse is constant for the relatively small changes in mixture ratio, that vapor pressure changes have no influence on the pump flow, and that the engine has no automatic control for mixture ratio.

5. The vehicle stage propelled by the rocket engine in Problem 4 has a design mass ratio  $m_f/m_0$  of 0.50 (see Eq. 4-6). How much will the worst combined changes in propellant temperatures effect the mass ratio and the ideal gravity-free vacuum velocity?
6. (a) What should be the approximate percent ullage volume for nitrogen tetroxide tank when the vehicle is exposed to ambient temperatures between about 50°F and about 150°F?
- (b) What is maximum tank pressure at 150°F.
- (c) What factors should be considered in part (b)?

*Answers:* (a) 15 to 17%; the variation is due to the nonuniform temperature distribution in the tank; (b) 6 to 7 atm; (c) vapor pressure, nitrogen monoxide content in the oxidizer, chemical reactions with wall materials, or impurities that result in largely insoluble gas products.

7. An insulated, long vertical, vented liquid oxygen tank has been sitting on the sea level launch stand for a period of time. The surface of the liquid is at atmospheric pressure and is 10.2 m above the closed outlet at the bottom of the tank. If there is no circulation, what will be the temperature, pressure and density of the oxygen at the tank outlet?

## SYMBOLS

$I_d$	density specific impulse, sec
$I_s$	specific impulse, sec
$k$	ratio of specific heat
$r$	mixture ratio (mass flow rate of oxidizer to mass flow rate of fuel)

## Greek Letters

$\delta_{av}$	average specific gravity of mixture
$\delta_f$	specific gravity of fuel
$\delta_o$	specific gravity of oxidizer
$\rho_{av}, \rho_f, \rho_o$	densities, kg/m <sup>3</sup> (lbm/ft <sup>3</sup> )

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