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Chemical Propellants

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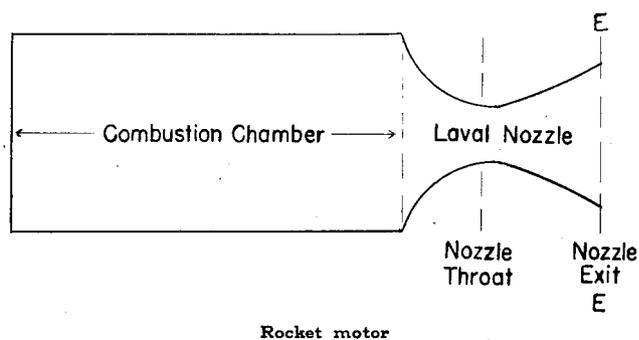
THE chemical propellants form a special class of compounds. Some of the members of this class are usually not considered as being important enough to warrant special discussion in chemistry courses. For this reason it appears to be of interest to present a catalogue of representative chemicals with emphasis on the particular characteristics which make them useful or usable rocket propellants.

In order to understand the function of chemicals in jet propulsion applications, it is necessary to consider the task which the chemicals are called upon to perform. In its bare essentials a rocket motor consists of a combustion chamber into which the propellants are injected, and from which the products of combustion flow out through a Laval nozzle (see the figure). Experience has shown that nearly complete thermodynamic equilibrium is reached in the combustion chamber and that the expansion of the combustion products through the Laval nozzle from the chamber pressure to the pressure of the surrounding atmosphere is nearly adiabatic.¹

An analysis of the forces acting on the rocket engine shows that the total thrust F is given by the relation

$$F = \dot{m}V_e \quad (1)$$

¹ The chamber pressure varies from one rocket engine to another. In liquid-fuel rockets it is usually 300 p. s. i., in solid-propellant motors 1000 to 3000 p. s. i., etc.



if a number of simplifying assumptions are made.^{2, 3} Here \dot{m} is the mass rate of flow of combustion products and V_e is the linear flow velocity in the direction of the nozzle axis at the exit position (*cf.* the plane $E-E$ in the figure). The exhaust velocity V_e , in turn, is determined by the enthalpy change during adiabatic expansion from the chamber (identified by the subscript c) to the nozzle exit (identified by the superscript e) according to the relation

$$V_e^2 = 2Jg\Delta H_c^e \quad (2)$$

² TSIEN, H. S., AND F. J. MALINA, *J. Aero. Sci.*, **6**, 50 (1938).
F. J. MALINA, *J. Franklin Inst.*, **230**, 433 (1940).

³ For an elementary account of the "Physics of Rockets" see SEIFERT, H. S., M. M. MILLS, AND M. SUMMERFIELD, *Am. J. Phys.*, **15**, 1, 121, 255 (1947).

where J represents the mechanical equivalent of heat, g is the acceleration of gravity, and ΔH_c^e equals the enthalpy change per unit mass during adiabatic expansion through the nozzle. From equations (1) and (2) it is apparent that we must make ΔH_c^e large in order to obtain a large thrust on the rocket motor per unit weight rate of flow of propellant.

By proper utilization of the equations for conservation of mass, energy, and momentum it can be shown for ideal gases that

$$F/\dot{m}g = \Phi \cdot \sqrt{T_c/\bar{M}} \quad (3)$$

where Φ is a function only of γ , *viz.*, of the effective ratio of the specific heat at constant pressure to the specific heat at constant volume during expansion, T_c represents the temperature in the combustion chamber, and \bar{M} is the average molecular weight of the combustion products during expansion through the Laval nozzle. In general, both γ and \bar{M} change during expansion because chemical changes are taking place while the gas is being cooled from the chamber temperature T_c to the exit temperature T_e . The chamber temperature T_c can be calculated for any given chemical propellant system by well-known thermodynamic methods.⁴ Since the specific heat ratio γ does not vary greatly from one chemical propellant to another, it is apparent from equation (3) that the selection of suitable propellants to yield large thrusts per unit weight rate of flow of propellant involves the selection of systems yielding high chamber temperatures T_c and low average molecular weights \bar{M} .

The requirement of small values of \bar{M} is met in practice by using reducing compounds containing a great deal of hydrogen as well as relatively light oxidizers, preferably compounds of fluorine and oxygen rather than of chlorine, bromine, and the like. In general, the heat released and hence the value of T_c will be large for those chemical reactions leading to the production of compounds with large negative standard heats of formation from reactants with small negative or even positive standard heats of formation. Here the standard heat of formation is defined in the usual way, *viz.*, as the heat evolved (standard heat of formation is negative) or absorbed (standard heat of formation is positive) when the given compound is formed at 298.16°K. and 1 atm. from the elements in their respective standard states.

The preceding considerations have emphasized the fact that large thrusts per unit weight rate of flow can be obtained from chemical compounds which produce large values of $\sqrt{T_c/\bar{M}}$. This parameter may therefore be considered to be a convenient factor for the evaluation of performance of given chemical propellants. In practice, operational problems, other than performance, will also have to be evaluated.

The particular chemical compound which is most useful for a given propellant application depends upon the

device which is to be built. A complete survey of propulsion units and of the chemical compounds used as driving fluids is outside of the scope of the present discussion. Instead, representative chemicals which have been used or may be useful for the more important propulsion units are listed below.

Chemicals Which May Be Used as Propellants

A. Oxidizers in Bipropellant Systems

nitric acid	nitrogen tetroxide
oxygen	chlorine trifluoride
ozone	hydrogen peroxide
fluorine	nitrogen trifluoride
fluorine oxide	bromine pentafluoride

B. Reducing Materials in Bipropellant Systems

hydrogen	gasoline
ammonia	kerosene
hydrazine (N ₂ H ₄)	aniline
hydrazine hydrate (N ₂ H ₄ ·H ₂ O)	methyl alcohol
diborane (B ₂ H ₆)	ethyl alcohol
tetraborane (B ₄ H ₁₀)	propyl alcohol
pentaborane (B ₅ H ₉)	acetylene
borazole (B ₃ N ₃ H ₆)	ethylene
borimide (B ₂ (NH ₂) ₂)	methane
aluminum borohydride (Al(BH ₄) ₃)	other hydrocarbons
disiloxane ((SiH ₃) ₂ O)	other alcohols
disilane (Si ₂ H ₆)	aldehydes
trisilane (Si ₃ H ₈)	ketones

C. Monopropellants

nitromethane	hydrogen peroxide
dinitroethane	hydrazine

D. Gas-generating Compounds

hydrazine	hydrogen peroxide
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E. Water-reactive Chemicals

aluminum borohydride (Al(BH ₄) ₃)	potassium
lithium	lithium hydride
sodium	sodium hydride

F. Fuels for Ramjets

Any suitable liquid reducing compound	carbon
carbon-metal mixtures	boron

G. Oxidizers in Solid Composite Propellants

potassium perchlorate	ammonium nitrate
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H. Fuels in Solid Composite Propellants

Polymers containing mostly carbon and hydrogen

J. Double-Base Propellants

Homogeneous colloidal mixtures of roughly 50 per cent nitrocellulose (containing in the neighborhood of 13 per cent N) with roughly 50 per cent nitroglycerin. In some double-base propellants the amount of nitroglycerin is reduced to about 20 per cent and such substances as dinitrotoluene, potassium nitrate, etc. are added to act as stabilizers, plasticizers, flash suppressors, coloring or darkening agents, etc.

Bipropellant mixtures consisting of a liquid oxidizer and a liquid reducing material are used extensively in rocket propulsion work. In general, satisfactory performance cannot be expected between any oxidizer listed in Group A and any reducing compound listed in Group B. A complete quantitative analysis of optimum

⁴ See, for example, WENNER, R. R., "Thermochemical Calculations," McGraw-Hill Book Co., Inc., New York, 1941, Chap. XI.

performance requires study of the thermodynamics of combustion. Practical utility depends on such factors as ease and speed of combustion, propellant density, toxicity, coolant characteristics, etc. It is, however, evident that the reducing and oxidizing compounds which have been chosen as liquid propellants generally yield combustion products of low molecular weight at high temperatures, thus assuring large thrusts per unit weight rate of flow of propellant.

A propellant is useful as a monopropellant for rocket applications if it can be made to burn with the evolution of heat and the production of low molecular weight decomposition products. Gas-generating compounds must have similar properties although it is generally desirable to have maximum production of gases at relatively low temperatures.

Water-reactive chemicals are substances which react exothermically with water with the production of large volumes of gas. They are used in such devices as the hydroduct and hypopulse.⁵

Ramjets, which do not carry their own supply of oxidizing agent, are best powered by the combustion products formed as the result of chemical reaction between a liquid reducing compound or a simple metal or nonmetal and atmospheric oxygen or nitrogen.

Composite solid propellants differ from double-base propellants by being more or less heterogeneous. Thus they consist of a nonuniform mixture of oxidizing and reducing materials. Solid double-base propellants, on the other hand, consist of homogeneously compounded materials, the discontinuities in physical and chemical properties being of colloidal dimensions.

The more important characteristics of desirable liquid propellant chemicals are summarized below. The reasons for emphasizing the listed characteristics are, in some cases, closely related to the results obtained from a study of the thermodynamics of combustion. On the other hand, some of the desirable physical characteristics follow rather obviously from handling or cooling requirements in liquid-fuel rocket engines.

A list of desirable physical and chemical characteristics of propellants for use in propulsion units, other than liquid-fuel rocket engines, can be prepared by rather obvious changes of the material which follows.

Desirable Physico-Chemical Properties of Propellants Used in Liquid-Fuel Rocket Engines

- (1) Small negative or preferably positive standard heats of formation of the reactants.
- (2) The reaction products should have low molecular weights and large negative heats of formation. If conditions (1) and (2) are met, then the reaction products will consist of low molecular weight compounds at high temperatures, thus assuring good performance.
- (3) The propellants should have large densities in order to minimize the dead weight of storage tanks.
- (4) The oxidizers and reducing agents are best handled as liquids. Hence it is desirable to obtain propellants which

⁵ The reader interested in a more complete discussion of jet engine design is referred to ref. (3) and also to the book "Principles of Jet Propulsion and Gas Turbines," by M. J. Zucrow, John Wiley & Sons, Inc., New York, 1948.

are normally liquid in the operating temperature range of service units (*i. e.*, from about -40 to $+60^{\circ}\text{C}$.). For substances such as liquid oxygen and hydrogen special cooling units must be provided. This refrigerating equipment represents added dead weight which the propulsion unit must carry and is warranted only in the case of very high energy propellant mixtures.

- (5) In normal propellant operation the combustion chamber temperatures may get excessively high. Hence it is necessary to provide special cooling equipment for the chamber walls. Cooling may be accomplished by forced convection involving passage of oxidizer and/or reducing agent through coils enveloping the chamber. In extreme cases this cooling technique is inadequate and it is necessary to resort to sweat cooling which is accomplished by passing a small amount of one or both of the propellants through small passages in the chamber wall, thus using the heat of vaporization as well as the specific heat of the oxidizer and/or reducing agent in order to cool the chamber wall. It is apparent that successful cooling can be accomplished the more readily the higher the specific heat and/or the heat of vaporization of the material involved. Hence it is customary to choose, if possible, at least one of the components of a bipropellant system with a high specific heat and/or large heat of vaporization.
- (6) Since it may be necessary to store the propellants for long periods of time before use, good propellants should have high storage stability, *i. e.*, they must not decompose or change chemically in any way during storage so that their use as a propellant is impaired.
- (7) Since propellants are chemicals which have to be handled by service personnel it may be desirable for some applications to use propellants of relatively low toxicity. Actually the art of propellant design has advanced at the present time to the point where practically every useful bipropellant component is toxic or represents a handling hazard for other reasons. As the result of this development it has become important to educate service personnel on the proper handling of dangerous chemicals.
- (8) For large-scale use it is, of course, imperative that propellants which are readily available and preferably also of low cost are employed. In practice this last requirement is inessential since experience has shown that rare and expensive chemicals which are needed in large quantities usually become cheap and readily available in the course of time.
- (9) The bipropellant mixture in a liquid-fuel rocket should be spontaneously combustible with minimum time lag. Spontaneously combustible propellants are said to be *hypergolic* whereas nonspontaneous⁶ propellants are said to be *nonhypergolic*. The time lag or ignition delay is the period of time preceding steady-state combustion. It is measured empirically and is a function of physical factors such as injection methods, motor configuration, etc., as well as of the chemical constitution of the propellant mixture. Long ignition delays may lead to the accumulation of large amounts of propellant in the combustion chamber before vigorous exothermic reaction occurs and initiates steady-state combustion. The accumulation of excessive amounts of propellant, before steady-state combustion occurs, is usually accompanied by severe initial shock and very high initial pressures which may lead to rupture of the combustion chamber.
- (10) The reaction products should not be excessively corrosive or form solid deposits thereby leading either to increased or decreased nozzle throat diameters. In the former case steady-state combustion may cease altogether or else occur at such low pressures as to impair over-all performance. Nozzle plugging, on the other hand, may lead to an excessive increase in chamber pressure followed by rupture of the combustion chamber.
- (11) For application to guided missiles the exhaust gases should not interfere with the guidance method which is being used.

⁶ Abbreviation for "nonspontaneously combustible."