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PROPERTY REQUIREMENTS FOR LIQUID ROCKET PROPELLANTS

by

E. M. GOODGER

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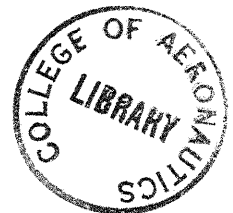
Property requirements for liquid rocket propellants

- by -

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SUMMARY

An analysis is made of the properties necessary for liquid
rocket propellants to give effective performance with acceptable
handling. Typical propellants are examined against this requirement
background, and their relative suitability assessed.

CONTENTS

1. Introduction

In the literature, there is a tendency to deal individually with rocket propellants, and to list their properties in the manner of a catalogue. This presentation is necessary eventually, when final details have to be settled after a choice of propellants has been made, but selection may be simplified by the comparison of individual properties over a range of propellant types. Furthermore, it is convenient to subdivide these properties into those which determine the performance of the rocket engine, and those which influence handling. In this Note, the following definitions are implied :-

Performance Characteristics - Factors with a major influence upon the project design and propulsive effectiveness of the rocket engine.

Handling Characteristics - Factors with a major influence upon the mechanical detail design of the rocket engine, the fuel system, the vehicle, and ground-handling equipment, and on the economics of supply.

In general terms, performance is the attraction in the search for improved propellants, whereas handling imposes the problems. In many cases, it is convenient to take liquid oxygen and a conventional hydrocarbon fuel of the kerosine type for reference purposes, so that the extent of improvements may be assessed quantitatively.

This Note has been prepared with the following objectives :-

i To compare the performance characteristics of typical liquid rocket propellants.

ii To compare the handling characteristics of these propellants.

iii To assess the overall suitability by examining the propellants individually.

2. Performance Characteristics

2.1. Reaction Energy

Since most propulsive systems are based upon a chemical reaction, a high reaction energy per unit mass of reactant is the first essential. Generally, the process is one of oxidation, although alternative reactions such as fluorination are both possible and desirable.

The gravimetric heat quantities released by the oxidation of a number of elements are charted in Fig. 1, and hydrogen is seen to have far and away the highest heating value, at 28,700 CHU/lb. Other promising

elements, in descending order of oxidation energy, are beryllium, boron, lithium, carbon, aluminium, silicon, and magnesium. Since difficulties may be encountered with the use of hydrogen alone, these alternative elements must also be considered, for use either as additives or as hydrogen carriers.

In chemistry, the reaction energy is defined as the heat <u>added</u> to the products in order to regain the standard state after a reaction with the reactants originally at the standard state. An <u>exothermic</u> reaction, therefore, is indicated by a <u>negative</u> sign. The reaction energy requirement may thus be written as max.neg. ΔH_r^o, where the superscript ^{o} represents the standard state of 25^oC. and 1 atmosphere. Reaction energy may be expressed in terms of the heats of formation of the reactants and of the resulting products :-

$$\Delta H_r^o = \Sigma \Delta H_f^o \text{ Products } - \Sigma \Delta H_f^o \text{ Reactants.}$$

It follows that max. neg. ΔH_r^o calls for products of max.neg. ΔH_f^o and reactants of max. pos. ΔH_f^o.

The heat of formation is derived from the following processes :-

Elemental Molecules ――→ Gaseous Atoms ――→ Compound Molecules
(at standard state)　　　　　　　　　　　　　　(at standard state)

Atomisation Heat	Bond Energy
Endothermic	Exothermic
Positive	Negative

Thus, $\Delta H_f^o = \Sigma \Delta H_a^o - \Sigma D(X - Y)$,

where ΔH_a^o represents atomisation (or sublimation) heat required to convert the elemental molecules into gaseous atoms, and $D(X - Y)$ represents the bond energy required to dissociate an X-Y bond into gaseous atoms.

As shown in Fig. 2, the requirement of max. neg. ΔH_r^o now develops into the four requirements of min. and max. pos. $\Sigma \Delta H_a^o$ for the products and reactants respectively, and max. and min. pos. $\Sigma D(X-Y)$ for products and reactants respectively. With individual hydrocarbons, values of these quantities included in Fig. 2 and plotted in Fig. 3 begin to show the fundamental requirements of molecular structure for high reaction energy. These may be summarised as low molecular weight with numerous multi carbon-carbon bonds, yet a high hydrogen content producing large concentrations of H_2O.

With hydrocarbon fuels produced commercially from petroleum feedstock, as shown in Fig. 4, gravimetric heating value is found to fall by about 10% for a 35% rise in specific gravity from 0.7 to 0.95. The combined effects result in a rise in the volumetric heating value of about 25%. An increased content of hydrogen, therefore, reduces the specific gravity and raises the gravimetric heating value until the ultimate is reached in hydrogen itself. The specific gravity of liquid hydrogen at its boiling point of -253°C. is 0.071. In airborne considerations, mass is a vital factor, so that the gravimetric energy requirement directs fuel selection towards low specific gravity fuels, and liquid hydrogen. With high-speed vehicles operating within a gaseous atmosphere, however, aerodynamic drag imposes a minimum volume requirement. In these applications, therefore, a heavy fuel may be advantageous, and specific gravity can be increased appreciably by loading liquid fuel with finely-pulverised solid to form a slurry. This arrangement offers a practicable compromise between the attractive high density and the difficult pumpability of the solid alone.

The importance of replacing carbon as a hydrogen carrier is emphasised by the realisation that, in aviation kerosine, carbon contributes about 86% of the mass of the fuel, yet only 62% of the energy. Hydrides are formed by boron, lithium, silicon, and magnesium in addition to carbon. Hydrides of nitrogen are also worth attention since the nitrogen can be utilised as a temperature-controlling diluent. Fuels of high-energy interest, therefore, resolve themselves into the following groups :-

   i   The hydrocarbons
   ii   Liquid hydrogen
  iii Slurries of beryllium, boron, lithium, carbon, aluminium, silicon, and magnesium in a suitable high-energy carrier fluid.
   iv Hydrides of beryllium, boron, lithium, silicon, magnesium and nitrogen.

The heating values plotted against specific gravity in Fig. 5 indicate dramatically the improvements available with the non-hydrocarbon high-energy fuels. Arbitrary curves have been constructed to connect the gravimetric, and volumetric, heating values of hydrogen, boron, and their compounds. The trends with specific gravity are similar to those noted with petroleum fuels. A 60/40 mass ratio boron-kerosine slurry is included, together with ammonia, hydrazine, and a typical alcohol.

Since both gravimetric and volumetric heating values are significant for high-speed applications within a gaseous atmosphere, the product of these two heating values can be compared with that for aviation kerosine, and expressed as the 'Performance Index', i.e.

$$\text{Performance Index} = \frac{\text{CHU/lb} \times \text{CHU/gallon}}{K}$$

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where K for aviation kerosine (AVTUR) is 840 x 10^{6} approximately in consistent units. Fig. 6 shows values of performance index plotted against specific gravity. Arbitrary curves have been constructed to connect the hydrogen-carbon and hydrogen-boron compounds. A more representative fuel for reference purposes might be RP-1, which is a pure, light-cut kerosine of low aromatic content, prepared especially for rocket applications. However, its properties are not far removed from Avtur, and its performance index is approximately 1.02.

2.2. Specific Impulse

Combustion in the absence of diluent gases results in temperatures of 3000°C. or more, compared with about 2000°C. met in most air-breathing engines. The thermodynamic behaviour of the product gases in their passage through the propelling nozzle (Fig. 7) now becomes significant, and the performance of the propellants cannot be assessed upon the reaction energy alone. An overall assessment becomes possible by applying the Bernouilli expression to the gas flow through the nozzle, and calculating the exit velocity, V_e. This leads to an expression for the specific impulse, I_{sp}, which is the thrust produced with unit mass consumption rate of propellants (see Appendix).

$$I_{sp} = \frac{1}{32.174} \sqrt{\frac{2\gamma}{\gamma-1} \frac{G\,T_c}{M} \left[1 - (p_e/p_c)^{\frac{\gamma-1}{\gamma}}\right]}$$

where p_e = nozzle exit pressure (= atmospheric pressure under optimum conditions).

p_c = combustion chamber pressure.

γ = ratio of specific heats for propelling gases

T_c = temperature of combustion chamber gases

M = mean molecular weight of propelling gases

The requirements for high specific impulse may now be written as follows :-

i Min. p_e/p_c (see Fig.8) For a given p_e, this represents a max. p_c, which is a function mainly of nozzle throat area and of propellant consumption rate.

ii Min. γ (see Fig.9) The value of γ is minimised by increasing the concentration of monatomic molecules in the propelling gases, and is thus a propellant function.

iii   Max. T_c
(see Fig. 9)
  Generally, the level of combustion temperature
follows that of the heating value, as shown in Fig. 1.
Some discrepancies occur, however, (e.g. Ti) due to
the relative values of specific heat of the resulting
products. The hydrocarbons show a striking example
of this (Fig. 10) where an increased heating value
is seen to result in a reduced T_c due to the influence
of the greater quantity of water vapour produced.
Hence T_c is a propellant function.

iv   Min. M
(see Fig. 9)
  This requires large concentrations of light products
(e.g. water vapour), and is therefore a propellant
function.

Mixture ratio is an additional variable which produces a change
in a derived parameter from a combination of changes in individual
parameters. Figs. 11A and B show mixture ratio curves for two typical
propellant pairs. Generally, although the maximum non-dissociated
temperature occurs at the stoichiometric ratio, the influence of
dissociation, together with the relative values of product heat
capacities, is such that the maximum dissociated temperature lies on
the fuel-rich side of stoichiometric. With fuels of high hydrogen
content, therefore, producing large concentrations of water vapour,
the reducing value of M with fuel enrichment brings the specific impulse
peak further over on the fuel-rich side. With these fuels, also, the
low specific gravity compared with most oxidants tends to move the peak
of the volume impulse curve back towards stoichiometric.

From the data presently available, a general direct relationship
is found to exist between peak specific impulse and CHU/lb propellant
mixture. This relationship is reflected in the fall in peak specific
impulse with increased specific gravity, shown in Fig. 12. Because
of the inclusion of specific gravity in the impulse term, a plot of
volume impulse shows a closer direct relationship with specific gravity,
as in Fig. 13A. The large-scale replot in Fig. 13B indicates a difference
of about 8% between shifting and frozen equilibrium values of peak
volume impulse.

Since it is difficult to predict the specific impulse from a
single characteristic property of a fuel, comparisons have been made
in the form of charts (Figs. 14 and 15) with the fuels arranged in
descending order of peak specific impulse and peak volume impulse
respectively. Arbitrary curves have been drawn to connect these
values for four different oxidants, and for fluorine. The charts
therefore also indicate the effectiveness of oxidants, and show that
maximum specific impulse is produced with hydrogen and fluorine as
a propellant pair, and maximum volume impulse with hydrazine and
fluorine.

2.3. Combustion Characteristics

Since liquid propellants are invariably sprayed into the combustion chamber, properties which provide for fine atomisation and rapid vaporisation are necessary for a compact flame and a short chamber length. These properties may be listed as follows :-

i. Spray Formation

Specific Gravity - Slight, direct, effect on droplet penetration.

Viscosity   - Direct effect on both droplet diameter and penetration.

Surface Tension - Direct effect on droplet diameter and penetration.

ii Spray Vaporisation

Volatility   - Direct effect on vaporisation rate

Thermal Conductivity - Direct effect on vaporisation rate.

Specific Heat - Inverse effect on vaporisation rate.

The required fuel properties, therefore, are a low viscosity, surface tension, and specific heat, and a high volatility and thermal conductivity.

Once flame has been initiated, and the supply of propellant vapour assured, the length of the combustion chamber can be minimised by means of a high flame speed. Flame speeds of the hydrocarbons lie at a very low level, ranging from about 2 to 4 ft/sec. when burning in air at atmospheric pressure, about ten times this when burned in oxygen, and increased further when burning under high pressure. The flame speeds of hydrogen, and the boron hydrides, are considerably greater than those of the hydrocarbons.

The mixture range of inflammability is normally associated with flame speed. A wide inflammable range is a valuable property where changes in propellant flow rate are likely to be encountered since flame stability is improved, and flame-out avoided. The inflammable range of hydrogen is very much wider than that of the hydrocarbons.

For extended operation, clean combustion is essential, with the absence of nozzle fouling by deposit build-up. With most fuels, this is achieved by control of mixture ratio to avoid over-enrichment of fuel. When condensation and freezing points of combustion products are high, the danger exists of liquid and solid particles forming in the propelling gas stream, and depositing on the internal surfaces of the nozzle. Deposit tendencies exist with hydrocarbons of high carbon content,

with boron fuel, and with slurries. Aluminium, with an oxide freezing temperature of about 2000°C., is particularly difficult in this respect, and Fig. 16 shows the extent of deposit accumulated in a 2 in. bore duct during a 30 second test burning a 30% aluminium-kerosine slurry in air at a low fuel/air ratio (Ref.7).

3. Handling Characteristics

3.1. Volume Impulse

Probably the foremost requirement for rocket operation within a gaseous atmosphere is a maximum volume impulse in order to minimise fuel system bulk and aerodynamic drag. Since this property is so closely dependent upon specific impulse, its discussion has been included in the Performance section. The associated controlling property, specific gravity of the propellant mixture, is seen to have a general direct relationship with volume impulse (Fig. 13) so that a high specific gravity is generally desirable for atmospheric operation.

3.2. Vapour Pressure

High-speed operation within a gaseous atmosphere leads to high bulk fuel temperatures due to kinetic heating. Thermal insulation or refrigeration may be necessary. Vapour pressure rises with temperature at an increasing rate (Fig.17) and must be either resisted by the strength of the tank structure, or relieved by tank venting. The former incurs weight penalties, whereas the latter gives rise to vapour loss, particularly at high altitude. A low vapour pressure is required, therefore, and Ref. 8 suggests a maximum limit of 20 p.s.i.a. at 230°C.

3.3. Thermal Stability

Prolonged exposure of hydrocarbon fuels to kinetic heating leads to the formation of a sediment of insoluble oxidation products which tend to filter blockage. Maximum thermal stability is essential for atmospheric operation due to kinetic heating, and for spatial operation due to radiation heating. The thermal stability of hydrocarbon fuels is currently assessed in a heated filter rig, and a thermally-stable kerosine (JP 6) is specified.

3.4. Viscosity-Temperature Relationship

A minimum viscosity-temperature dependence is desirable in order to retain pumpability at low temperatures (e.g. starting conditions in arctic regions, or low-speed operation at high altitude) yet provide at high temperature a viscosity level sufficient to lubricate metering valves in the control system. The fall in viscosity with temperature rise for some rocket propellants is shown in Fig. 18.

3.5. Heat Capacity

A high specific heat, together with a high latent heat of vaporisation, permit smaller heat transfer surfaces and lower flow rates of coolant. Some values of specific and latent heats are included in Table 1.

3.6. Combustion Characteristics

Fuels burning with high luminosity, caused by glowing particles in the flame, are liable to form smoke, and to promote metal fatigue due to radiant heat transfer to the combustor walls. The aromatics fall into this category. One valuable property which helps to ensure ignition, flame stability, and relight at altitude, is the spontaneous ignitibility of the propellants on contact in the liquid phase. This phenomenon is termed 'hypergolic' ignition, and is exhibited by hydrazine and HTP, aniline and nitric acid, and some other propellant pairs. It simplifies the detail design of the rocket engine by the elimination of electrical ignition equipment, but inevitably, increases the risk of fire in handling. A valuable development is the system of 'thermal' ignition, in which HTP is decomposed catalytically in the combustion chamber, the decomposition temperature being sufficient to ingite kerosine spontaneously. This preserves the convenience of spontaneous ignition within the chamber, without the increased fire danger outside it.

3.7. Uniformity, Availability, Cost

Greater constancy of purity and quality permits smaller tolerances in design and hence saves weight. Specification limits ensure uniformity of product quality, but limits can be set only as uniformity of supplies, control of processes, and reproducibility of test techniques permit. Cost of the finished product depends upon availability of supplies, and complexity of processing. Beryllium, for example, is in such small supply that its consumption as a rocket propellant is impracticable. Boron, on the other hand, exists in nature mainly in the oxide form as a borate. Since this is also the resultant combustion product, reaction energy must be supplied during processing in order to produce elemental boron, and this adds to the cost.

3.8. Storage, Transfer, Transport

For ease of handling, propellants should exist in the liquid phase at normal temperatures. Gases require either pressurised containers which are bulky and heavy, or cryogenic equipment which tends to be expensive and fragile. Solids provide maximum density, but are difficult to pump. Propellants should be inert and stable, with no physiological hazards or corrosive tendencies. Stability at extremes of temperature is required, with maximum fire safety. These requirements dictate a boiling point well above ambient, and a freezing point well below, compatibility with a wide range of structural materials, a high flash point, a high spontaneous-ignition temperature, and a high cracking (decomposition) temperature. Some of these properties are plotted for petroleum fuels in Fig. 19. Acetylene, with a high heating value/lb.,

is rejected due to its detonability when pressurised.

4. Overall Suitability

4.1. Hydrocarbons

Petroleum fuels offer the immediate attractions of high
availability and relatively low cost, coupled with reasonable perform-
ance and an extensive backlog of handling experience (Ref.8). Aviation
kerosine and RP-1 represent the optimum types of rocket fuel within
the commercial product range, but certain individual hydrocarbons,
although of reduced availability, offer overall improvements.
Conclusions drawn from such an overall assessment (Ref.9) suggest
that the polycyclic naphthenic type hydrocarbons provide the best
compromise of high hydrogen content, high density, low vapour pressure,
good thermal stability, and good low temperature characteristics. The
materials examined include decalin, phenanthrene, fluoranthene, and
isopropyl bicyclohexyl. The supply situation would be eased by
specifying petroleum fuels rich in polycyclic naphthenes rather than
the pure hydrocarbons alone.

4.2. Liquid Hydrogen

Hydrogen is seen to exhibit the ultimate in gravimetric heat
content and, since it realises a fairly high combustion temperature
with products of low molecular weight, it also produces a maximum
specific impulse. With its attractive combustion characteristics of
high flame speed, wide mixture range of inflammability, and clean
burning, hydrogen represents the optimum in performance.

On the handling side, the very low density of hydrogen renders
the liquid phase essential for aircraft use, and the low density of
liquid hydrogen completely eliminates the superiority in impulse
when expressed on a volume basis. The low boiling point of liquid
hydrogen incurs problems of vapour pressure and of material suitability.
The vapour loss when stored in a double-walled vacuum container is of
the order of 4% per day. Shielding with a layer of liquid nitrogen
(b.p. -196°C.) can reduce this to 0.017% per day. The latter type of
vessel is comparatively fragile, and will not withstand pressure
differences in excess of about 20 p.s.i. For storage in aircraft,
attention is turning more towards the 'polar vacuum' technique, where
the vacuum chamber is filled with a powdered mixture of aluminium with
silica, 'Perlite', or other solid. This reduces the radiation heat
loss, which is proportional to the fourth power of the temperature
difference, but increases slightly the conduction heat loss. When
paired with liquid oxygen, the oxidant might be used to replace
liquid nitrogen for shielding purposes to give a compact, but highly
inflammable, installation.

Most ferrous alloys and many other metals undergo recrystal-
lisation and become embrittled between ambient temperature and
-253°C., although their tensile strength may increase. Metals which
are considered suitable for use with liquid hydrogen are copper,
18-8 stainless steel, inconel, and monel. Natural rubber is useless
at these low temperatures, but p.t.f.e. retains resistance to shock.
An interesting side effect is the solidification of oxygen if permitted
to approach the surface of liquid hydrogen. The oxygen crystals sink
in the liquid hydrogen to form a highly inflammable slurry. On
pumping, it is found that the crystals collect a charge of static
electricity, and that the sparks produced during fracture of the
crystals are capable of initiating a violent explosion.

The low viscosity of liquid hydrogen permits high pumping
efficiencies. Ball bearings have been operated successfully at high
speeds, using liquid hydrogen as the lubricant. The high specific
heat is attractive for coolant purposes, but the low boiling point
means that the fuel rapidly vaporises. Since hydrogen is the earth's
ninth most abundant element, availability is no problem, and the
production of gaseous hydrogen has developed on a wide scale.
Liquefaction demands fairly extensive equipment due to the large heat
extraction necessary. Hydrogen exists in both an ortho and a para
form, and the natural ortho-para conversion in the liquid phase
releases more than sufficient energy to boil off the converted para
hydrogen. For long-term storage, the para form is essential, and can
be achieved by catalysis.

4.3. Slurries

Inspection of Fig. 20 shows that the introduction of solid
materials into a hydrocarbon carrier fluid results in a progressive
reduction in specific impulse expressed on a fuel mass basis, and
a slight increase only in specific impulse expressed on a basis of
mixture with air. When based on air alone, the concentration of
solid is seen to be effective in increasing performance, so that
slurry fuels appear to be attractive for ramjet applications. For
rocket operation in a gaseous atmosphere, volume impulse is significant,
and calculations made with the fuel-air results from Fig. 20 show
an increase of 12.75% on volume impulse for the 80% magnesium-octene
slurry :-

Propellant	Mixture Volume Impulse Lb.sec./gallon of liquid propellant
Stoic. octene-1 & air	1,420
Stoic. 80% boron/20% octene-1 & air	1,567
Stoic. 80% aluminium/20% octene-1 & air	1,552
Stoic. 80% magnesium/20% octene-1 & air	1,601

Similar improvements would be expected with oxygen as the oxidant.

Combustion tests reported in Ref. 11 showed that magnesium-hydrocarbon slurries burned readily and efficiently without deposition even under conditions where the liquid hydrocarbon alone would not burn. Successful flight tests were also conducted with a small ramjet. Boron slurries burned less readily than petroleum-based jet fuels, and gave rise to objectionable deposits in the combustor. Aluminium slurries generally suffer from deposition troubles, unless porous-walled combustors are used.

On the handling side, the maximum mass concentration of solid is limited to about 50 or 60% from considerations of pumpability and of settlement. Research at Cranfield into the preparation and physical behaviour of a 50% mass slurry of powdered aluminium, of six micron average particle size, in aviation kerosine showed that suspension stability can be achieved by the incorporation of 0.5% mass of aluminium octoate which, on heating, increases the viscosity of the kerosine by the formation of a gel (Ref.12). Since the resulting slurry is difficult to pump or spray, a surface-active agent must also be added to act as a dispersant. One constituent of the surface-active agent dissolves in the kerosine, and the remainder attaches itself to the surface of the solid particles, so relieving the inter-facial tension, and promoting fluidity. Of the materials tested at Cranfield, polyoxyethylene sorbitol mono-oleate was found to be satisfactory when used in a mass concentration of 0.1% in the above slurry.

Abrasion of pumps and systems would be a severe problem with slurries, particularly when using boron which is second only to diamond in hardness.

4.4. Hydrides

Of the possible replacements for carbon in the hydrocarbons (i.e. carbon-hydrides), only beryllium, boron, and lithium offer a greater energy content. The heating value of beryllium hydride is some 60% higher than that of aviation kerosine, but beryllium is not a practicable fuel in view of its extreme scarcity, toxicity, and the demands of the nuclear power industry. The heating value of lithium hydride is little better than that of aviation kerosine. The boron hydrides (i.e. boranes) of interest have been shown to be diborane (B_2H_6), pentaborane (B_5H_9), and decaborane $(B_{10}H_{14})$, which exist in the gaseous, liquid, and solid phases respectively at normal temperatures. Diborane condenses at -92°C., pentaborane freezes at -46.7°C. and boils at 63°C., whereas decaborane melts at 99.4°C. Boron itself melts at about 2200°C.

Gaseous diborane ignites spontaneously in air, and is readily explosive. Its violent reaction in the presence of moisture makes handling difficult, but offers possibilities of underwater propulsion. As with many boron compounds, diborane is toxic, and has a disagreeable odour.

As a liquid fuel, pentaborane is more attractive from the handling viewpoint. It does not ignite spontaneously in air when cool, but may explode when hot. It is liable to decompose on standing, giving off hydrogen gas and forming heavier boranes which are solid but dissolve in the parent pentaborane. This decomposition is slow even in the presence of moisture, and results in boric acid. Pentaborane also is toxic. Decaborane is solid and has a lower performance, but it is less toxic and has a low vapour pressure. Most structural metals, except lead and copper, appear to be compatible with the boranes. Mild steel cannot be used for storage vessels due to embrittlement following the release of hydrogen gas.

In view of these problems, a valuable expedient is the compounding of carbon with boranes to produce carboboranes. The carbon is added in the form of alkyl groups, such as the ethyl radical. Performance suffers slightly, but alkylation creates a stabilising effect and reduces the toxicity of the combustion gases. In America, the Olin-Mathieson Chemical Corp. produces carboboranes under the designation HEF, i.e. high energy fuels, whereas the Callery Chemical Co. designation is HiCal.

In ramjet applications, fuels of a pyrophoric (spontaneously ignitible in air) nature are attractive, since their inflammable mixture range is much wider than that of hydrocarbon fuels, and they burn at lower pressures. These properties permit the use of smaller, lighter, and more reliable ramjets, capable of economic high-speed operation at very high altitudes. They may also be used as turbojet ignition fluids, and as anti-screech additives in rocket engines. The pyrophoric nature of some boron compounds, although giving rise to handling difficulties, is attractive performance-wise, and tests are proceeding with triethyl borane (TEB), as well as triethyl aluminium (TEA) and trimethyl aluminium (TMA).

Of the nitrogen hydrides, useful performance is exhibited by ammonia (NH_3), hydrazine (N_2H_4), unsymmetrical dimethyl hydrazine or UDMH ($N_2C_2H_8$), and 'Hydyne', which is a 60/40 mass mixture of UDMH and diethylenetriamine (DET). In general, nitrogen hydrides are toxic, but their combustion products are inert. They are inflammable, and form explosive mixtures with air. Ammonia has a high vapour pressure, but a high specific heat.

Hydrazine is spontaneously ignitible with nitric acid, and with HTP. Hydrazine is generally used in the hydrate form, which is equivalent to a hydrazine concentration of 64%.

4.5. Oxidants

Discussion of the properties of oxidants has received a thorough treatment in the literature but, for completeness, a brief review is included. Fluorine is considered in this category since its reaction with a fuel results in the evolution of energy. Fluorine is the most powerful 'oxidising' agent known, reacting with practically all organic and inorganic materials. It provides the highest specific impulse and, with its high specific gravity, the highest volume impulse. It has a very high vapour pressure, and its low boiling point makes necessary the insulation of storage equipment. Reaction with many metals is slow at ambient temperature, resulting in a protective film of metallic fluoride. For this reason, such metals as iron, aluminium, magnesium, copper, and brass are compatible if the temperature is controlled. Fluorine is very toxic.

Liquid oxygen also provides rapid reactions, high flame speeds, and high combustion temperatures. It, too, is a cryogenic material, with its attendant problems of vapour loss and low-temperature compatibility. Vacuum jacketing reduces vapour losses to about 0.1% per day in bulk storage, but losses from current designs of aircraft tank are of the order of 7% per hour. Thermal insulation reduces tankage costs, but the most effective insulants are also inflammable. The mixture ranges of inflammability of most fuels are widened considerably in combination with oxygen, compared with those in air, and the fire hazard is further increased since the freezing of water from the surrounding atmosphere makes for easier generation of sparks. Since the spontaneous ignition temperature of most materials is lower in oxygen than in air, liquid oxygen cannot be used as a wall coolant. Availability of oxygen is no problem, and liquefaction can be carried out in mobile plants if necessary. Liquid ozone is more attractive from the performance and density points of view, giving an increase in specific impulse of about 10%. Explosive decomposition is likely on contamination by dust or other small impurities, unless the mass concentration of ozone is reduced below 30% by dilution with oxygen. The higher volatility of oxygen results in a progressive rise in ozone concentration during storage, and this risk is not eliminated by refrigeration since ozone and oxygen then tend to separate out. Ozone is extremely toxic above a concentration of about 0.1 parts per million.

High Test Peroxide provides a useful level of performance with most fuels and is stable in storage. If protected from temperature rise and the ingress of contaminants, the decomposition loss does not exceed about 1% per annum in temperate zones, and 3% in the tropics. The decomposition temperature ranges from 450 to 996°C.

(80 to 100% concentration), and the vapour is very active, so that flushing of the system is necessary after draining. A number of materials, including silver and the permanganates, catalyse decomposition and permit the use of HTP as a monopropellant or a source of auxiliary power. Pure aluminium and stainless steel are suitable structural materials for use with HTP.

High strength ('fuming') nitric acid, which is prefixed 'red' when it contains up to 30% of dissolved oxides of nitrogen, gives a performance comparable with HTP. It is slightly hygroscopic, and its corrosivity to aluminium increases with water content. It reacts with most organic materials, and may cause fires on contact with wood or other cellulose products. Fuming nitric acid does not inflame, but will ignite spontaneously with some fuels. The low surface tension enables the liquid to creep over surfaces, and the fumes evolved are highly toxic. Aluminium, stainless steel, and high silicon irons are suitable structural materials, particularly when corrosion inhibitors are incorporated in the acid.

The nitrogen peroxides, in the form of the mixed oxides also give comparable performance. A typical mixture of 70% N_2O_4 and 30% NO appears to meet the engineering requirements of high chemical stability, good corrosion resistance, low freezing point, and reasonably low vapour pressure. With dry peroxides, carbon steel and many other structural materials are suitable, but stainless steels are necessary under wet conditions.

5. Conclusions

i. A high heat of reaction is a basic requirement for a rocket propellant pair, but this is modified by the thermodynamic behaviour of the combustion gases in the propelling nozzle. Consequently, any realistic indication of propellant performance must be based upon the resultant thrust.

ii. A high combustion temperature is necessary for high thrust, but cooling problems are intensified, and certain propellants only are suitable as coolants.

iii. A general increase in specific impulse is found with a decrease in specific gravity of the propellant mixture.

iv. Liquid hydrogen offers the ultimate in specific impulse for chemical propellants, but handling difficulties are severe.

v. Liquid fluorine is the most energetic reacting medium available for use with rocket fuels.

vi. A general increase in volume impulse is found with an increase in specific gravity of the propellant mixture.

vii. Hydrocarbon fuels still represent a practicable compromise for rocket applications.

viii. Non-carbon hydrides appear to be the next most attractive fuels for rocket applications.

ix. Slurry fuels are more suited to air-breathing propulsive units.

Some typical rocket applications of liquid bi-propellants are shown in Table 3.

6. Acknowledgements

Figs. 9 and 11 included with permission from G. P. Sutton, 'Rocket Propulsion Elements', 1956, John Wiley & Sons Inc.
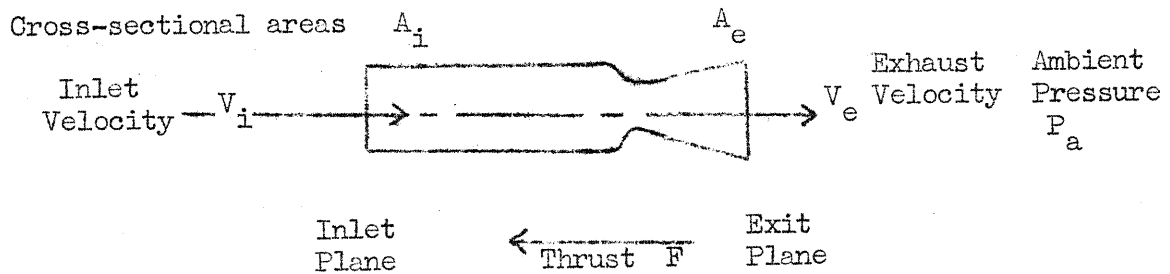
Table 3 prepared by R. W. Stutchbury, Aircraft Propulsion Department, College of Aeronautics, Cranfield.

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APPENDIX

Derivation of Specific Impulse

Cross-sectional areas A_i ... A_e. Inlet Velocity V_i. Exhaust Velocity V_e. Ambient Pressure P_a. Inlet Plane. Thrust F. Exit Plane.

The total force exerted on a duct in the direction of flight

$$= F + P_a(A_e - A_i) = \text{change of stream thrust}$$

$$= (\dot{m}_e V_e + p_e A_e) - (\dot{m}_i V_i + p_i A_i).$$

In rocket engines, V_i, A_i, and $\dot{m}_i$ are all zero, hence,

$$F = \dot{m}_e V_e + (p_e - p_a)A_e.$$

In the optimum case, the nozzle will be designed to give an exit pressure equal to ambient, and the thrust expression reduces to :-

$$F = \dot{m}_e V_e .$$

Thrust is a measure of the size and performance of the rocket engine, but a comparison of the performance of propellants is available in the thrust produced by unit consumption rate of propellant mass. This parameter is termed 'specific impulse', and represented by the symbol I_{sp}.

Hence, $I_{sp} = F/\dot{m}_e = V_e$, in consistent units.

Since it is more convenient to deal with thrust in units of pounds force, and with propellant mass in units of pounds, this expression may be written in terms of the British mixed (Engineers') unit system, as follows :-

$$I_{sp} = \frac{F \ (Lb)}{\dot{m}_e \ (lb/sec)} , \quad \text{by definition.}$$

Therefore, $\quad I_{sp} = \dfrac{F\ (pdl)}{32.174\ \dot{m}_e\ (lb/sec)}$, in consistent British absolute units,

and also, $\quad I_{sp} = \dfrac{F\ (Lb)}{32.174\ \dot{m}_e\ (slug/sec)}$, in consistent Perry units,

$$= \dfrac{V_e}{32.174}\ , \quad \text{where } 32.174 \text{ is the conversion factor}$$

between the various systems of units.

V_e can be determined by applying the Bernouilli expression to the inlet and exit planes of the propelling nozzle :-

$$\tfrac{1}{2} V_c^2 + C_p\, T_c = \tfrac{1}{2} V_e^2 + C_p\, T_e\ , \text{ for isentropic conditions}$$

where subscripts c and e represent combustion chamber (nozzle inlet) and nozzle exit planes respectively. Since V_c is nominally equal to zero, this expression may be rearranged to :-

$$V_e = \sqrt{2\, C_p\, T_c - 2\, C_p\, T_e}$$

In an ideal gas, C_p is constant, hence :-

$$V_e = \sqrt{2\, C_p\, T_c\, (1 - T_e/T_c)}.$$

This may be developed from thermodynamics as follows :-

$$V_e = \sqrt{\dfrac{2\,\gamma}{\gamma - 1}\ RT_c \left[1 - (p_e/p_c)^{\frac{\gamma-1}{\gamma}}\right]}$$

$$= \sqrt{\dfrac{2\,\gamma}{\gamma - 1}\ \dfrac{GT_c}{M} \left[1 - (p_e/p_c)^{\frac{\gamma-1}{\gamma}}\right]}$$

where M is the mean molecular weight of the product gases.

This expression is sometimes written as $V_e = \Theta\ \sqrt{GT_c/M}$, since the term comprising Θ appears in a number of other performance parameters. Hence,

$$I_{sp} = \dfrac{\Theta}{32.174}\ \sqrt{\dfrac{GT_c}{M}}$$

For simplicity, the chemical composition of the combustion gases may be assumed to remain constant throughout the expansion in the propelling nozzle. Specific impulse calculated under these 'frozen equilibrium' conditions is slightly less (approximately 8%) than that obtained in the 'shifting equilibrium' case which includes the heat released by recombination of the free atoms and radicals due to the falling temperature.

For operation within a gaseous atmosphere, where aerodynamic drag is significant, specific impulse may be based upon propellant liquid volume, in the same way as heating value. This is expressed as the product of I_{sp} and density, and is termed the volume impulse (or density impulse).

In the ramjet engine, designed for operation within the earth's atmosphere, fuel effectiveness may be expressed in terms of the air specific impulse, which is the thrust produced with unit mass consumption rate of air. This parameter also indicates the size of engine necessary for a given thrust level.

TABLE 1. REPRESENTATIVE PROPERTIES OF LIQUID ROCKET PROPELLANTS

PROPERTY / MATERIAL	HYDROCARBONS				LH_2	60/40 BORON AVTUR SLURRY	HYDRIDES					OXIDANTS			
	AVTUR	RP-1	POLY CYCLIC NAPHTHENES	ETHANOL			B_2H_6	B_5H_9	NH_3	N_2H_4	UDMH	LF_2	LO_2	HTP	HNO_3
LOWER HEATING VALUE CHU/lb	10,250	10,280	10,270	6,650	28,700	12,500	17,400	16,200	5,720	4,720	7,870				
CHU/gall	82,000	83,000	88,900	52,700	20,090	164,000	74,800	98,800	35,000	47,700	61,400				
PERFORMANCE INDEX	1.00	1.02	1.09	0.42	0.69	2.44	1.55	1.90	0.24	0.27	0.58				
S.G. @ 60/60°F	0.8	0.8	0.886	0.792	0.071 b.p.	1.31	0.43 b.p.	0.61	0.61	1.01	0.78	1.51	1.14 b.p.	1.35	1.56
SPEC. HEAT @ 60°F CHU/lb°C.	0.50			0.61	2.33 b.p.		0.48	0.57	1.12	0.75	0.65	0.37	0.4 b.p.	0.61	0.42
VAPORISATION HEAT CHU/lb	67			204	109		125	122	326		134	41	51	346	115
BOILING POINT °C	150/300	185/274	201/275	80	-253	150+	-93	63	-33	114	63	-188	-183	152	86
FREEZING POINT °C	-40	-40	-60	-118	-259	-40	-165	-47	-78	2	-58	-220	-220	-22	-42
FLASH POINT °C	37.8	43.3		21						52	1				
SPONTANEOUS IGN. TEMP. IN AIR @ 1 atm. °C	254			439	570				651		250				

TYPICAL

TABLE 2. RELATIVE SUITABILITY RATINGS OF LIQUID ROCKET FUELS (Derived from Ref.9)

BEST = 1   WORST = 5

	PROPERTY	HYDRO-CARBONS	LH$_2$	SLURRIES	NON-CARBON HYDRIDES	HYDRAZINE
PERFORMANCE	HEAT CONTENT	3	1	3	2	5
	I$_{sp}$ WITH LO$_2$	4	1	5	3	2
	COMBUSTION	3	1	5	4	2
HANDLING	SPECIFIC GRAVITY	3	5	1	4	2
	VAPOUR PRESSURE	1	5	2	2	4
	THERMAL STABILITY	2	1	3	4	4
	VISCOSITY – TEMPERATURE	1	5	4	2	3
	SPECIFIC HEAT	2	1	2	4	4
	UNIFORMITY	4	1	5	3	2
	AVAILABILITY & COST	1	4	2	4	3
	STORAGE, TRANSFER TRANSPORT	1	5	4	3	2
OVERALL RATING	AIR-BREATHING	2	1	4	3	4
	ROCKET	2	1	5	4	3

TABLE 3. TYPICAL LIQUID - PROPELLANT ROCKETS

VEHICLE	ENGINE	SEA-LEVEL THRUST. Lb.	FUEL	OXIDANT	REMARKS
'THOR'	ROCKETDYNE IR-79 SUSTAINER	150,000	RP-1	LO_2	I.R.B.M. (R.A.F.)
'ATLAS'	ROCKETDYNE 2-IR93 BOOST 1-IR105 SUSTAINER	165,000 60,000	RP-1 RP-1	LO_2 LO_2	I.C.B.M. (U.S. STRAT. AIR COMMAND)
De-H. PROP. 'BLUE STREAK'	ROLLS-ROYCE 2 ENGINES	ASSUMED 150,000 EACH	ASSUMED HYDROCARBON	ASSUMED LO_2	L.R.B.M.
SAUNDERS-ROE 'BLACK KNIGHT'	BRISTOL-SIDDELEY GAMMA. MK.201	16,400	KEROSINE	H.T.P.	UPPER ATMOSPHERE & RE-ENTRY
L.R.B.A. 'VERONIQUE'	L.R.B.A.	8,800	TURPENTINE *	NITRIC ACID *	UPPER ATMOSPHERE (I.G.Y.)
AEROJET-GENERAL 'AEROBEE'	AEROJET	4,000	ANILINE *	NITRIC ACID *	UPPER ATMOSPHERE
MARTIN 'VIKING'	REACTION MOTORS XIR 10	20,000	ETHANOL	LO_2	SOUNDING
'VANGUARD' STAGE 1 STAGE 2 STAGE 3	G.E.C. AEROJET	27,000 8,000(ALT) 2,300(ALT)	RP-1 U.D.M.H. SOLID	LO_2 NITRIC ACID	SATELLITE CARRIER
'NOVA' STAGE 1 STAGE 2 STAGE 3 STAGE 4 STAGE 5		4 x 1,500,000 1,500,000 80,000 40,000 6,000	RP-1 RP-1 LH_2 LH_2 STORABLE LIQUIDS	LO_2 LO_2 LO_2 LO_2	N.A.S.A. ADVANCED SPACE-LABORATORY PROJECT

* Hypergolic pairs

Turpentine (Pinene) $C_{10}H_{16}$ b.p. 155°C.   f.p. -55°C.   S.G. 0.858

Aniline $C_6H_5NH_2$ b.p. 184°C.   f.p. - 8°C.   S.G. 1.03
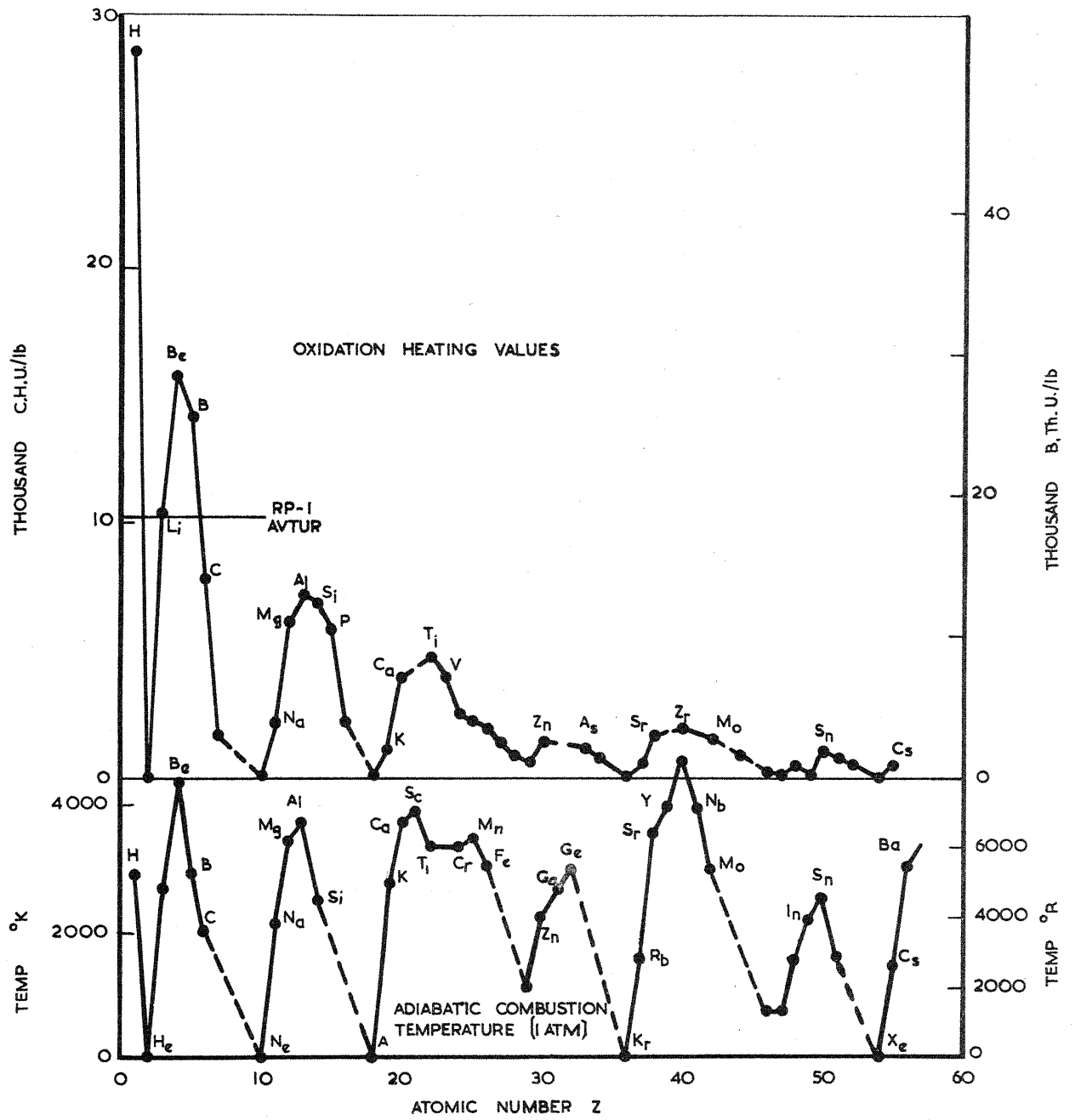
FIG. I. ELEMENTAL HEATING VALUES AND COMBUSTION TEMPERATURES (REF I)

MAX. REACTION ENERGY/UNIT MASS (ΔH_r)

Reactants at standard state $\longrightarrow$ Products at changed state

Products at changed state $+ \Delta H_r$ = Products at standard state

ΔH_r = Heat added to regain standard state after
reaction from standard state.
= negative, if reaction exothermic

ΔH_r = $\Sigma \Delta H_f$ Products $-$ $\Sigma \Delta H_f$ Reactants

Thus, Max. Neg. ΔH_r requires :-

MAX. NEG. ΔH_f PRODUCTS & MAX. POS. ΔH_f REACTANTS

ΔH_f = Heat of Formation

Element Molecules $\longrightarrow$ Gaseous Atoms $\longrightarrow$ Compounds

Atomisation Heat   Bond Energy
Endothermic   Exothermic
Positive   Negative

$\therefore$ ΔH_f = Atomisation Heat $-$ Bond Energy

= $\Sigma \Delta H_a$ $-$ $\Sigma D(X - Y)$

PRODUCTS

MAX. NEG. ΔH_f

REACTANTS

MAX. POS. ΔH_f
(or min. neg.)

MIN. POS. $\Sigma \Delta H_a$

C (11.3)

better than

H_2 (52.1)

MAX. POS. $\Sigma D(X-Y)$

H_2O (12.3)

better than

CO (8.0) or

CO_2 (8.0)

MAX. POS. $\Sigma \Delta H_a$

H_2 (52.1)

better than

C (11.3)

MIN. POS. $\Sigma D(X-Y)$

Min. (C-H) bonds

C $\equiv$ C better

than C - C

All values in kcal/gm.

FIG. 2. REACTION ENERGY DIAGRAM
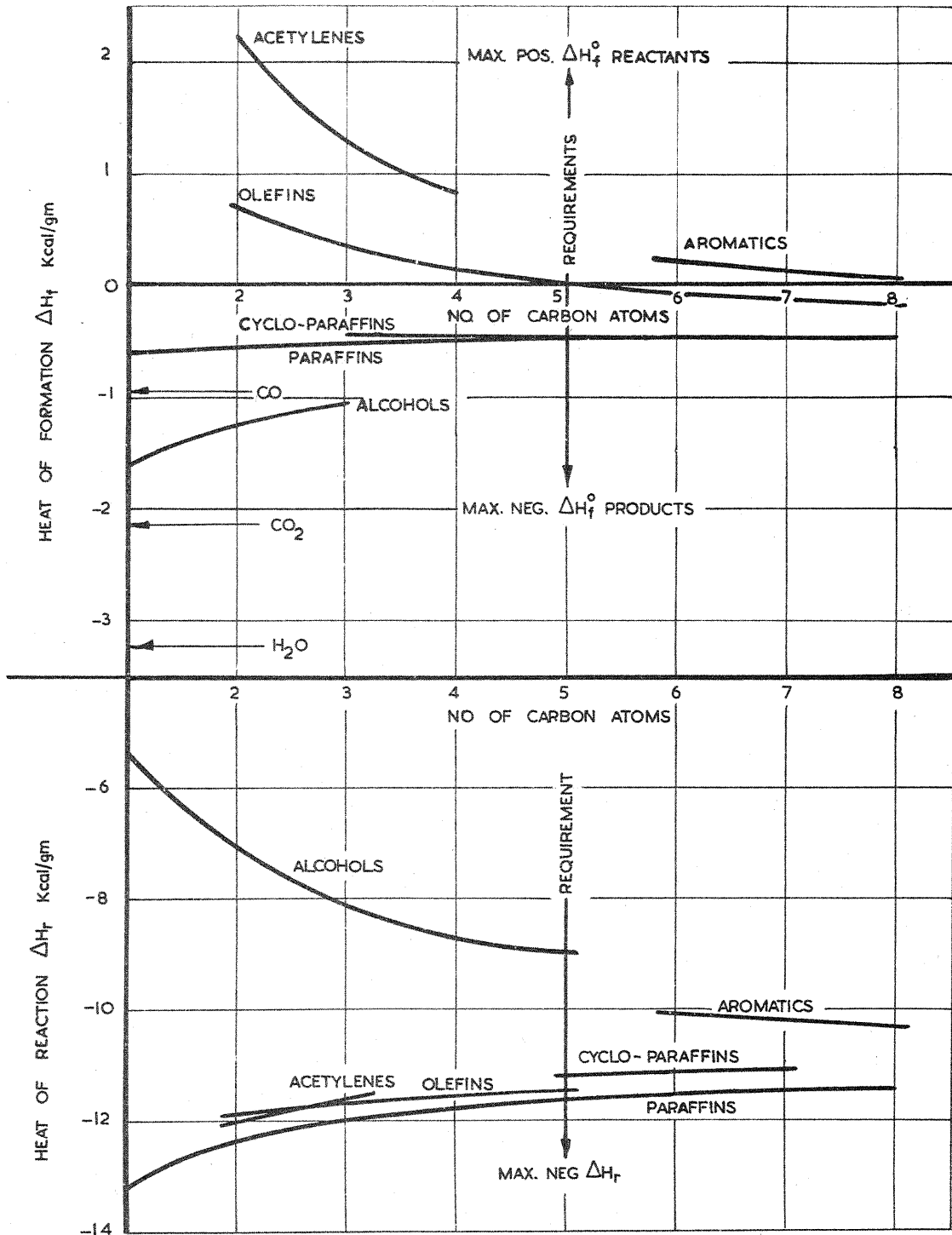
FIG. 3. HEATS OF FORMATION AND REACTION OF HYDROCARBONS

N.B. ΔH_f VALUES DERIVED FROM REF 2
ΔH_r " " " " 3

CODE	FUEL	D. Eng.R.D. N°
AVGAS	AVIATION GASOLINE	2485
AVTAG	AVIATION WIDE-CUT GASOLINE	2486
AVTUR	AVIATION KEROSINE	2482
AVCAT	AVIATION HIGH FLASH KEROSINE	2488
R.P-1	ROCKET KEROSINE	
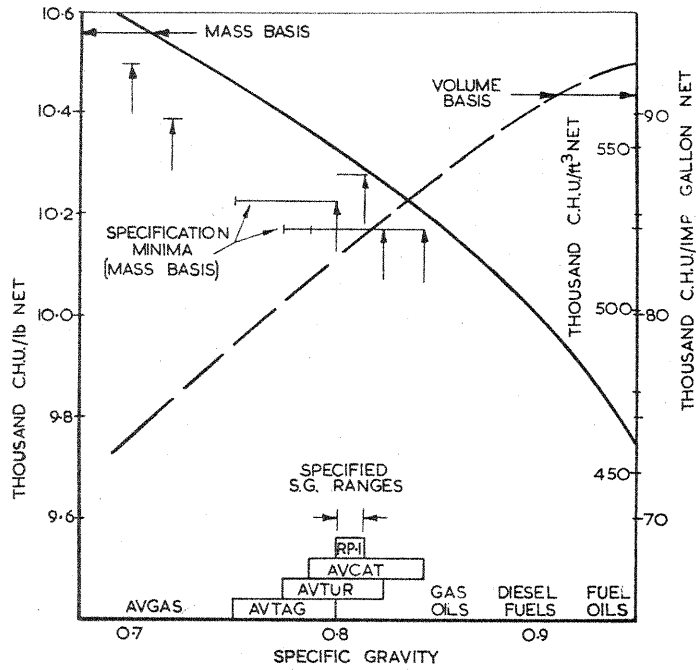
FIG. 4. TYPICAL HEATING VALUES OF PETROLEUM FUELS
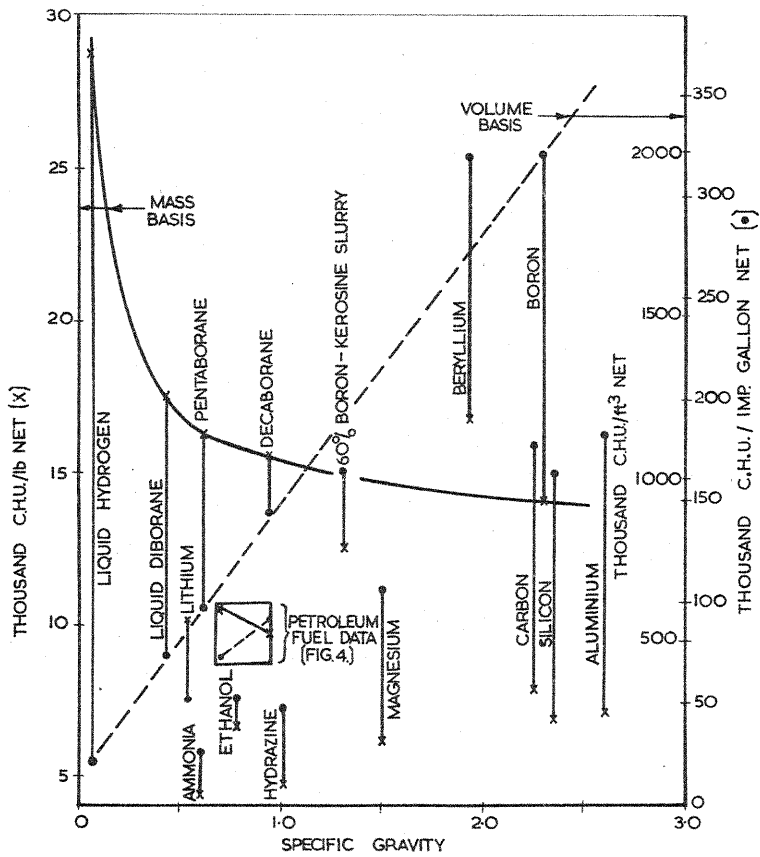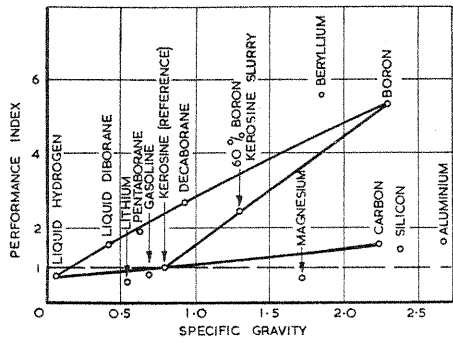

FIG. 5. HEATING VALUES OF PETROLEM AND NON-HYDROCARBON FUELS

FIG. 6. VALUES OF PERFORMANCE
INDEX

$$\theta = \sqrt{\frac{2\gamma}{\gamma-1}\left[1-\left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}\right]}$$
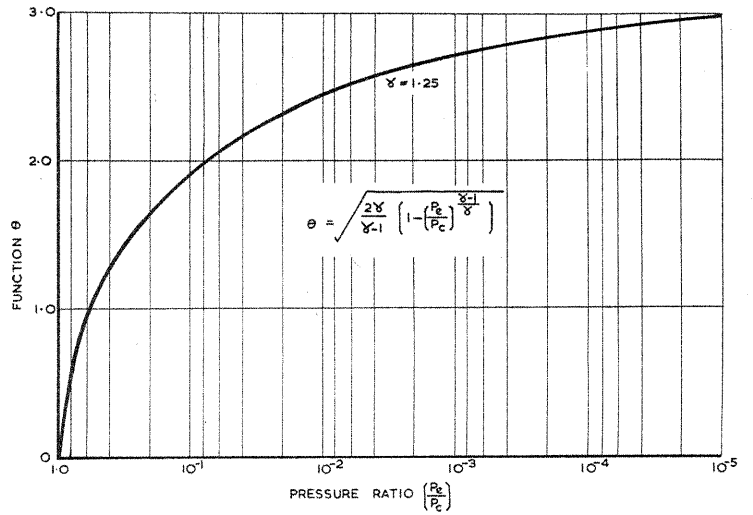
FIG. 8. INFLUENCE OF PRESSURE RATIO UPON FUNCTION θ
(SEE ALSO REF. 4.)
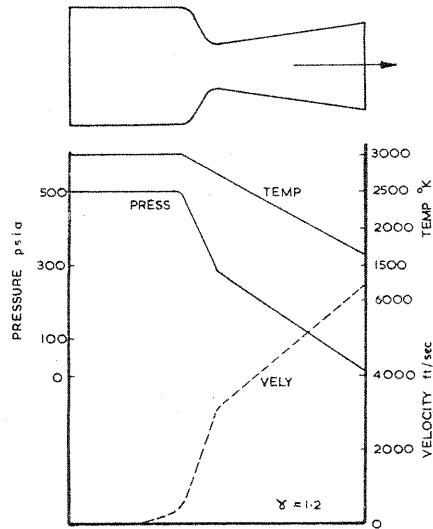
FIG. 7 TYPICAL VARIATIONS OF
T.P. & V. IN A ROCKET NOZZLE
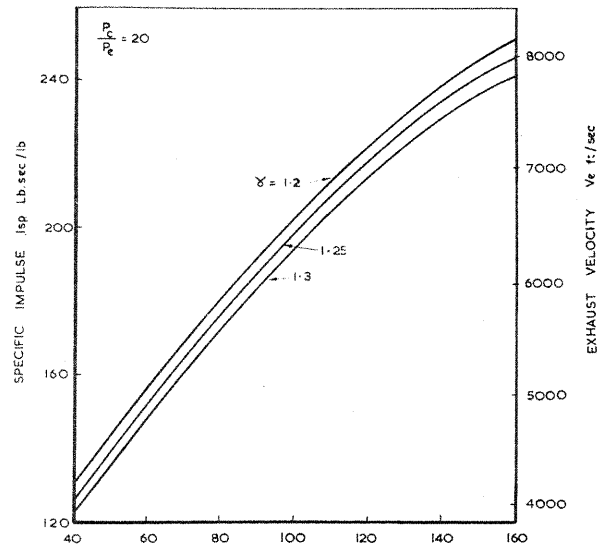
FIG 9 INFLUENCE OF $\frac{T_c}{M}$ RATIO AND γ
UPON Isp AND Ve (REF. 5. BY PERMISSION)

PARAFFINS ALCOHOLS | NAPHTHENES | OLEFINS | AROMATICS

C.H.U./lb STOIC. MIXTURE

700
680
660

C.H.U./lb STOIC. MIXTURE

C.H.U./lb FUEL

C.H.U./lb FUEL

12,000
11,000
10,000
9,000

3050
3000
2725

T_c' °C

NON DISSOCIATED TEMP T_c'

OTTO ENGINE
5/I C.R.
100°C INLET

2700
2675
2650

T_c °C

DISSOCIATED TEMP T_c

5   7   9   11

$\frac{C}{H}$ RATIO
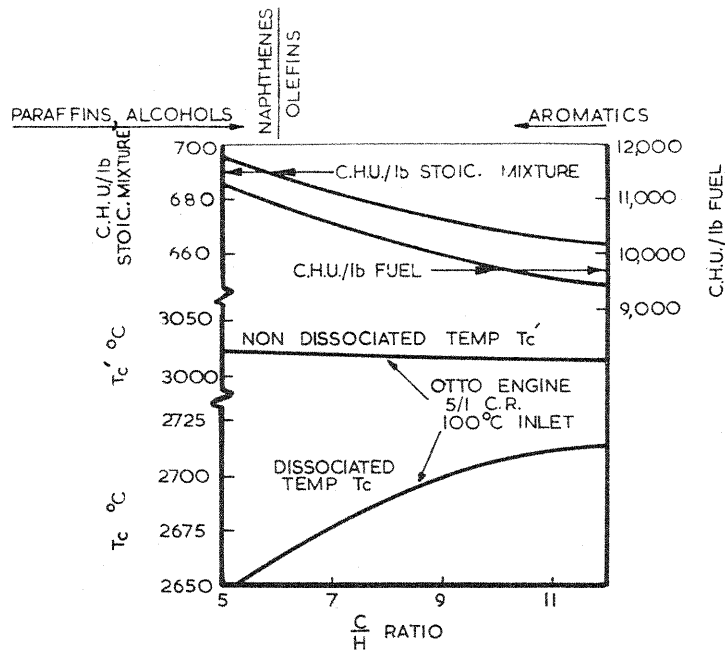
FIG. 10. VARIATION OF GRAVIMETRIC HEATING VALUES AND
COMBUSTION TEMPERATURES WITH CARBON / HYDROGEN RATIO

COMBUSTION TEMP °C

3500
3000
2500
2000

P_c = 300 p.s.i.a.

$\frac{P_c}{P_e}$ = 20.4

T_c

M

MEAN MOLECULAR WEIGHT

20
16
12
8

SPECIFIC IMPULSE Lb.sec/lb

340
320
300
280

Isp

(A) LH_2 / LO_2

STOIC.

2   4   6   8

OXIDANT / FUEL MASS RATIO

COMBUSTION TEMP °C

3500
3000
2500
2000

P_c = 20 ATM

$\frac{P_c}{P_e}$ = 20

M

T_c

MEAN MOLECULAR WEIGHT

20
16
12
8

SPECIFIC IMPULSE Lb.sec/lb

260
250
240
230

Isp

(B) HYDRAZINE/LO_2

STOIC.

0.25   0.5   0.75   1.0

OXIDANT/ FUEL MASS RATIO

FIG. 11. MIXTURE - RATIO PERFORMANCE CURVES (REF. 5. BY PERMISSION)
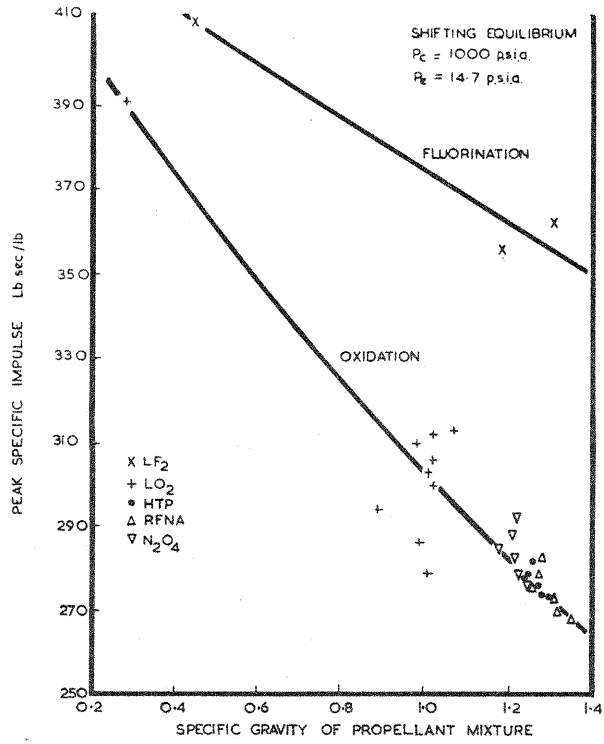
FIG. 12. RELATIONSHIP BETWEEN PEAK SPECIFIC IMPULSE AND SPECIFIC GRAVITY (DERIVED FROM REF 6)
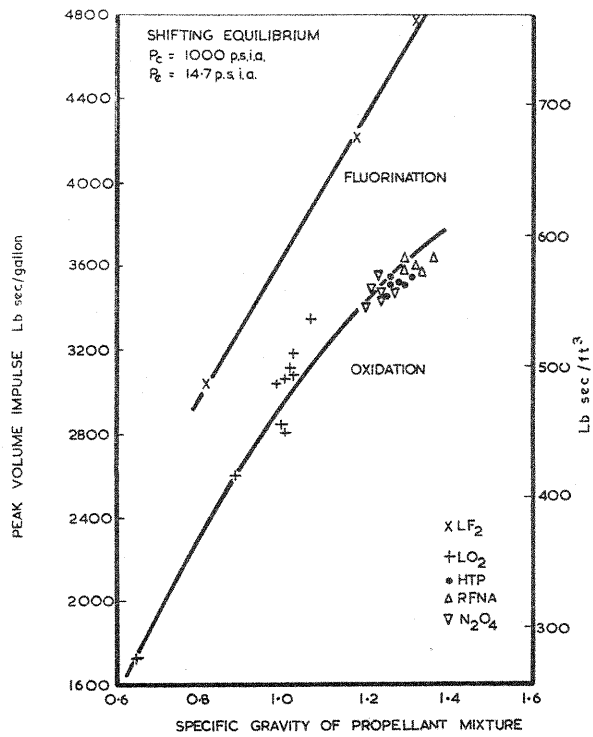
FIG. 13A. RELATIONSHIP BETWEEN PEAK VOLUME IMPULSE AND SPECIFIC GRAVITY (SMALL SCALE PLOT) (DERIVED FROM REF 6)
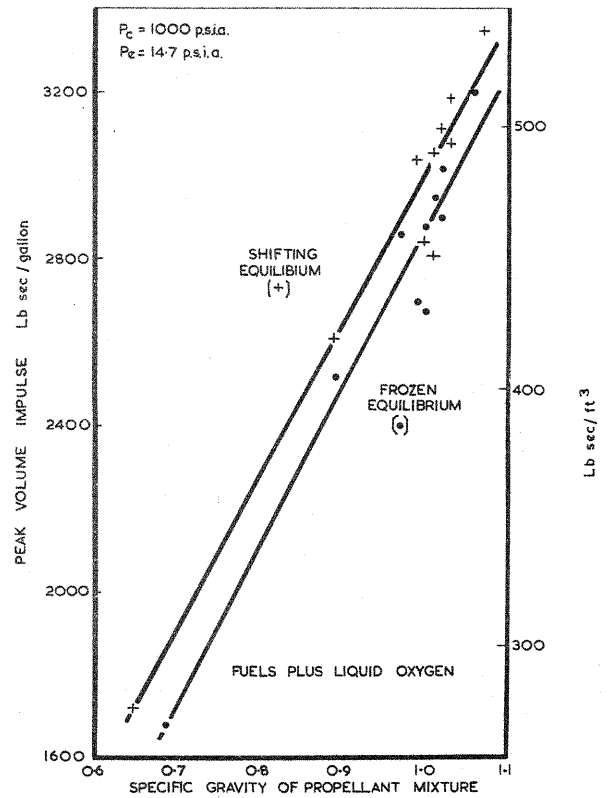
FIG 13B RELATIONSHIP BETWEEN PEAK VOLUME IMPULSE AND SPECIFIC GRAVITY (LARGE SCALE PLOT) (DERIVED FROM REF 6)

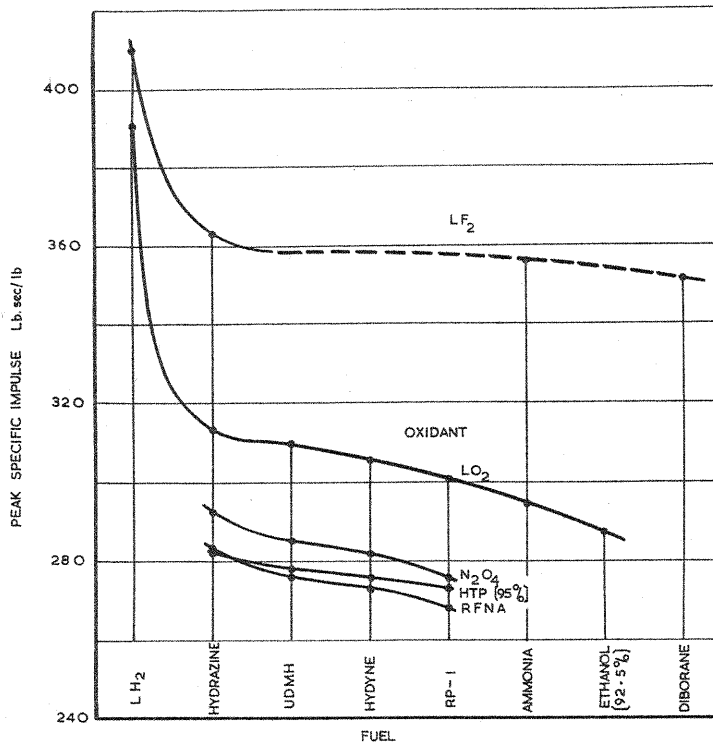FIG. 14. COMPARISON OF PEAK SPECIFIC IMPULSE VALUES FOR BI – PROPELLANTS (DERIVED FROM REF. 6)
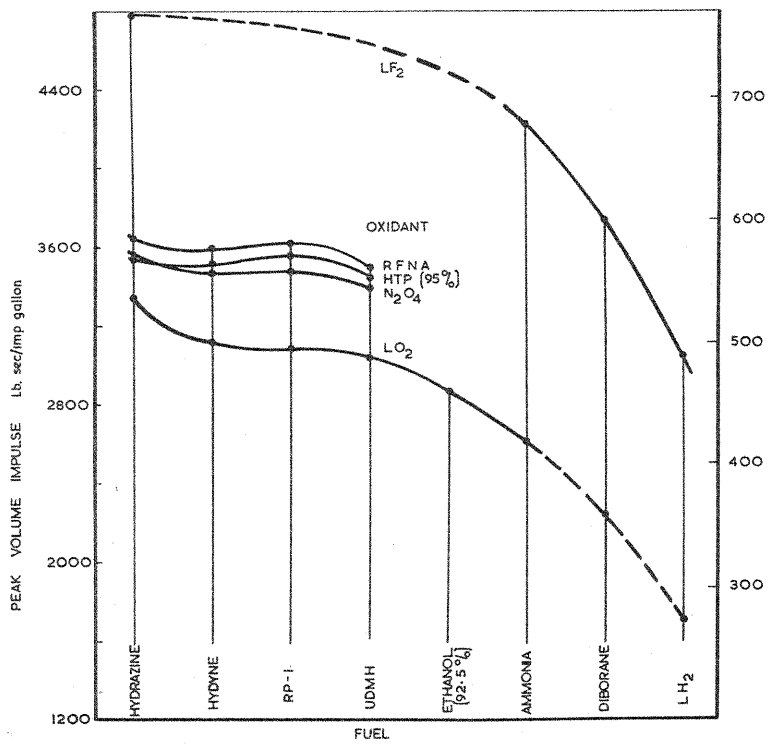

FIG. 15. COMPARISON OF PEAK VOLUME IMPULSE VALUES FOR BI–PROPELLANTS (DERIVED FROM REF. 6.)
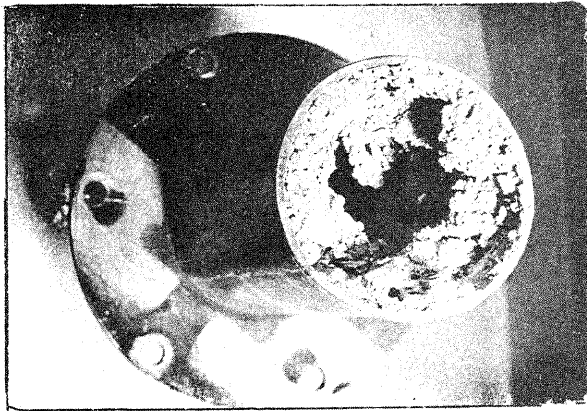
FIG.16. COMBUSTION CHAMBER DEPOSITS
WITH ALUMINIUM SLURRY FUEL (REF.7)
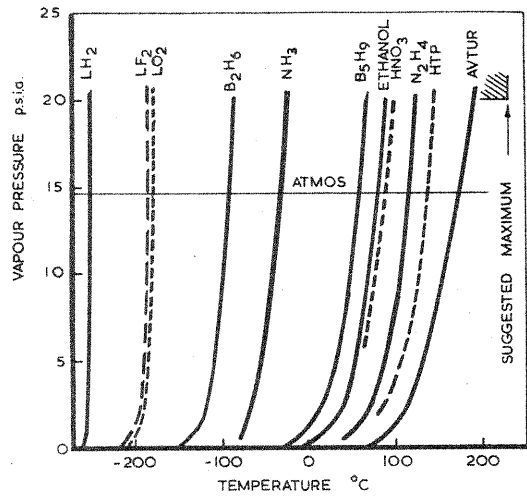
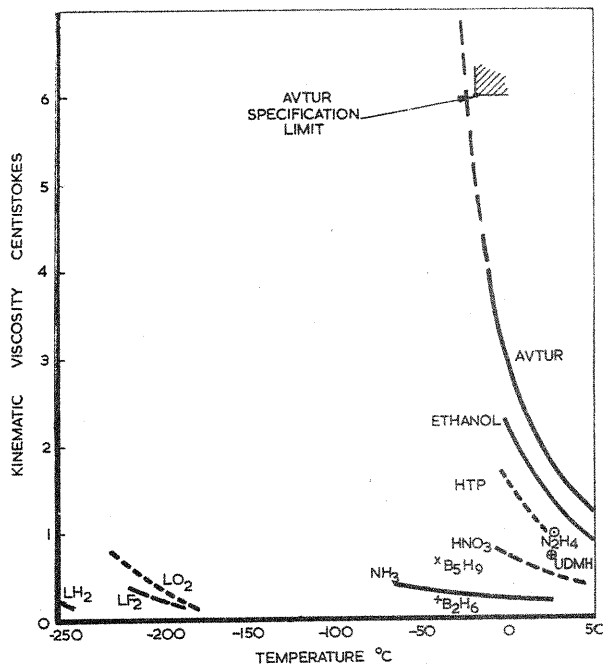FIG. 17. TEMPERATURE VARIATION OF
PROPELLANT VAPOUR PRESSURE

FIG 18 TEMPERATURE VARIATION OF
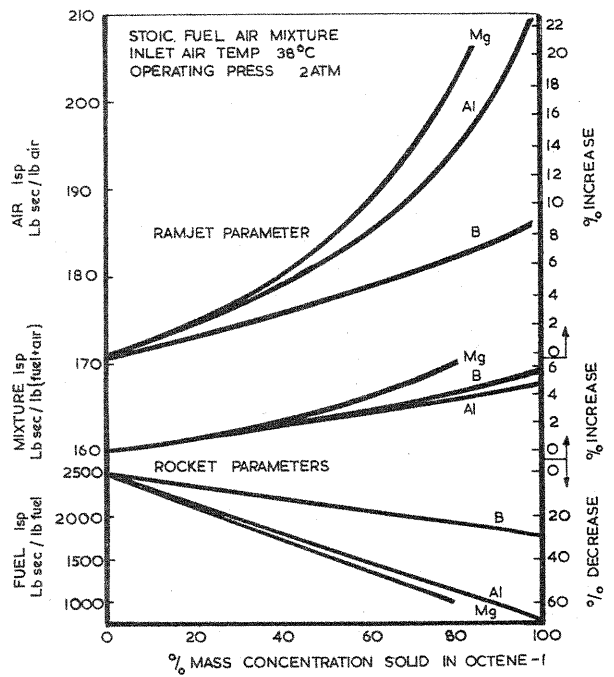PROPELLANT VISCOSITY

FIG 20 SPECIFIC IMPULSE VALUES
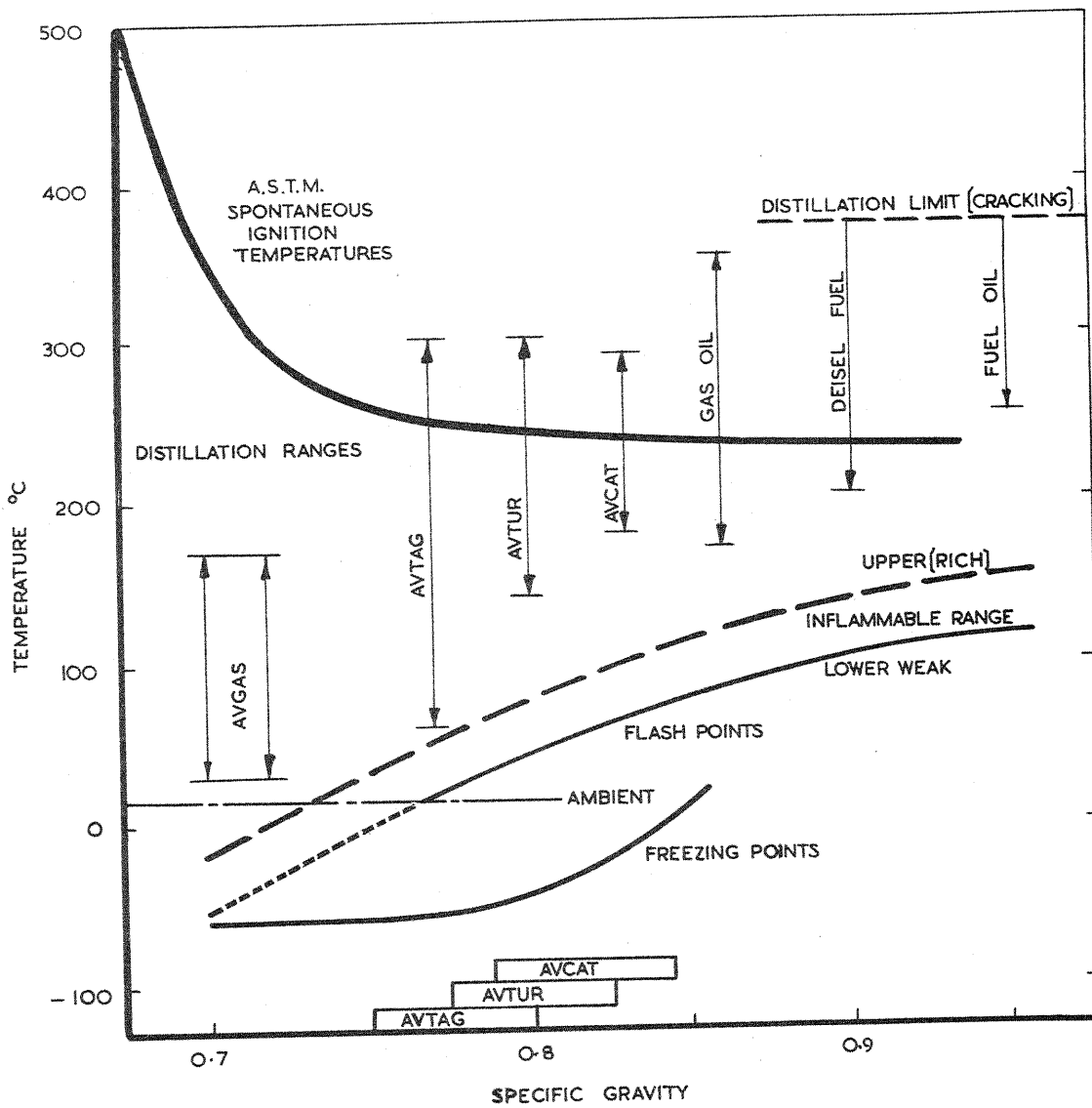FOR SLURRY FUELS (DERIVED FROM REF.6)

FIG. 19. TYPICAL VALUES SHOWING TRENDS IN
PETROLEUM FUEL PROPERTIES (REF. 8.)