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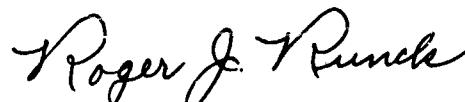
## **IGNITION OF METALS IN OXYGEN**

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**Columbus, Ohio 43201**

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IGNITION OF METALS IN OXYGEN

by

E. L. White and J. J. Ward

to

OFFICE OF THE DIRECTOR OF DEFENSE  
RESEARCH AND ENGINEERING

DEFENSE METALS INFORMATION CENTER  
Battelle Memorial Institute  
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## IGNITION OF METALS IN OXYGEN

E. L. White and J. J. Ward\*

### SUMMARY AND CONCLUSIONS

The ignition of metals in oxygen and oxygen atmospheres was reviewed from the viewpoints of (a) methods that have been used to study behavior, (b) experimental values that have been obtained, and (c) the status of theories that permit the calculation of ignition temperatures.

While no clearcut definition of ignition temperature has been developed, it appears probable that a definite or an absolute ignition temperature does exist for a particular metal-oxygen system. In general terms, if the energy input as converted to heat is greater than the heat dissipation, a temperature will be reached at which ignition of the metal will occur. Practically, this temperature appears dependent on many factors some of which are relatively static (e.g., atmosphere, composition, purity, metal surface area and condition, etc.) and others that may be dynamic (e.g., pressure, impact, impact velocity, vibration, etc.). No standard test procedures or methods have been developed to evaluate the ignition temperatures of metals. The net result is that varying values have been reported for the same or similar metal-oxygen systems.

Despite these differences, the following generalizations can be offered on the basis of the experimental evaluations performed to date:

- (1) All metals, with the possible exception of gold and platinum, can be expected to ignite in oxygen at some elevated temperature.
- (2) Alloys of several systems have been shown to ignite in oxygen systems at relatively low temperatures and some at LOX temperatures if some external source of energy input is present. Generally, the presence of a fresh metal surface is also necessary to cause ignition at these low temperatures. These ignition-sensitive alloy systems include the alloys of titanium, zirconium, thorium, uranium, lead, tin, and magnesium.
- (3) A number of secondary energy input sources have been shown to cause ignition of these sensitive alloys in oxygen systems. These sources also probably produce a fresh metal surface and are identified as follows:

#### In Gaseous Oxygen

Electric spark	Stress rupture
Puncture	Explosive shock.

#### In Liquid Oxygen

Mechanical impact	Puncture
Explosive shock.	

- (4) A number of other methods of secondary energy input and methods of exposing fresh metal do not produce ignition. These are as follows:

#### In Gaseous Oxygen

High-velocity flow	
Low-cycle fatigue cracking	
Impact on the outside of a container	
without puncture	
High-velocity flow through a small	
orifice	
Rapid pressurization	

#### In Liquid Oxygen

Impact on the outside of a container	
without puncture	
Rapid pressurization	
Machining	
Friction and galling	
Tensile rupture	
Mechanical vibration	
Sonic vibration	
Ultrasonic vibration	
High-velocity flow through an orifice.	

- (5) An increase in pressure of a gaseous oxygen system tends to promote ignition at lower temperatures or with lower secondary energy inputs. The dilution of oxygen with an inert material, gaseous or liquid, tends to reduce sensitivity of metals in oxygen systems. However, propagation is not affected much until the dilution is very great, on the order of 90 percent inert gas or liquid.

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- (6) A number of alloy systems have been shown to be relatively insensitive to ignition in an oxygen environment either at high temperatures or at low temperatures with high secondary energy inputs. These alloy systems include: austenitic stainless steels, nickel alloys, cobalt alloys, copper alloys, and silver alloys. Alloys of these systems show the best service record and also show the least sensitivity in laboratory tests.
- (7) Another group of alloys appears to be somewhat intermediate between the sensitive and insensitive groups cited in Items 2 and 6. This group includes aluminum alloys, the 400 series stainless steels, and carbon and low-alloy high-strength steels. These materials would be expected to find limited use in relatively nonsensitive applications.

A review of the theoretical analysis of the spontaneous ignition of metals in oxygen has shown the following:

- (1) A theoretical model for the spontaneous ignition of massive metal in gaseous oxygen at high temperatures (above 1500 F) has been developed, based on low-temperature oxidation-reaction data and thermophysical property data.
- (2) Several theoretical models for the calculation of ignition temperature of metal particles in gaseous oxidation have been developed that agree qualitatively. These models explain why particle radius is an important variable in powder combustion. Much of this work has been directed to the application of metal powder as a fuel.

- (3) Practically no quantitative method is available for the calculation of ignition temperatures of massive metal in cryogenic oxidizers, such as liquid oxygen. Several good qualitative descriptions of the possible mechanism for massive metal-liquid oxygen reactions have been made. For this reason, the possible role of shock loading and energy input sufficient to give local ignition temperatures has been considered and reviewed in this report.

In the development and discussion of theoretical calculational models, a number of thermochemical and thermophysical constants are required. Therefore, a literature search was made, and a compilation of data for these constants was given. The data included standard free energy of oxide formation as an extent of metal-oxygen reaction. Also, heat-capacity values, vapor-pressure data, and thermophysical properties of melting and boiling points were included. Thermal-conductivity values of metals and oxides were included when they could be found. Heats of metal-oxide formation were tabulated. These values, with heat-capacity data, were used in calculating temperature rise on reaction.

For those who may be interested in pursuing the theoretical-calculation ignition temperatures, this report also summarizes the following thermochemical and thermophysical data for most metals and their oxides:

- (a) Standard free energy of formation
- (b) Heat capacity
- (c) Vapor pressure
- (d) Melting and boiling points
- (e) Thermal conductivity.

## INTRODUCTION

The spontaneous ignition and burning of metals in oxidizing media have been recognized as a problem in the missile industry. In the past, several accidents and at least one disastrous fire have resulted from inadequate knowledge concerning the relative performance of various metals in an oxidizing atmosphere. In recognizing this problem, the Air Force requested that the Defense Metals Information Center undertake the preparation of a state-of-the-art report on the subject of metal reactions in oxidizing environments. It was further requested that this report emphasize such areas as current test methods for evaluating metal combustion, mechanisms of the metal-oxygen reaction, experimental and theoretical work that attempts to correlate basic properties of metals to predict reactivity, and a summary of the relevant test data available. This report was prepared in answer to that request.

In the pursuance of this task, two basic conditions were laid down. First, it was necessary to limit the oxidizing environments of primary concern to those of gaseous and liquid oxygen (hereafter referred to as GOX and LOX, respectively) and to other gaseous oxygen mixtures (i.e., with nitrogen, water or steam, carbon dioxide, inert gases, etc.) in which the ignition of metals has been studied. Specifically, experiences with the combustion of metals in such oxidizers as hydrogen peroxide, fluorine, chlorine trifluoride, etc., are not covered in this report. Second, it was assumed that all who are concerned with the storage and handling of LOX are familiar with the elaborate precautions that are used to prevent contamination of the LOX from all foreign objects and impurities. Hence, LOX as defined and described in this report refers only to high-purity liquid oxygen, and no effort has been made in this report to consider the possible effects of impurities in LOX on metal-ignition reactions.

In preparing this report, the authors gratefully acknowledge helpful discussions with and valuable suggestions received from Mr. W. K. Boyd, Chief of the Corrosion Research Division, and Dr. G. W. Cunningham, Chief of the Materials Thermodynamics Division at Battelle. The authors also wish to acknowledge the assistance of Mr. E. G. Bodine, Research Associate in the Fabrication Dynamics Division, who authored Appendix B.

## METHODS OF MEASURING IGNITION TEMPERATURE

### Basic Considerations

A number of experimental methods have been used to determine the ignition temperature of solid metals and alloys in oxygen gas, air, various mixtures of inert gases with oxygen, and liquid oxygen. In addition to the input of energy from

heat sources, the effects of electrical-energy input, and various types of mechanical-energy input on the ignition temperature have also been studied. The experimental procedures and equipment vary widely because the objectives of the tests were different. Generally, two types of problems have been investigated:

- (1) The determination of safety hazards, such as the ignition of dust clouds and layers of particles, and the ignition of massive metal by heating or mechanical shock
- (2) The use of metal powders as fuels in torches and rocket engines.

A wide range of ignition temperatures has been reported for the same or similar materials by these different experimental methods. Even though these wide variations in ignition temperatures do exist, many investigators maintain that the real ignition temperature is a fixed absolute value just as is the melting point or boiling point. The explanation of the variations in measured ignition temperatures is based on the concept that the heat balance of a system can greatly influence the measured temperature.

When a metal is heated in an oxidizing atmosphere, there are two sources of heat input to the system:

- (1) External heat energy, such as from a furnace, electrical resistance heating of a specimen, a hot gas, etc.
- (2) Internal heat, energy released within the system by the reaction of the oxidizer with the metal surface, as a gas-solid, a gas-liquid, or a gas-gas reaction, depending upon the temperature of the metal surface and its environment.

Simultaneously, heat is being lost from the system. These heat losses may occur as a result of several mechanisms, such as:

- (1) Radiation
- (2) Conduction
- (3) Convection
- (4) Heat of fusion of the metal or its oxide
- (5) Heat of vaporization of the metal or its oxide
- (6) Heat to cause dissociation.

The concept that variation in ignition temperatures can be explained by a heat balance is schematically illustrated in Figure 1. The solid line represents heat input to the system. The internal heat is produced at an ever-increasing rate, being a function of the temperature of the metal surface. It is also a logarithmic function of  $1/T$  (Arrhenius vs  $1/T$  relationship). At point a,

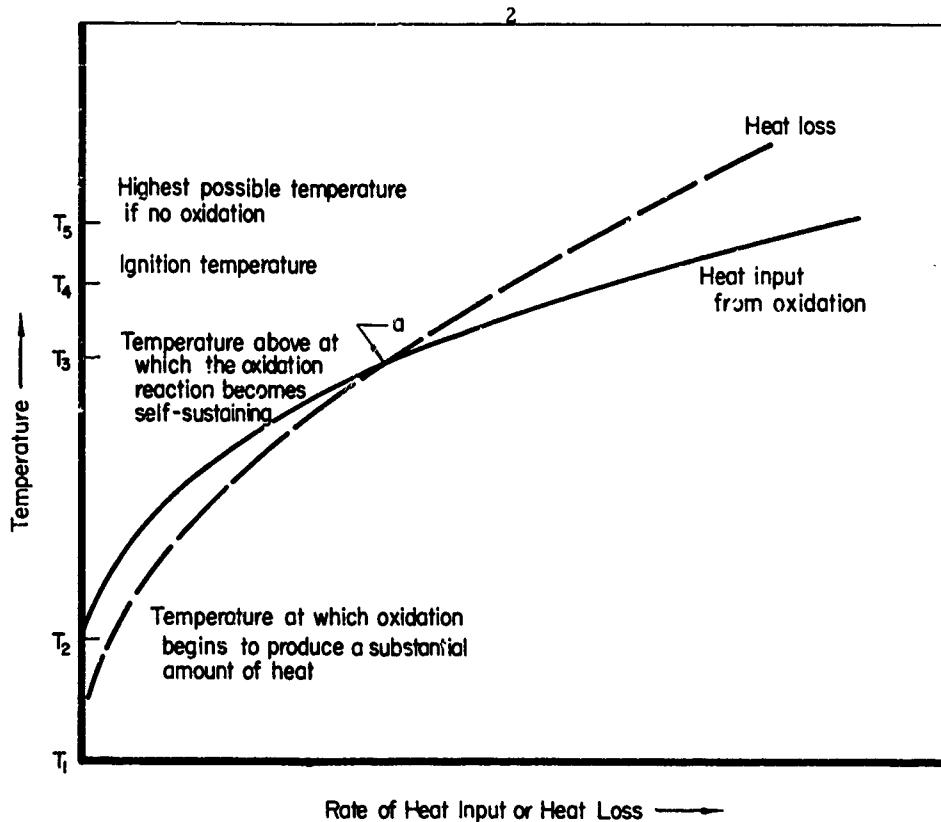


FIGURE 1. SCHEMATIC DIAGRAM OF A METAL BEING HEATED IN AN OXIDIZING ATMOSPHERE

the internal heat input is equal to the total heat loss. Therefore, the oxidation reaction will be self-sustaining, even if the external heat input is discontinued. In a sense the surface temperature at this time can be defined as the ignition temperature because ignition will certainly occur. The dependence of ignition temperature, so defined, upon the heat balance of a system is very marked. For example, the heat balance at a given point may not persist for a sufficiently long time to yield the normal manifestation of ignition (i. e., a flash of light, explosion, or sharp temperature rise). Thus, quenching after ignition must be considered. This can occur as a result of unsteady state-heat transfer conditions that may exist in any actual system. This means that if the heat losses increased rapidly, immediately after ignition, the heat-loss curve would be shifted to a point above point a and the spontaneous reaction situation would no longer exist and quenching would take place. This shift in the heat balance would be very apt to occur in a liquid-oxygen system in which the high temperature of point a is reached only in a very localized spot in the overall cold system. Another similar condition may exist in a relatively high-temperature system in which the melting point of the oxide or the metal is between the temperature associated with point a and the real ignition temperature, and a heat-balance shift would be caused by heat lost to the heat of fusion.

The concept of the control of ignition temperature by controlling the heat balance of the sys-

tem then indicates that the observed or measured ignition temperatures can be either below or above the actual ignition temperature of a material, depending on how and at what point in the system the temperature is measured. In the following paragraphs, a number of the experimental methods that have been used to determine ignition temperature will be described. The results obtained from these investigations are summarized by metal or alloy system in later succeeding sections.

#### Ignition by Heating

##### Ignition of Massive Metals by Heating

Ignition temperatures have been determined by heating a piece of metal in a crucible in an electric furnace under argon.<sup>(1)</sup> The temperature was measured with a thermocouple near the specimen. When the desired temperature was reached, the argon was flushed out with oxygen and ignition was determined visually by observing the emission of light. The following observations can be made about this experimental method:

- (1) The ignition was determined by the emission of light
- (2) The surface temperature of the specimen may have risen above the measured furnace temperature before ignition because of oxidation, but this rise was not measured

- (3) The reaction with the oxygen started in a dilute oxygen-argon mixture
- (4) The specimen and the oxygen may not have been at the same temperature, so heat may have been flowing from one to the other
- (5) The specimen could have melted before the oxygen was admitted, and thus, ignition temperatures above the metal melting point could be measured, which cannot be done by some other methods
- (6) Scaling of the metal during heating of the specimen was kept to a minimum, thus reducing the complicating factor of scale thickness, which would affect heat transfer and contact of the gas with the metal surface.

A second experimental method that has been used<sup>(2,3,4)</sup> to measure ignition temperatures consists of resistance heating of wire, or ribbon-type, specimens in a container that can be pressurized with the desired gas. The specimen temperature is measured by an optical pyrometer. The specimen either ignites or melts. The following observations can be made about this method:

- (1) The specimen is heated and ignited in an atmosphere of the desired composition, so scaling during heating can affect the ignition temperature
- (2) The specimen is continually heating the surrounding gas, which is at a lower temperature at the time of ignition, resulting in an unsteady heat-transfer condition
- (3) Ignition is determined by the emission of light
- (4) Ignition temperatures above the melting point cannot be determined because the heating is stopped at the melting point
- (5) If specimens break by rapid creep, heating will stop below the melting point.

A method similar to the one described above substitutes tubes for wires or ribbons.<sup>(4)</sup> This means the specimen temperature could be measured by thermocouples inside the specimen as well as optically from the outside. In general, the same remarks can be made about this method as the one above, except that by using two methods of temperature measurement, a better estimate of the real temperature and the heat-transfer condition can be obtained. Ignition would be indicated by both emission of light and by the sharp temperature rise.

Ignition temperatures have been determined by heating small cylinders of the metal in a tube furnace through which a slow flow of oxygen was passing. The specimen temperature was measured by a thermocouple inserted in the specimen. The oxygen was preheated in the lower part of the furnace. The ignition temperature was determined by a sharp break in the time-temperature heating curve of the specimen.<sup>(5)</sup> A second method was used in which a small metal bell was placed over the specimen and fed with argon, which protected the specimen until the desired temperature was reached. When the specimen and the surrounding oxygen attained the same temperature, the bell was removed. If the temperature went up rapidly, ignition had occurred.<sup>(5)</sup>

From the practical aspect, the investigator wishes to produce the heat-transfer conditions that are avoided when attempting to determine the real ignition temperature. An example of this is the study of ignition in high-velocity air. Wire-type specimens have been heated by electrical resistance in high-velocity air streams<sup>(2)</sup> and the ignition temperatures measured optically. In other studies, cone-shape specimens were exposed to a high-velocity stream of hot air, with the cone temperature measured by a thermocouple imbedded inside the cone near the tip.<sup>(2)</sup> The temperature of the air was raised slowly and the ignition temperature was indicated by a sharp rise in the specimen temperature.

Another method of measuring the effect of high-velocity flow was to preheat specimens to a desired temperature and quickly swing them into a high-velocity air stream.<sup>(3)</sup>

A modification of the preceding method allowed the specimen to remain for some time at a temperature below ignition temperature. This method showed that under these conditions, the temperature of the specimen would slowly rise above the temperature of its surroundings, and upon reaching a somewhat higher temperature, would ignite. This temperature was about the same as the previously determined ignition temperature.

#### Ignition Temperatures of Small Particles

The ignition temperatures of small particles have been measured by different methods. These methods generally can be divided into three groups: (1) single particles, (2) clouds of powder, and (3) layers of powder.

The ignition temperatures of single particles have been measured by dropping the particles through a furnace in which gas was slowly flowing. The gas temperature was measured by a thermocouple and ignition was determined by observation.<sup>(6,7)</sup> The sizes of particles varied widely in the different experiments from 2 to 5 microns in diameter up to 500 microns.

Single-particle ignition temperatures have also been determined by feeding particles with a small flow of nitrogen into a flame produced on a flat flame burner. Various gas-oxygen mixtures could be used to obtain the desired temperatures and flue gas-oxygen content.<sup>(8)</sup>

Dust clouds have been treated in a similar manner by dropping them through a furnace tube.<sup>(7)</sup> Another method that has been used is to lift particles through a furnace by a stream of air. This method tends to separate the particles according to size as they are fed to the equipment. In both methods, the powder must be sized first by screening or by other mechanical means. This introduces another factor, that is, the effect of different particle sizes in the same cloud.

Powder clouds have been shown to ignite in several places at nearly the same time, indicating that the heat balance is about the same at these points and somewhat different from the bulk of the cloud. Also, the particle size or the cloud density may vary at these points.

The ignition temperatures of layers of particles have been investigated. These layers are usually in some sort of container, so that only the surface is exposed. Also, the flow rate of the atmosphere is slow to prevent the formation of a cloud. In one method, the powder and gas are heated together in a tube furnace. In another, the powder is heated in one section of a furnace and the gas is preheated in another and continuously and slowly fed to the reaction area.<sup>(9)</sup> Still another method involves filling a hole in a large metal block with powder, heating the block, and passing the gas over the hole.<sup>(10)</sup> Usually the temperature is measured by a thermocouple in the powder layer. Ignition is indicated by a sharp rise in the powder temperature<sup>(9)</sup> or by visually noting the emission of light.

It has been found that the depth of a powder layer has an effect on the ignition temperature.<sup>(9)</sup> Also, heat transfer through the powder layer is greatly affected by the degree of compaction of the powder.

#### Introduction of Energy From Sources Other Than Heat

The effect on ignition of introducing energy in forms other than as heat has been studied. These experiments have been done for the most part in LOX or in gaseous oxygen, air, or oxygen-inert gas mixtures, at LOX or near room temperature. Generally, these effects have not been studied at higher temperatures, say a few hundred degrees below the ignition temperature.

The forms of energy input other than heat that have been studied are as follows:

- (1) Mechanical shock by impact of the metal surface while exposed to the test medium

- (2) Impact on the outside of a container
- (3) Effect of stress rupture of the metal
- (4) Puncture by impact
- (5) Rapid pressurization
- (6) Friction, galling, and machining
- (7) Vibration
- (8) High-velocity flow through orifices
- (9) Cyclic fatigue.

#### Mechanical Shock by Impact in the Medium

The most commonly used method is impact by dropped weight<sup>(1,11-18)</sup> The specimen, usually a small section of sheet metal, is placed in a metal cup or other container and covered with LOX, or a small container is flushed with a gaseous atmosphere. A weight is dropped that drives a striker through the medium to the test piece. Generally, one of two striker assemblies is used:

- (1) The striker rests on the plate, and when impacted, transmits the shock to the specimen
- (2) The striker may be attached to the falling weight or be suspended above the specimen and struck by the falling weight.

Strikers with various cross sections have been used, varying from large flat strikers to knife-edge and ball strikers. Thus, the contact areas have differed widely. Various size weights have been dropped from different heights. There appears to be no common denominator among the variety of combinations used. That is, such units of measure of impact energies as ft-lb, ft-lb/in.<sup>2</sup>, velocity, and other factors do not necessarily take into consideration all of the variables. For example, other factors that may be involved are: hardness of the striker, hardness of the base plate, mass of the base, container material, and configuration, specimen thickness, striker area, and shape. Ignition does not occur 100 percent of the time under most conditions and not at all under some conditions. Thus, a number of tests is required to evaluate a given type of specimen. The more or less accepted means of evaluating drop-weight data is to conduct a minimum of 20 tests. The specified impact energy is 10 Kg-M delivered by a 20-pound plummet through a 1/2-inch-diameter striker. If no reaction occurs in 20 tests, or if no more than one occurs in 60 tests, the material is not considered to be sensitive to the test conditions used. As mentioned above, there are many variables in the test conditions, so probably at least specimen thickness, striker area, and height of drop to produce the same impact could be varied to obtain a better evaluation of impact sensitivity.

#### Impact on the Outside of a Container

Energy input by impact on the outside of a container has been investigated.<sup>(16)</sup> Drop-weight tests have been used for this type of shock input

at energy levels that badly deform the metal but do not puncture it. Most materials have been found to be much less sensitive to this type of energy impact than to impact on the inside of the container.

#### Stress Rupture

The ignition of metals upon rupturing under stress in LOX and gaseous oxygen has been studied by several investigators. The equipment used in these experiments usually has been quite similar, (16, 19, 20) e.g., a small tensile-type specimen is pulled apart in a container of the desired atmosphere. The effect of atmosphere concentration, pressure, and temperature has been studied.

The effect of various strain rates and various size specimens has also been studied. The cross-sectional area at the break appears to have some effect on ignition, other factors being constant. The rupture of large cross sections appears to cause ignition under lower temperature and pressure conditions than the rupture of small cross-sectional areas. Ignition is not affected by change in strain rate from tensile impact to very low rates.

#### Impact Puncture

The effect of impact puncture has been shown to be more likely to ignite a metal than tensile rupture or simple impact in an oxygen medium. Under these conditions, impact shock, a fresh metal surface, and high-velocity flow are all present.

Puncture has been achieved by a number of different techniques. First, a thin diaphragm on any oxygen container has been punctured by driving a pin or chisel through the diaphragm. (20) Power has been derived from dropped weights or from spring-loaded strikers. Though it is not always done, the puncture probably should be made from the side or bottom in contact with the liquids.

A second method of puncturing metal-specimen diaphragms or actual tank walls is with high-velocity projectiles. These projectiles have included regular jacketed slugs or incendiary types, as well as darts and pellets fired from air guns. The effect of very small particles fired at high velocities has also been studied. These very small particles were formed from larger particles that were fired onto a heavy plate on which they shatter before puncturing the test diaphragm alongside.

The size, shape, or velocity of puncturing particles and tools appears to have very little effect on ignition. Also, the temperature of the projectile seems to have little effect. An illustration is the little differences between the effect of regular and incendiary bullets, and between projectiles fired through air and those fired through vacuum. The greatest differences occur between punctures from the inside and from the outside.

That is, a projectile fired through both sides of a tank or through a container with a diaphragm at both ends is more likely to ignite the metal on the exit side than on the entrance side. The difference between the two conditions is primarily that the impact on the exit side occurs in the active medium.

#### Rapid Pressurization

Ignition by rapid pressurization has been studied by two methods. (16, 18) Rapid pressure increases have been produced using quick opening valves between high- and low-pressure containers of either LOX or gaseous oxygen. Rapid pressurization has also been obtained by impacting a piston, which in turn compresses either LOX or gaseous oxygen against a specimen. In some experiments, the rapid pressurization was repeated in a cyclic manner for hundreds of cycles.

This type of energy input usually does not result in the ignition of metals but may cause ignition of organic materials.

#### Machining, Wear, and Galling

Ignition of metals by rubbing action has been studied in both horizontal reciprocating and rotary types of equipment. These experiments have been done in LOX only. Frictional heat is produced in all of these tests, but whether machining, wearing, or galling occurs depends on the hardness and shape of the tools. It probably can be assumed that fresh metal surfaces are produced in all cases, but to a greater extent by machining. On rotating machines, the effect of high velocities up to 220 ft/sec and contact pressures up to 2600 psi has been tested. High local temperatures have been indicated, in the range of 1000 F. Ignition of the more active metals such as titanium has occurred, but propagation does not usually occur.

#### Vibration

Experiments to determine if ignition can be produced by vibration have been conducted in several ways. (17) First, mechanical tapping of the outside of a LOX tank in a "Rotap" machine has been done. Higher vibration levels, up to 200 cycles per second or 20 G's with a double amplitude of 0.03 inch have been produced by mechanical means. LOX containers have also been exposed to vibration by sonic energy produced by rocket motors. Specimens have also been subjected to ultrasonic energy from a 400-watt 25-kc magnetostrictive transducer. In these tests, vibrational energy input has not caused ignition even of metals that can be easily ignited by other means.

#### High-Velocity Flow Through Small Orifices

Both LOX and gaseous oxygen have been forced through small orifices. (16) This has been

done by impacting an hydraulic cylinder or by pressurization. The orifices have been formed by several means; by drilling, or by using a small pinhole or small crack already in the metal. High-velocity flow through small holes and cracks has not resulted in ignition with either LOX or gaseous oxygen, even with the more sensitive metals.

#### Fatigue Tests

A few fatigue tests have been conducted in gaseous oxygen. These were in 60-psi oxygen at room temperature.<sup>(17)</sup> Though actual ignition did not occur in these tests, tarnished spots indicated that it is possible to ignite at least the active metals by fatigue failures. It is probable that ignition would not occur until the piece actually cracked completely through or at least under conditions under which the crack begins to propagate very rapidly.

#### EXPERIMENTAL VALUES OF IGNITION TEMPERATURE

The following sections of this report describe the results of tests that have been performed with a variety of conditions and methods to determine the ignition temperatures of metals in oxygen systems. Both reactions with liquid and gaseous oxygen are considered.

Most of the data generated have been for titanium and its alloys with somewhat lesser attention being given to aluminum, magnesium, and stainless steels. Correspondingly less information is available for other metals and their alloys. Also, more attention has been given to the ignition of metals in gaseous oxygen and oxygen mixtures than in liquid oxygen. To assist the reader in comparing the ignition temperatures that have been measured for all of these metals and alloys in gaseous oxygen and oxygen mixtures, Appendix A summarizes the available data.

#### Titanium Alloys

##### Ignition in Gaseous Oxygen at High Temperatures

It has been shown that titanium and its alloys will ignite in gaseous oxygen when they are heated to temperatures several hundred degrees below the metal melting point of titanium, 3034 F (1668 C). Relatively massive specimens (1/16-in. wires to 0.5-in. tubes) have been shown to ignite in the range of 2372 to 2912 F (1300 to 1600 C), when resistance heated in static oxygen atmospheres.

Effect of Oxygen Pressure. An increase in oxygen pressure above atmospheric pressure has been shown to lower the ignition point several hundred degrees C. At oxygen pressures of 300 to 500 psi, the ignition temperature is lowered to 1598 to 2012 F (870 to 1100 C).<sup>(3,4)</sup>

Effect of Dilution of Oxygen. Titanium also will ignite in air in the same temperature range as in oxygen.<sup>(2)</sup> Some titanium alloys (Ti-8Mn and Ti-5Al-2.5Sn) ignite at somewhat higher temperatures in air than in oxygen.<sup>(2)</sup> This ignition takes place at temperatures at or just above their melting points.

It has been shown that titanium will ignite in more dilute mixtures than air, such as 50O<sub>2</sub>-50CO<sub>2</sub> mixture, if the range is the same as in oxygen at 300 psi. Titanium will also ignite in CO<sub>2</sub> atmospheres and in nitrogen at temperatures below the melting point under pressure.<sup>(3,4)</sup>

Effect of Velocity. The ignition temperatures of titanium and its alloys have been shown to be nearly the same in high-velocity air streams as in static or slow-moving air.<sup>(2)</sup>

##### Ignition in Gaseous Oxygen at Ambient and Moderate Temperatures

Massive titanium will not ignite in air or oxygen at ambient or moderate temperatures, unless there is a secondary input of energy usually accompanied by the exposure of a fresh metal surface. Titanium powders will ignite at as low as 680 F (360 C) in clouds or 950 F (510 C) in layers.<sup>(21)</sup>

Ignition by Electric Spark. An electric spark with an energy input of 25 millijoules will ignite a cloud of titanium powder at room temperature and atmospheric pressure.<sup>(21)</sup> Massive titanium can also be ignited by an electric spark in gaseous oxygen at room temperature and atmospheric pressure with a spark energy of 1 to 10 joules.<sup>(16)</sup> Lower energies were required for 0.005-in. sheet than for 0.007- and 0.010-in. sheet. The test was performed by bringing a steel needle close to a titanium plate and allowing a spark to jump from one to the other. A modification in which the needle was the titanium sample gave similar results. Neither steel nor aluminum ignited in the same type of test. The oxygen flow rate, the extent of confinement, and the point of spark impingement appeared to affect the results.

The variations observed would indicate that the heat balance of the system is one of the controlling factors in ignition by spark, as has been found with ignition in high-temperature oxygen. Also, since the point of impingement seemed to be involved, there may be spots on a titanium surface that are more active than others or have a thinner or cracked scale.

Ignition by Stress Rupture. Massive metal will ignite in gaseous oxygen at room temperature at pressures above atmospheric pressure, if there is also a secondary input of energy from tensile rupture of the metal, accompanied by exposure of a fresh metal surface.<sup>(16)</sup> The pressure required was shown to be 350 psi.<sup>(20)</sup>

These effects of pressure on ignition temperature are shown in Figure 2. Ignition at somewhat lower pressures (about 60 psi) was indicated in other tests,(22) as shown in Figure 3. The Ti-6Al-4V alloy required a slightly higher pressure than the pure metal. The dilution of oxygen with helium increased the pressure required to cause ignition. At 65 percent oxygen about 1000 psi pressure is required. Below 35 percent oxygen (see Figure 4) titanium would not be expected to ignite, even at very high pressures. Under dynamic flow conditions such as caused by puncturing a pressure vessel, the pressures required for ignition are approximately 250 psi less than under static conditions.(20)

An increase in temperature above room temperature lowers the pressure required to ignite titanium under stress-rupture conditions. The pressure decreases from 350 to 50 psi at 1200 F (Figure 2).

The observation has been that once a piece of titanium is ignited, it continues to burn until all of the metal or all of the oxygen is gone. Propagation data have been developed that indicate that even in dilute mixtures of oxygen, burning can propagate at moderate pressures of 200 psi even though ignition cannot occur. Therefore, dilution of the oxygen after ignition would not be expected to cause quenching until the oxygen became very dilute or the temperature was lowered rapidly.

Effect of Low-Cycle Fatigue. The energy concentration by low-cyclic fatigue is probably smaller than with stress rupture. However, as a crack propagates, fresh metal surfaces are exposed. Fatigue tests in gaseous oxygen at 60 psi and room temperature did not result in burning at the bare metal areas.(17) However, slightly tarnished spots were observed, which indicated that high temperatures had been reached.

Effect of Mechanical Impact on the Outside of a Gaseous-Oxygen Container. No reactions occurred when the outside of a gaseous-oxygen (50 psi) container was struck with 140 ft-lb force. In four trials, the blow crushed the container but did not puncture it.(16) This indicates the energy input in the form of heat was not concentrated enough to cause ignition.

#### Ignition of Titanium in Gaseous Oxygen Below Room Temperature

Effect of Stress Rupture. At the low temperatures associated with LOX (-250 F), titanium ruptured under stress requires a higher pressure for ignition to occur than when ruptured at room temperature (see Figure 3). (19)

Effect of Flow Through a Small Orifice. A specimen of welded titanium containing a minute orifice was pressurized twice to 100 psig, which caused a stream of oxygen to flow through the orifice. No reaction occurred. In another experiment, a specimen containing a small crack was

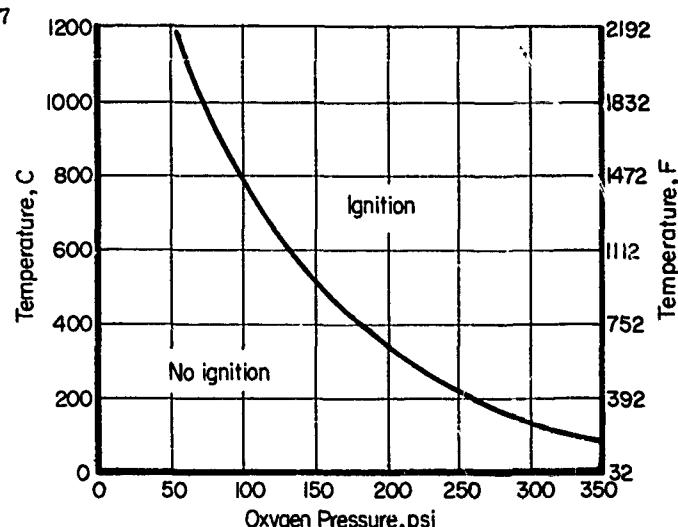


FIGURE 2. EFFECT OF TEMPERATURE ON SPONTANEOUS IGNITION OF RUPTURED TITANIUM IN OXYGEN(22)

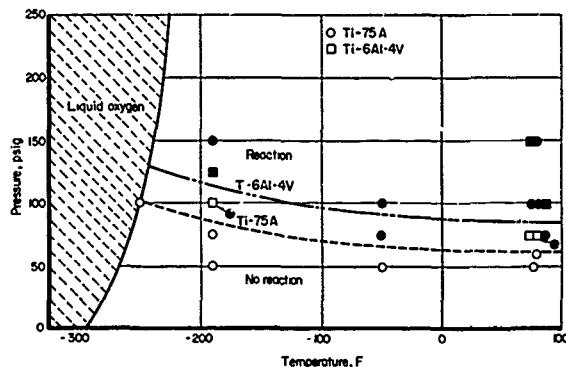


FIGURE 3. REACTIVITY OF TITANIUM RUP-TURED IN GASEOUS OXYGEN(18)

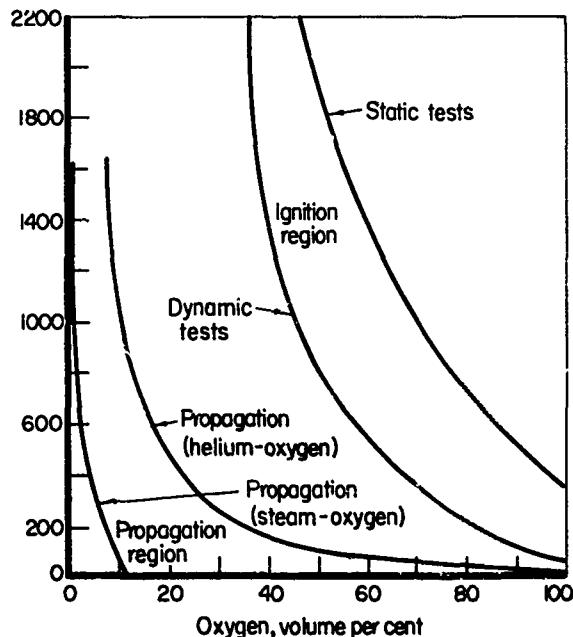


FIGURE 4. IGNITION AND PROPAGATION LIMITS OF TITANIUM IN HELIUM-OXYGEN AND STEAM-OXYGEN MIXTURES(22)

pressurized with 100-psig oxygen until it propagated to 1-1/2 inches in length. No reaction occurred. (16)

#### Reaction of Titanium Alloys With Liquid Oxygen

Titanium and its alloys are not expected to react violently with LOX under static conditions at the boiling point of the liquid. The normal oxidation rate is quite low at this temperature. However, it has been found that, under these conditions, titanium and its alloys can be caused to ignite with only a small amount of energy input. The factors that appear critical here are those that lead to concentrations of energy in the form of heat to raise the temperature at local sites, and the exposure of fresh metal surfaces.

Ignition by Impact. Investigators are agreed that mechanical impact is one source of energy that causes the ignition of titanium and its alloys in LOX. In the study of impact ignition of titanium and other materials, it has been found that organic materials, such as oils and greases, that are often found on metals, are very sensitive to impact. If the titanium surface were contaminated with organic compounds, ignition of the metal would occur more readily. Therefore, the degree of cleanliness of the surface may affect test results or cause unexplained field failures. Other types of dirt, such as metal filings and grit on the metal surface, produce more reactivity in impact tests.

The effect of impacting titanium in LOX has been investigated by a number of people using drop-weight-type testers. (11-12, 14-18, 23-24) In these experiments, various weights were dropped from different heights with various striker designs and areas of impact. These variations in equipment resulted in the same ft-lb input with different heights of fall and different velocities and area effects.

In addition to titanium, the following alloys have been evaluated:

- Ti-5Al-2.5Sn
- Ti-6Al-4V
- Ti-40A
- Ti-13V-11Cr-3Al
- Ti-25Zr (experimental alloy).

After examining data from various sources, it was concluded<sup>(25)</sup> that the unalloyed titanium is slightly less sensitive to impact in LOX than the titanium alloys studied. Most of the data show impact sensitivities in the 10 to 70 ft-lb range, and many ignitions in the 10 to 30 ft-lb range. As has been mentioned before, no ignitions in 20 tests or one ignition in 60 tests are the accepted limits of impact sensitivity for safe practice. By these criteria, titanium alloys have been ranked

as unacceptable as a LOX container material and are ranked as being similar to such organic materials as Buna N, polyethylene, and Styrofoam. (16)

A number of surface treatments and coatings have been evaluated as to their effect on the impact sensitivity of titanium alloys in LOX. Some treatments found either to increase or to have little effect on impact sensitivity are noted as follows:

- (1) Mechanical polishing was shown to improve the resistance by one investigator, (18) whereas in another case, it seemed to increase sensitivity. (16)
- (2) Pickling was shown to increase both the frequency and the violence of the ignition reactions. (16)
- (3) Passivation with  $H_2O_2$  increased the sensitivity to LOX. (16) Passivation in boiling nitric acid also increased the sensitivity. (19) Treatment in boiling potassium hydroxide may have produced some slight reduction in sensitivity. (16)
- (4) A number of phosphate-coating treatments have been tried on titanium. These include manganese phosphate, iron phosphate, and others. None of these conversion-coating treatments produced a substantial improvement in the impact-sensitivity situation. (16) The fluoride-phosphate treatment, which forms a heavy coating, produced only a small decrease in sensitivity. (26)
- (5) Anodizing of a titanium surface by several methods to prepare both thin or thick coatings did not improve the resistance of the base metal to impact sensitivity. (16)
- (6) The ceramic coatings that have been tried have produced no improvement in LOX sensitivity over that of the base metal. (16)
- (7) Teflon coatings reduced the LOX sensitivity, but not enough to be useful. (16)
- (8) Flame-sprayed aluminum coatings<sup>(16)</sup> and vapor-deposited aluminum coatings<sup>(26)</sup> provide some protection, but not enough to be useful.
- (9) Oxide films produced by annealing in vacuum and air cooling decreased the sensitivity somewhat, but not enough to be of any real value. (16)

- (10) Although the data regarding the method of application or thickness were not discussed in detail, gold and silver coatings were ineffective in reducing impact sensitivity.

Other types of coatings appear to provide enough reduction in impact sensitivity so that they might find limited use. Even these protective measures would be limited by the fact that damage to the coatings probably would destroy their effectiveness. These coatings are described as follows:

- (1) A nitrided layer can be formed on titanium alloys by heating at 1500 F in a nitrogen atmosphere for 3 hours. This surface treatment produced good results in that no burning occurred in the tests and only two flashes were produced.<sup>(16)</sup> This treatment might be undesirable because the metal becomes slightly embrittled by the treatment.
- (2) Electroplated coatings (about 0.5 mil thick) of copper and nickel effectively reduce the impact sensitivity of titanium in LOX.<sup>(16)</sup> These coatings may be of some practical value, although they are difficult to apply to large items.
- (3) Electroless copper and nickel coatings would be much easier to apply to the inside of such items as tanks. Thin coatings, about 0.2 mil thick, effectively reduce impact sensitivity to an acceptable level for limited use. The weight added is somewhat less than with the electroplated coatings, but the adherence may be somewhat less.<sup>(16)</sup> The latter may be a function of the method of application.
- (4) It has been found that aluminum cladding, probably a thick coating, prevents the spontaneous ignition of titanium when exposed to pressurized LOX.<sup>(28)</sup>

Ignition by Explosive Shock. Titanium and titanium alloys can be caused to ignite in LOX by explosive shock waves.<sup>(16)</sup> Three different test methods were used in this study. In the first test procedure, the spacing between the charge and the acceptor (test specimen) was fixed and the size of the charge was varied. No direct measure was made of the shock, but the variations in amount of charge required to ignite several materials can be compared. It was found that in the equipment for 0.010- and 0.035-in. -thick Ti-5Al-2.5Sn alloy sheet, only the cap (M36Al) was required to cause ignition. Only 0.84 inch of No. 40 primacord had to be added to the cap to ignite

0.063-in.-thick specimens. In contrast, Mg-HK31XA-H24, Al 5052-H34, or stainless Type 301 required much larger charges (see Table 1). Titanium was more sensitive than two gasket materials, Alipax 500 and Johns Manville 76, and was even more sensitive than No. 400 or No. 200 primacord in the same system, with water substituted for the LOX.

The other test methods were designed so that the spacing could be varied and the donor charge and the specimens kept constant.<sup>(16)</sup> Titanium was again found to be far more sensitive than either an aluminum alloy or a stainless steel (Table 1).

Copper or nickel electroless plating on unalloyed titanium results in some improvement over the uncoated Ti-5Al-2.5Sn alloy. However, the slight improvement gained with these coatings would not be sufficient protection. Nickel- and copper-coated titanium are rated more sensitive than a magnesium alloy, an aluminum alloy, or stainless steel.

Ignition of Titanium in Liquid Oxygen by Puncture. A number of experiments have been conducted to determine the effect of puncturing a container of LOX. In the standard gun-fire test, a 50-calibre, armor-piercing incendiary bullet was fired through a plywood sheet to produce tumbling upon entry into a titanium pressure bottle. Upon impact, a huge flash was observed together with a violent reaction.<sup>(14)</sup> The pressure bottle was fragmented. Fusion and burning had occurred on some of the fractured faces. However, the reaction did not propagate and the LOX was not consumed. Similar tests showed that the reactions were more violent when the LOX was not dry (i.e., when it contained ice particles).

In other tests,<sup>(16)</sup> nonincendiary bullets and 1/8-in. pointed rods were fired into Ti-5Al-2.5Sn tanks filled with LOX. With the rods, one of two burned fast and then detonated; another rod sealed the hole, but later the tank exploded by an unexplained mechanism. With the bullet, the LOX tank first burned and then exploded. The burning started immediately after the puncture, then subsided slightly before the explosion.

In tests on Ti-5Al-2.5Sn<sup>(16,29)</sup> and Ti-6Al-4V,<sup>(29)</sup> LCX containers were punctured by pins driven by falling weights. The containers did not burn every time, but the frequency was very high, i.e., in 12 of 15 times in one test and in 20 of 21 times in another. No reactions occurred with aluminum or stainless steel under these conditions. It has also been reported that punctures of LOX tanks caused by small steel and nylon pellets resulted in violent explosions.<sup>(16)</sup>

From the above experiments, it is clear that the puncture of a titanium-alloy LOX tank will

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TABLE 1. SUMMARY OF SHOCK-SENSITIVITY RESULTS

Material	Test Method I - Stimulus From Donor (Cap and Primacord)			Test Method II - Stimulus From Donor (Cap and Primacord)			Test Method III - Stimulus From Donor (Cap and Primacord)		
	Thickness, inch	Inches of Prima- cord(b)	Size of Primacord, gr/ft(b)	Inches of Prima- cord(b)	Size of Primacord, gr/ft(b)	Gap(a) for Ignition, inches	Inches of Prima- cord(b)	Size of Primacord, gr/ft(b)	Gap(a) for Ignition, inches
<u>Reactions With LOX</u>									
Ti-5Al-2.5Sn	0.063	0.84	40	2	400	2.88	Cap only	--	1.55
Ditto	0.063	--	--	--	--	--	2	400	2.92
"	0.035	Cap only	--	--	--	--	12	400	2.44
"	0.035	--	--	--	--	--	12	400	3.00
"	0.010	Cap only	--	Cap only	--	0.36	12	400	3.90
A1-5052-T34	0.063	12	238	2	400	0.61	12	400	0.95
Ditto	0.035	12	224	--	--	--	12	400	2.10
Type 301 stainless steel	0.035	>>12	400	--	--	--	--	--	--
Titanium, copper plated	0.010	12	100	--	--	--	12	400	2.50
Titanium, nickel plated	0.010	12	84	--	--	--	12	400	2.50
Mg-HK31XA-H34	--	12	189	--	--	--	--	--	--
<u>Reactions in Gaseous Oxygen</u>									
Ti-5Al-2.5Sn	0.063	1.5	40	--	--	--	12	400	2.13
Ditto	0.032	--	--	--	--	--	12	400	2.75
"	0.010	Cap only	--	--	--	--	--	--	--
A1-5052-H34	0.063	12	283	2	400	0.46	12	400	1.37
Ditto	0.035	12	224	--	--	--	--	--	--

(a) Larger gap indicates the material is more sensitive.

(b) Smaller size or shorter primacord means more sensitive.

almost certainly result in burning that may be accompanied by a violent detonation. Three sensitizing mechanisms appear to be at work:

- (1) Impact by the puncturing tool
- (2) Exposure of fresh titanium surface
- (3) High-velocity flow past the bare metal surface.

A secondary mechanism may be that rapid pressurization, due to liquid evaporation, takes place because of the heat produced from the initial reaction. This accompanying pressure increase results in the violent detonation.

The effect of the size of the puncturing tool is illustrated by micrometeoroid puncture tests.<sup>(29)</sup> These tests, using very small "bullets" (0.1 to 0.2 gram) fired at high velocities of 9,100 to 15,000 ft/sec, resulted in ignition of the titanium at the side of entry about half the time, and on the opposite side in 15 of 16 times.

The data indicate that puncture caused by either small particles at high velocity or larger tools at much lower velocities results in ignition of titanium alloy in contact with LOX.

Effect of Mechanical Impact on the Outside of a Liquid-Oxygen Container. Experiments were conducted at as high as 140 ft-lb impact to determine if mechanical impact on the outside of a LOX container would have the same effect as impact in contact with the LOX. These tests did not result in ignition; the input of energy is probably

less than that from the detonation-type tests but is at least 7 times as great as the "in LOX" type of impact that produces ignition.<sup>(16)</sup>

Similar tests<sup>(18)</sup> showed no reaction when titanium tubes containing LOX were crushed with 70 ft-lb of impact.

Effect of Rapid Pressurization. Titanium-alloy LOX tanks have been shown to withstand 250 pressurization cycles 0 to 1500 psi without ignition. The pressurization cycle consisted of almost instantaneous rise to 1500 psi in 0.6 second and back to 0 psi in a total of 2 seconds.<sup>(16)</sup> LOX was also compressed in an hydraulic cylinder by application of 70 ft-lb of force from a dropped weight. A titanium specimen at the bottom of the pressurized cavity did not ignite.

Effect of Dilution by Liquid Nitrogen. Experiments have shown that titanium is impact sensitive in LOX even when it is diluted with large amounts of liquid nitrogen (LN<sub>2</sub>).<sup>(16)</sup> Only when the LN<sub>2</sub> dilution reaches 70 percent (almost liquid air) does the titanium become nonreactive at the 70 ft-lb level (see Table 2).

TABLE 2. EFFECT OF LIQUID-NITROGEN DILUTION ON LIQUID-OXYGEN IMPACT SENSITIVITY OF Ti-5Al-2.5Sn TITANIUM<sup>(16)</sup> (0.063 in. thick)

LN <sub>2</sub> , percent	Reactions per No. of Tests at Indicated Impact, ft-lb						
	72	65	58	51	43	36	22
0	11/20	--	--	--	--	3/20	1/20
50	1/20	3/20	3/20	0/20	0/20	--	--
60	2/20	--	--	2/20	1/20	0/20	--
70	0/20	0/20	--	--	--	--	--
100	0/20	--	--	--	--	--	--

Machining or Galling. Titanium panels were machined under LOX with no reaction.<sup>(16)</sup> The chips thus produced were shiny and bright. However, when heat was generated with galling under a rotating stainless-steel cylinder, an observable reaction occurred. Propagation did not occur at contact pressures of 2600 psi and speeds of 220 ft/min.

In experiments on the effect of galling under LOX, tests were conducted by rotating the end of a stainless-steel rod on a titanium specimen in an aluminum cup filled with LOX. The rod was mounted in a drill press and operated at peripheral speeds of up to 40 in./sec (200 ft/min) and different pressures up to 1600 psi. The reaction, as indicated by the intensity of the light flash, increased when speed and/or pressure increased. The temperature generated was estimated to be about 1000 F, as observed from the color of the stainless-steel rod.

An explanation for propagation not occurring even though ignition can be made to take place by heat generated by friction is that propagation probably is dependent upon the heat balance of the system. In the above experiments, it is clear that a high enough temperature does exist at some points in the overall cold system. The titanium-oxygen interface, however, only momentarily reaches ignition conditions, after which the heat balance shifts and quenching occurs.

Ignition by Tensile Rupture. The reactivity of a freshly formed titanium surface was investigated by rupturing titanium tensile specimens exposed to LOX. No propagating reactions were obtained in over 30 experiments at strain rates from 100 to 10,000 in./in./min. One small discolored spot was found only on one specimen. However, a bright flash of light was observed when the specimen ruptured.<sup>(26,27)</sup> Aluminum foil also flashes when ruptured. It is believed the flash is the result of the rapid oxidation of the fresh surface.

Effect of Vibration. High vibration levels, as associated with space vehicles, were studied. Vibration tests<sup>(16)</sup> of LOX-filled tanks, made with up to 200 cycles per second at 20 G's with a 0.03-inch double amplitude, caused no reactions.

In other experiments, a "sloshing" vibration was investigated using a LOX-filled tank in a Rotap machine for 10 minutes in each of 5 tests. In a similar test, the top vent port was left open and tapped lightly by the machine as dense vapors passed over the impact area. No reaction occurred.

Effect of Ultrasonic Energy. Titanium coupons were placed in LOX and subjected to ultrasonic energy from a 400-watt, 25-kc magnetostrictive transducer.<sup>(16)</sup> Three runs using disks 0.010, 0.025, and 0.063 inch thick, for 15 minutes' duration produced no reaction.

Effect of Sonic Energy. Two 0.010-in.-wall titanium tanks filled with LOX and pressurized to 50 psig were located 8 feet from a rocket motor.<sup>(16)</sup> A 4000-pound thrust LOX-kerosene rocket engine was fired to produce a 150-db acoustic pressure level. Four tests for a total of 210 seconds produced no reactions.

Simulated Loose Equipment in a Liquid-Oxygen Tank. The effect of components breaking loose and vibrating in a LOX tank during flight was simulated.<sup>(16)</sup> A 2-in. cube of Type 321 stainless steel was rough cut with a power hack saw and placed in a Ti-5Al-2.5Sn tank. The tank was filled with LOX and pressurized with 35 to 40 psig oxygen. The tank was then vibrated in a Rotap machine. After about 15 minutes, the LOX evaporated, and the cube rattled around in gaseous oxygen. Examination of the tank showed a surface peppered with minute dents but no reaction was indicated. Similar results are reported in gaseous oxygen on compressive impact studies.<sup>(18)</sup> Steel balls were impacted up to 20 mils deep into a titanium sample with no reaction.

Effect of Flow Through an Orifice. LOX was forced through a small orifice using an hydraulic cylinder. There was no apparent reaction.<sup>(18)</sup>

#### Summary of Oxygen-Titanium Reaction Information

The following conclusions can be drawn about ignition reactions of oxygen-titanium alloy systems.

##### Gaseous Oxygen

- (1) Ignition of titanium in gaseous oxygen occurs at temperatures about 482 F (250 C) below its melting point at atmospheric pressure
- (2) An increase in pressure lowers the ignition temperature
- (3) Dilution of oxygen up to the amount in air causes little change in ignition temperatures
- (4) Titanium will ignite in both carbon dioxide and nitrogen at temperatures somewhat higher than in oxygen at the same pressures
- (5) The ignition temperature in high-velocity air streams is about the same as under static conditions
- (6) Massive titanium will not ignite at ambient and moderate temperatures in air or oxygen unless some secondary source of energy other than heat is available

- (7) As with other metals, clouds and layers of powder can be ignited at substantially lower temperatures than can massive metal
- (8) Titanium can be ignited in both powder and massive form by electric spark at room temperature
- (9) The massive metal can be ignited by stress rupture at room temperature at oxygen pressures above about 60 psi but not at atmospheric pressure. If the temperature is increased, ignition occurs at lower pressures
- (10) Titanium is not ignited by low-cycle fatigue cracking at pressure up to 60 psi. Ignition is likely at higher pressure
- (11) The metal is not ignited by impact up to 70 ft-lb in gaseous oxygen at low temperatures and atmospheric pressure
- (12) Impact on the outside of a gaseous oxygen container is not likely to cause ignition if puncture does not occur
- (13) Ignition can be expected when titanium containers of gaseous oxygen are punctured either by large low-velocity projectiles or small high-velocity projectiles
- (14) High-velocity flow through small orifices is not expected to ignite titanium.

#### Liquid Oxygen

- (1) Titanium will not ignite in LOX without an external energy source and exposure of a fresh metal surface
- (2) Ignition may occur when titanium is impacted in LOX, even at impact levels as low as about 10 ft-lb
- (3) Unalloyed titanium may be slightly less sensitive to impact than some of its alloys
- (4) The following surface treatments, to some extent, reduce the impact sensitivity of titanium alloys: nitriding, electroplated nickel or copper, electroless nickel or copper, and cladding with a thick layer of aluminum

- (5) Titanium alloys are much more sensitive to ignition by explosive shock than magnesium, aluminum, and stainless steel. Plating the titanium alloys with nickel or copper gives some small improvement
- (6) Puncture of titanium-LOX tanks is almost sure to result in ignition
- (7) Impact of the outside of a tank that does not puncture is not likely to cause ignition
- (8) Ignition is not likely to occur in LOX-titanium systems by rapid pressurization, by machining, friction and galling, tensile rupture, mechanical vibration, sonic vibration, ultrasonic vibration, or high-velocity flow through an orifice.

#### Aluminum Alloys

##### Ignition in Gaseous Oxygen at High Temperatures

Aluminum in the massive form has been shown to ignite only at temperatures above its melting point 1220 F (660 C) at atmospheric pressure. (4) If the molten metal is confined, the ignition temperature may be as high as 1832 F (1000 C). At higher pressures of oxygen, up to 800 psi, the ignition temperature is still higher than the melting point. (3,4)

Aluminum has been broken by stress rupture to expose a fresh surface in 2000-psi gaseous oxygen at 572 F (300 C). No reaction occurred. (22)

Experiments involving impact and puncture of a diaphragm of a container of gaseous oxygen at 35 to 40 psi resulted in no reactions in 47 tests with pure aluminum, Aluminum 2014-T6, and Aluminum 6061-T6. (16) These tests were conducted at both room temperature and LOX temperature. Diaphragms pressurized with gaseous oxygen at 60 psi were punctured by simulated micrometeoroid particles traveling at 9,100 to 15,000 ft/sec. No reactions occurred, but there was some oxidation around the holes. (30) No reaction occurred as a result of puncturing Al-2024 diaphragms in LOX by metal shot traveling at 25,000 to 29,000 ft/sec through vacuum.

Aluminum can be ignited by explosive shock when in contact with gaseous oxygen. (16) Table 1 shows the effects under three different conditions. (16) In these tests, based on the amount of explosive needed and on the spacing between the charge and specimen, Aluminum

5052 is shown to be much less sensitive than titanium, but more sensitive than stainless steel.

Small particles of aluminum or aluminum-magnesium alloys can be ignited in clouds in air by low-energy sparks (50 to 80 millijoules). (21) Massive aluminum can be sparked with very much higher energies (10 joules) in pure oxygen and no evidence of reaction is found. (16)

Small particles of aluminum in clouds or layers have been ignited in air at 1202 and 1382 F (650 and 750 C), respectively. (21) In more dilute mixtures than air, ignition temperatures of 3632 F (2000 C) are indicated. (31)

#### Ignition in Liquid Oxygen

When aluminum foil is ruptured in LOX, bright flashes of light are emitted, but there is no other evidence of ignition. (18, 27) It is believed that these flashes are merely the result of rapid oxidation of the fresh metal surface and cannot really be called ignition. (25)

Aluminum and its alloys are not usually ignited by impact energies up to 70 ft-lb of force. (16, 18) There was some indication that if grit is impacted on aluminum, ignition may occur.

In puncture tests, the effect of both rupture and impact was studied. When a 30-calibre bronze-jacketed bullet was fired through an aluminum-LOX tank, the slug passed through both sides, leaving clean holes; no reaction occurred. Milder tests on aluminum tanks punctured by steel pins produced no reaction. (16)

Diaphragms pressurized with LOX were punctured by very small, high-velocity particles (9,100 to 15,000 ft/sec) to simulate micro-meteoroids. (30) There were no reactions when the particles penetrated Aluminum 2024 alloy diaphragms. However, there was a small amount of oxidation around the holes. When 1/16-in. shots traveling at 25,000 to 29,000 ft/sec in vacuum passed through diaphragms in LOX, no reaction occurred, but the metal was mechanically ruptured. (16)

It has been shown that aluminum alloys can be ignited by explosive shock in LOX. In these experiments, the amount of explosive required to ignite Aluminum 5052 was much greater than that necessary for titanium, and somewhat more than for magnesium (Table 1). However, this aluminum alloy was shown to be more sensitive than stainless steel. (16) The same trend was indicated in tests in which the spacing between the explosive and the specimen was varied. (16)

The experimental data above indicate that aluminum and its alloys are not easily ignited in

either gaseous oxygen or in LOX. However, the data show that stainless steel is even less sensitive, indicating that stainless steel would be the choice between the two materials, based on ignition reactions.

#### Stainless Steels

##### Ignition in Gaseous Oxygen

It has been found that the austenitic stainless steels in massive form ignite at or above their melting points at oxygen pressures up to 300 psi. (2, 4) At 800 psi, Types 302, 304, and 347 ignite at their melting points, while Types 310 and 210 ignite at slightly lower temperatures. (4) The precipitation-hardening steels, 17-7PH and AM-350, ignite at their melting points at 50 psi and slightly lower at 300 and 800 psi. (4) Types 410 and 430 steels behave more like carbon steels than like the 300-series steels and ignite at temperatures between 2372 and 2480 F (1300 and 1360 C) at pressures up to 300 psi, (2, 4) and as low as about 2192 F (1200 C) at 800 psi. (4)

At lower temperatures, the 300-series stainless steels do not ignite when ruptured in 2000-psi gaseous oxygen at 572 F (300 C). (22) Type 301 stainless steel diaphragms at 60 psi were impacted and ruptured by small particles traveling 9,100 to 15,000 ft/sec; no reaction occurred. (30) Type 301 diaphragms on gaseous oxygen containers, at 35 to 40 psi at room temperature and LOX temperature, have been punctured with 1/16-in. steel shot; no reaction occurred. (16) In the above experiments, the effects of impact, rupture, and high flow rates were involved, and no reactions occurred.

In other experiments, higher velocity flows were used. Oxygen gas at pressures of 12,000 psi was released through small orifices, 0.005 to 0.013 inch in diameter. No reaction occurred, but some erosion of the orifices took place. (32)

In air as in oxygen, the ignition temperature of Type 302 is above the melting point. (2) A higher temperature is required to ignite Type 430 steel in air than in oxygen. The temperature is at or above the melting point of the alloy. (2) High-velocity air flow, Mach 1.25, also had little effect on the air ignition temperature. In 50O<sub>2</sub>-50CO<sub>2</sub>, the 300-series steels ignite at or above their melting point.

It is reported that 18-8 stainless steel in fine powder form does not ignite at temperatures up to 1832 F (1000 C) either in clouds or layers. (21)

The effect of sudden increases in pressure has been studied. Stainless steel receivers were suddenly pressurized by releasing oxygen gas at 10,000 to 16,000 psi into low-pressure receivers.

The pressure in the receiver rose quickly from 15 to 8,000 psi, raising the bulk temperature 21 to 42 F. These pressure surges did not produce ignition. (32)

#### Ignition in Liquid Oxygen

The effect of impact and rupture of LOX tanks has been investigated. Type 301 stainless steel diaphragms on LOX containers have been punctured by micrometeoroid particles traveling at 9,100 to 15,000 ft/sec. No reaction was observed under these conditions. When 1/16-in. steel spheres traveling at 25,000 to 29,000 ft/sec were shot through diaphragms 0.010 inch thick, no reaction occurred, but the diaphragms ruptured mechanically. (16)

Type 304 LOX pressure bottles penetrated by incendiary 50-calibre bullets do not ignite and burn, but they do exhibit tearing. Occasionally, the bottles shatter if the material has defects at the grain boundaries. (33)

The effect of friction and galling on the ignition of stainless steels has been investigated. When a stainless-steel cylinder was rotated on a titanium plate at 2600 psi contact pressure at 220 ft/min in LOX, the titanium reacted, but the stainless steel showed no reaction. (18) A stainless-steel rod was rotated on a titanium plate at 200 ft/min at 1600 psi contact pressure in LOX. The temperature of the stainless steel reached about 1000 F, but there was no ignition of the stainless steel. (27)

It is possible to ignite stainless steel in LOX by explosive shock. (16) In this respect, Type 304 stainless steel requires much larger explosive charges to cause the LOX metal reaction than does aluminum.

All of the experiments that have been reported indicate that the 300-series stainless steels are among the materials most resistant to ignition in both LOX and gaseous oxygen. The various methods of additional external heat input that have been investigated have substantiated this insensitivity. The instances in which stainless steels have been ignited in oxygen can usually be traced to the ignition of another material that in turn ignited the stainless steel.

#### Copper Alloys

#### Ignition in Gaseous and Liquid Oxygen

Copper does not ignite in gaseous oxygen at atmospheric pressure and below its melting point. (2, 4) An increase in pressure up to 500 psi does not change this situation. (3, 4) Berylco 25 also does not ignite at its melting point at least at 50 psi. (2) However, Berylco 10 does ignite at about 1760 F (960 C) in oxygen. (2)

Copper, Berylco 10, and Berylco 25 behave about the same in air as in oxygen. (2) Data for copper in high-velocity air indicate that its ignition temperature is still above the melting point of the metal. Also, copper did not ignite at its melting point in a 50O<sub>2</sub>-50CO<sub>2</sub> mixture. (3)

Small particles of copper in a cloud in air will ignite at 1292 F (700 C). (21) Berylco 25 powder does not ignite at 1832 F (1000 C) in either a cloud or a layer. (21) Brass powder (70-30) will ignite as low as 374 F (190 C) in a layer and 698 F (370 C) in a cloud. (21) Manganese bronze would not ignite in a cloud at 1832 F (1000 C) but did in a layer at 1670 F (910 C). Cu-50Al ignited in a cloud at 1706 F (930 C) and in a layer at 1526 F (830 C).

The effect of high-velocity-oxygen gas flow was studied with 0.005- to 0.013-in. orifices in copper and brass. The oxygen was released through the orifices from a container at 12,000 psi. No reaction occurred, but a fair amount of erosion did appear on the orifices. (32)

Impact studies in LOX have shown that copper alloys have a low sensitivity to ignition by this means. At the 72 ft-lb force level, Ampco 24, Cu-34Zn-1Pb, bronze, and 70-30 cupro-nickel showed no reactions in 20 tries. (34)

#### Nickel Alloys

#### Ignition in Gaseous and Liquid Oxygen

It has been shown that nickel does not ignite at its melting point at oxygen pressures up to 800 psi. (4) Inconel, Monel, Hastelloy C, Hastelloy B, and Hastelloy X behave in a similar manner up to 300 to 500 psi. (2, 4) Inconel X may ignite at slightly below its melting point at 300 psi. Monel, Hastelloy B, and Hastelloy X may ignite slightly below their melting points at 800 psi. (4)

In air, nickel and Inconel in massive form do not ignite at their melting points at pressures up to 300 to 500 psi. (2, 3) The ignition temperature of Inconel is not affected by high-velocity air flow. (3) Nickel powder in clouds or layers does not ignite at 1832 F (1000 C). (21) The ignition point of nickel powder in clouds and layers is lowered by alloying with 50 to 60 percent aluminum, being as low as 1022 to 1202 F (550 to 650 C) in layers and 1724 F (940 C) in clouds. (21)

The effect of various mechanical inputs of energy and the exposing of fresh metal has not been extensively investigated for nickel alloys. Drop-weight sensitivity tests on the K6 alloy (Karl Harrison Co.) and Kovar A show no reaction at 72 ft-lb impact in LOX. (34)

The effect of high-velocity flow through orifices in Monel was investigated by releasing

12,000-psi oxygen gas through 0.005- and 0.013-in. orifices.<sup>(32)</sup> Only a small amount of erosion was observed and no reactions occurred.

The data available, although not so complete as for the stainless steels, indicate that nickel alloys can be classed as being very resistant to ignition in oxygen.

#### Iron Alloys

##### Ignition in Gaseous and Liquid Oxygen

Pure iron in massive form has been shown to ignite in gaseous oxygen at atmospheric pressure at 1706 F (930 C).<sup>(1)</sup> The ignition temperature of mild steel in oxygen has been shown to be about the melting point at 50 psi and decreases to 1904 F (1040 C) at 800 psi.<sup>(4)</sup> The alloy steels 4130 and Graphma tool steel ignited at similar temperature levels.<sup>(3)</sup>

Steels behave much the same in air as in pure oxygen, igniting in the range of 2192 to 2372 F (1200 to 1300 C).<sup>(2)</sup> High-velocity air streams also have little effect on the ignition temperature.<sup>(3)</sup> Likewise, dilution of oxygen with 50 percent CO<sub>2</sub> does not change this ignition temperature.<sup>(4)</sup>

Finely divided powders ignite in air at much lower temperatures than the massive metal. Pure iron powder in clouds or layers ignites at about 590 to 608 F (310 to 320 C) in air.<sup>(21)</sup> Very fine powder will ignite at room temperature in air. Alloying iron with large additions of aluminum, silicon, chromium, manganese, vanadium, and even titanium (descending order) raises the ignition temperature of clouds of particles.<sup>(35)</sup> The Fe-50Al alloy did not ignite at 1832 F (1000 C). The others ignited in the range between 680 and 1652 F (360 and 900 C).<sup>(21)</sup>

The data on the effect of the various other factors such as impact, rupture, puncture, and explosive shock are very limited. Steel wool has been shown to be sensitive to impact in LOX with three out of four reactions at 72 ft-lb impact.<sup>(34)</sup> However, no reaction occurred when iron was ruptured in 2000-psi gaseous oxygen at 572 F (300 C).<sup>(22)</sup>

Although the data are somewhat limited, iron and low-alloy steels probably should be rated as having a moderately high sensitivity in oxygen systems. Therefore, these alloys probably should not be used in critical conditions.

#### Cobalt Alloys

##### Ignition in Gaseous Oxygen

Limited data on cobalt alloys suggest that they may be nearly as resistant to ignition as the nickel systems in oxygen. Multimet and Haynes 25 do not ignite until above their melting points

at atmospheric pressure, but may ignite at or slightly below their melting points at higher pressures.<sup>(4)</sup>

Ignition data for cobalt powder in layers and clouds in air suggest that cobalt is more susceptible to ignition than cobalt alloys or nickel. The data show ignition of cobalt at 1454 F (790 C) in clouds and 1238 F (670 C) in layers as compared with no ignition of nickel at 1832 F (1000 C) under similar conditions.<sup>(21)</sup>

#### Magnesium Alloys

##### Ignition in Gaseous and Liquid Oxygen

The ignition temperature of magnesium in oxygen at atmospheric pressure has been shown to be slightly below its melting point at 1033 F (623 C).<sup>(5)</sup> At 500 psi, the ignition temperature was shown to be near the melting point of 1202 F (650 C).<sup>(3)</sup> The ignition point of a number of alloys has been investigated.<sup>(5)</sup> Parts of the following alloy systems were studied: alloys of magnesium with the following metals; (binary alloys) aluminum, nickel, antimony, silver, bismuth, cadmium, cobalt, copper, calcium, indium, lithium, manganese, silicon, tin, lead, zinc; (ternary alloys) aluminum-zinc, aluminum-cadmium, cadmium-silver, and cadmium-zinc.<sup>(5)</sup> Except for alloys over 80 percent aluminum, these alloy additions usually resulted in lowering the melting point and the ignition temperature. The ignition temperature ranged from 932 to 1112 F (500 to 600 C). Merely being in contact with some other metals also changed the ignition temperature of magnesium. Contact with nickel, brass, and aluminum lowered the ignition temperature, while contact with steel and silver did not affect it.

Massive magnesium has been shown to ignite in air at the same temperature as in oxygen.<sup>(1)</sup> Also, in other oxygen-inert gas mixtures the ignition temperatures were found to be 1141 to 1200 F (616 to 649 C) for 10O<sub>2</sub>-90N<sub>2</sub><sup>(5)</sup> and 1202 F (650 C) for 20O<sub>2</sub>-80A mixtures.<sup>(36)</sup>

Magnesium powder in air as a cloud ignites at 1148 F (620 C) and in a layer at 914 F (490 C).<sup>(21)</sup> Other investigations show that the density of particles in a cloud affects the apparent ignition temperatures. Less dense clouds require high temperatures for ignition, ranging as high as 1292 to 1472 F (700 or 800 C), much above the melting point.<sup>(7)</sup> It has been shown that the smaller particles, in the size range of 12 to 70 microns, may require a higher temperature to cause ignition. The ignition temperatures of powder clouds in oxygen is about the same range as in air.

Impact studies in LOX show that magnesium and its alloys must be considered sensitive to this type of ignition. Tests have been conducted on

pure magnesium, Mg-Li alloys, HK-31 alloy, and AZ-31 alloy. All these alloys were shown to be sensitive to impact at the 72 ft-lb level. Reduction in the impact force to about 35 ft-lb would not be expected to produce any reaction in 20 tries. (34)

In contrast to the above results, magnesium did not react when ruptured in 2000-psi oxygen at 572 F (300 C). Diaphragm-puncture tests with MgHK31 at room temperature and 2 to 40 psig oxygen resulted in one flash of light in 20 tests. At higher pressures of 60 and 100 psig, reactions were more frequent, i.e., 9 times in 20 tries at each pressure. (16) These results can be compared with ignition and burning with titanium and no reactions with aluminum.

From the above data, it can be concluded that though magnesium alloys are not so sensitive to ignition as titanium alloys, they are probably sensitive enough to be rated as unusable in oxygen systems.

#### Tin and Lead Alloys

##### Ignition in Gaseous and Liquid Oxygen

The ignition temperature of massive tin in oxygen at atmospheric pressure is reported as 1589 F (865 C), which is above the melting point of tin. (1) Likewise, powdered tin has been shown to ignite at 1220 F (660 C) in clouds and 966 F (520 C) in layers in air. (21) No data are available for massive lead in oxygen, but powdered lead has been shown to ignite in clouds at 1310 F (710 C) and layers at 518 F (270 C) in air. (21) The above data indicate that both lead and tin ignite only above their melting points in oxygen or air. But, since the melting points of tin and lead are low, they could still be sensitive to ignition by mechanical sources of energy.

Tin as tin plate has been shown to ignite at as low as 35 ft-lb impact and react about 2 out of 20 times at 72 ft-lb in LOX. Lead alone has not been tested in impact but many commercial solders have been studied. These soft solders containing lead or tin were all sensitive to impact in LOX at 70 ft-lb and most of them at 35 ft-lb. (34)

Generally speaking, the above results suggest that lead, tin, and soft solders should be avoided in LOX systems. They may be satisfactory in gaseous systems since, due to their low strength, they are not usually used under high pressures.

#### Silver and Silver Solders

##### Ignition in Gaseous and Liquid Oxygen

No ignition data are available for silver in oxygen or air. However, thermodynamic data indicate that the oxide is unstable at moderate

temperatures. These data, coupled with the location of silver in the periodic table, suggest that silver will not ignite easily.

Drop-weight impact data on silver solders show that some of these solders, usually the higher melting types are not impact sensitive at the 72 ft-lb level in LOX. Silver plating on stainless steel was not impact sensitive. (34)

#### Other Metals and Alloys

##### Ignition in Gaseous Oxygen

Ignition temperatures for both massive and powdered forms of a variety of other metals are given in Appendix A. These include antimony, barium, beryllium, bismuth, boron, cadmium, calcium, chromium, lithium, manganese, molybdenum, sodium, strontium, tantalum, tellurium, thorium, tungsten, uranium, vanadium, and zinc. Either from actual data on massive metal or inferred from powder data, the following metals are expected to ignite below their melting points: barium, beryllium, calcium, strontium, thorium, vanadium, tantalum, chromium, molybdenum, tungsten, uranium, manganese, silicon, and boron. The following probably would ignite above their melting points: lithium, sodium, potassium, cesium, platinum, gold, mercury, antimony, bismuth, silicon, and tellurium. Though the metals in the second group, which also includes nickel, copper, aluminum, and cobalt, possess the desirable property of igniting above their melting points, some of the melting points are so low that their use is limited. Conversely, some metals in the first group may be relatively insensitive because they have a high melting point and ignite only slightly below these temperatures. These exceptions include beryllium, chromium, and possibly columbium, tantalum, molybdenum, and tungsten.

#### THEORETICAL ANALYSIS AND CALCULATION OF IGNITION TEMPERATURES

##### Basic Data Required

The theoretical evaluation of the compatibility of metals with liquid or gaseous oxygen involves a number of thermochemical and thermophysical constants. Data for these constants are available in the literature but are widely scattered. For this reason, the data were collected in this section in tabular form. A discussion of the data and their application follows.

##### Thermochemical Data for Metal Oxides of Interest

In Table 3, the standard heat of formation,  $\Delta H_f$ , of the metal oxides is shown at several temperatures. The negative value indicates that the metal reacts exothermically, that is, heat is evolved in the oxide formation. The negative sign

TABLE 3. THERMOCHEMICAL DATA FOR OXIDES OF METALS OF INTEREST

Oxide	Oxide Temperature, K					Reference
	100	298	1500	2000	2500	
Standard Heat of Formation, $\Delta H_f$ kcal/g mole						
TiO <sub>2</sub> (c)	-225.012	-225.500	-224.145	--	-226.175	(38)
ZrO <sub>2</sub> (c)	-260.958	-261.500	-258.608	-258.198	-263.001	(38)
FeO (c,l)	--	-63.500	-62.700	-57.850	-57.050	(37)
Cu <sub>2</sub> O (c,l)	--	-41.800	-48.300	-35.000	-35.100	(37)
CuO (c,l)	--	-38.300	-40.100	-36.700	-36.100	(37)
Cr <sub>2</sub> O <sub>3</sub> ( $\alpha$ , $\beta$ )	--	-272.650	-270.150	-270.700	-279.600	(37)
NiO (c)	--	-57.300	-55.880	-60.400	-60.850	(37)
MgO (s)	-143.156	-143.700	-175.712	-174.008	-172.295	(38)
B <sub>2</sub> O <sub>3</sub> (c)	-303.062(38)	-303.640(38)	-296.550(38)	-292.655(38)	-305.800	(37)
Ag <sub>2</sub> O (c)	--	-7.200	-10.150	-8.900	-129.300	(37)
CaO (c)	--	-151.790	-153.000	-187.450	-185.450	(37)
Na <sub>2</sub> O (c,l)	--	-99.400	-131.500	-126.500	-121.590	(37)
CdO (c)	--	-62.200	-85.800	-83.800	--	(39)
BeO (c)	-142.620	-143.100	-142.287	-144.639	-144.064	(38)
Al <sub>2</sub> O <sub>3</sub> (c)	-398.697	-400.400	-402.581	-400.075	-397.172	(38)
CoO (c)	--	-57.100	-56.900	-60.500	-60.500	(37)
SiO <sub>2</sub> (c) (quartz)	-216.938	-217.500	-215.147	-225.941	-224.322	(38)
MoO <sub>2</sub> (c)	--	-140.800	-130.800	-130.800	-130.800	(37)
MoO <sub>3</sub> (c,l,g)	--	-178.100	-157.000	-113.800	-113.800	(37)
WO <sub>2</sub> (c)	-140.437	-140.940	-136.659	-133.822	-130.394	(38)
WO <sub>3</sub> (c)	-201.012	-201.460	-195.771	-193.177	-190.285	(38)
SnO (c)	--	-68.350	-68.400	-67.150	-65.900	(37)
Ta <sub>2</sub> O <sub>5</sub> (c)	--	-488.800	-478.750	-472.950	-428.300	(37)
ThO <sub>2</sub> (c)	--	-293.200	-292.300	-292.700	--	(39)
UO <sub>2</sub> (c)	--	-259.200	-261.300	--	--	(39)
V <sub>2</sub> O <sub>3</sub> (c)	--	-296.000	-289.000	-285.500	-287.000	(37)
MnO (s,l)	--	-92.050	-93.450	-97.800	-137.200	(37)
ZnO (c)	--	-83.250	-110.350	-108.100	--	(39)
HfO <sub>2</sub> (monoclinic)	--	-266.050	-261.200	-258.650	--	(39)
SrO (c)	--	-141.100	-140.800	-172.400	--	(39)
BaO	--	-133.500	-132.500	-167.000	-150.700	(37)
PbO (c) red	-52.341	-52.407	-49.785	-46.677	-84.935	(38)
PbO (c) yellow	-52.066	-50.387	-48.181	-87.655	-87.655	(38)
Au <sub>2</sub> O <sub>3</sub> (c)	--	-0.800	500 K = +0.100			(39)
HgO (c)	-20.969	-21.699	1000 K = -33.489			(38)
Standard Free Energy of Formation, $\Delta F_f$ kcal/g mole						
TiO <sub>2</sub> (c)	-220.919	-212.283	-160.942	--	-118.190	(38)
ZrO <sub>2</sub> (c)	-256.705	-247.704	-193.878	-172.373	-150.077	(38)
FeO (c,l)	--	-58.150	-39.850	-33.600	-27.650	(37)
Cu <sub>2</sub> O (c,l)	--	-36.400	-13.300	-6.100	+1.000	(37)
CuO (c,l)	--	-31.700	-5.400	+5.700	+16.400	(37)
Cr <sub>2</sub> O <sub>3</sub> ( $\alpha$ , $\beta$ )	--	-253.150	-178.600	-147.900	-115.600	(37)
NiO (c)	--	-50.570	-25.810	-15.100	-3.700	(37)
MgO (s)	-140.918	-135.981	-101.261	-76.699	-52.572	(38)
B <sub>2</sub> O <sub>3</sub> (c)	-297.080(38)	-284.725(38)	-211.576(38)	-183.855(38)	-164.800	(37)
Ag <sub>2</sub> O (c)	--	-2.500	+15.800	+24.700	+36.000	(37)
CaO (c)	--	-144.390	-114.200	-96.500	-73.500	(37)
Na <sub>2</sub> O (c,l)	--	-89.900	-131.500	-126.500	-121.500	(37)
CdO (c)	--	-55.100	-14.400	+9.000	--	(39)
BeO (c)	-140.561	-136.120	-108.276	-96.200	-84.157	(38)
Al <sub>2</sub> O <sub>3</sub> (c)	-392.241	-378.078	-286.086	-247.619	-209.834	(38)
CoO (c)	--	-51.500	-30.700	-21.400	-11.700	(37)
SiO <sub>2</sub> (c) (quartz)	-212.933	-204.530	-153.835	-131.315	-107.844	(38)
MoO <sub>2</sub> (c)	--	-126.100	-79.600	-62.500	-45.400	(37)

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TABLE 3. (CONTINUED)

Oxide	Oxide Temperature, K					Reference
	100	298	1500	2000	2500	
<u>Standard Free Energy of Formation, <math>\Delta F_f</math> kcal/g mole (continued)</u>						
MoO <sub>3</sub> (c,1,g)	--	-159.700	-95.900	-88.100	-81.600	(37)
WO <sub>2</sub> (c)	-136.293	-127.597	-76.989	-57.511	-38.818	(38)
WO <sub>3</sub> (c)	-195.006	-182.619	-111.379	-83.631	-56.574	(38)
SnO (c)	--	-61.400	-30.800	-18.150	-5.450	(37)
Ta <sub>2</sub> O <sub>5</sub> (c)	--	-456.550	-334.500	-287.300	-247.600	(37)
ThO <sub>2</sub> (c)	--	-279.200	-223.750	-200.900	--	(39)
UO <sub>2</sub> (c)	--	-246.600	-197.700	--	--	(39)
V <sub>2</sub> O <sub>3</sub> (c)	--	-277.000	-206.000	-179.000	-152.000	(37)
MnO (s,1)	--	-86.750	-65.600	-55.200	-42.900	(37)
ZnO (c)	--	-76.100	-38.950	-15.500	--	(39)
HfO <sub>2</sub> (monoclinic)	--	-251.750	-198.050	-177.400	--	(39)
SrO (c)	--	-134.000	-106.600	-88.400	--	(39)
BaO (c)	--	-126.500	-99.000	-86.000	-68.000	(37)
PbO (c) red	-49.977	-45.134	-16.634	-6.031	+13.598	(38)
PbO (c) yellow	-49.692	-44.949	-16.573	-5.622	+14.619	(38)
Au <sub>2</sub> O <sub>3</sub> (c)	--	+18.550	500 K = +31.450	--	--	(39)
HgO (c)	-18.741	-13.983	1000 K = +11.440	--	--	(38)
<u>Heat Capacity of the Oxide or Reaction Product, Cp cal/mole/K</u>						
TiO <sub>2</sub> (c)	4.430	13.196	18.390	--	19.250	(38)
ZrO <sub>2</sub> (c)	4.524	13.397	17.800	--	17.800	(38)
FeO (c,1)	--	11.502	14.630	--	1800 K 16.30	(40)
Cu <sub>2</sub> O (c,1)	--	16.599	21.74 (1200 K)	--	--	(40)
CuO (c,1)	--	10.70	15.27 (1250 K)	--	--	--
Cr <sub>2</sub> O <sub>3</sub> ( $\alpha$ , $\beta$ )	--	24.975	31.665	--	1800 K 32.370	(40)
NiO (c)	--	10.589	14.21	--	200 K 15.22	(40)
MgO (s)	1.865	8.906	12.701	--	13.035	(38)
B <sub>2</sub> O <sub>3</sub> (c)	4.987	15.050	35.000	--	--	(38)
Ag <sub>2</sub> O (c)	--	15.74	--	--	--	(40)
CaO (c)	--	10.235	13.221	--	2000 K 13.790	(40)
Na <sub>2</sub> O (c,1)	--	17.309	21.100 (1000 K)	--	--	(40)
CdO (c)	--	10.382	12.810	--	2000 K 13.820	(40)
BeO (c)	0.675	12.628	13.078	--	13.368	(38)
Al <sub>2</sub> O <sub>3</sub> (c)	3.069	18.889	31.620	--	34.100	(38)
CoO (c)	--	12.598	14.618	--	2000 K 15.630	(40)
SiO <sub>2</sub> (c) (quartz)	3.720	10.634	17.320	--	18.750	(38)
MoO <sub>2</sub> (c)	--	--	--	--	--	--
MoO <sub>3</sub> (c,1,g)	--	17.567	2.00	--	--	(40)
WO <sub>2</sub> (c)	4.560	13.414	20.736	--	24.395	(38)
WO <sub>3</sub> (c)	7.280	17.630	24.930	--	27.690	(38)
SnO (c)	--	10.993	14.406 (1273 K)	--	--	(40)
Ta <sub>2</sub> O <sub>5</sub> (c)	--	32.289	46.580	--	2000 K 49.972	(40)
ThO <sub>2</sub> (c)	--	14.896	20.090	--	2000 K 21.560	(40)
UO <sub>2</sub> (c)	--	15.224	21.456	--	2000 K 22.341	(40)
V <sub>2</sub> O <sub>3</sub> (c)	--	24.665	36.252	--	1800 K 37.750	(40)
MnO (s,1)	--	10.697	13.981	--	1800 K 14.575	(40)
ZnO (c)	--	9.619	13.444	--	2000 K 14.095	(40)
HfO <sub>2</sub> (monoclinic)	--	14.092	20.357	--	2000 K 21.047	(40)
SrO (c)	--	10.760	13.952	--	1800 K 14.350	(40)
BaO (c)	--	11.359	14.571	--	2000 K 15.530	(40)
PbO (c) red	6.422	10.943	16.600	--	20.600	(38)
PbO (c) yellow	6.581	10.958	15.110	--	17.847	(38)
Au <sub>2</sub> O <sub>3</sub> (c)	--	--	--	--	--	--
HgO (c)	6.796	10.331	1000 K = 14.200	--	--	(38)

of the standard free energy of formation of the metal oxide, also listed in Table 3 shows that the metal reacts spontaneously with oxygen. That is, a thermodynamic driving force for reaction of a metal with oxygen exists if  $\Delta F_f^\circ$  is negative in sign.

It should be noted that all metals listed in Table 3, excepting gold and possibly platinum, are thermodynamically reactive with oxygen at room temperature and lower temperatures. The fact that a number of metals may be used to contain and transport oxygen at room and lower temperatures is dependent upon a low reaction rate or upon the presence of a barrier, such as an oxide film, for protection. These latter factors on which compatibility of metal-oxygen systems are dependent are in the field of kinetics or reaction mechanism, a science that is more difficult and less understood today than the study of chemical thermodynamics. Any situation that will lower the activation energy, such as mechanical stress or shock, can promote oxidation of metals. If an oxide film is involved, any flow or force that removes oxide can promote reaction of metal-oxygen and, therefore, failure of the system.

Thermodynamically, it is surprising that, at room temperature, any metal excepting gold is compatible with oxygen. Further, it can be seen from the literature data that with halogens all metals listed in Table 3 are thermodynamically unstable. Thus, an oxidizer such as chlorine trifluoride,  $ClF_3$ , is completely dependent on reaction kinetics and mechanism for compatibility with metals. A similar situation exists for nitrogen tetroxide in contact with metals.

From the standard free energy of formation of an oxide, its dissociation pressure can be calculated. In general, if  $\Delta F_f^\circ$  of an oxide is -10,000 cal/mole or more negative, the oxide will not dissociate in liquid oxygen-metal systems, nor will the oxide dissociate in gaseous oxygen-metal systems at a chamber pressure of one atmosphere or higher.

For some metal oxides the value for  $\Delta F_f^\circ$  becomes positive at higher temperatures, as seen in Table 3. When  $\Delta F_f^\circ$  is negative, the tendency is for metal to react with oxygen. But a  $\Delta F_f^\circ$  positive value indicates dissociation of an oxide to free metal and oxygen.

In calculating ignition temperatures, a heat or energy balance must be made. The values of the heat of formation of the metal oxides as well as the heat capacity of the oxide are required in the energy balance. For this reason, the heat capacity of various metal oxides is also given in Table 3.

#### Heat-Capacity Values

As stated above, the heat capacity of the metal is required in an energy balance needed in ignition-temperature calculations. Heat capacities for the metals are given in Table 4.

TABLE 4. HEAT CAPACITY OF METALS<sup>(41)</sup>

Metal	Heat Capacity, cal/deg/GFW, K		
	298	1500	2500
Fe (s,1)	5.98 (s)	8.06 (s)	8.00 (1)
Zr (s,1)	6.01 (s)	7.27 (s)	8.00 (1)
Fe (s,1)	5.99 (s)	8.77 (s)	10.78 (1)
Cu (s,1)	5.85 (s)	7.50 (1)	7.50 (1)
Cr (s,1)	5.56 (s)	9.23 (s)	9.70 (1)
Ni (s,1)	6.23 (s)	8.70 (s)	9.20 (1)
Mg (s,l,g)	5.96 (s)	4.97 (g)	4.98 (g)
B (s,1)	2.63 (s)	6.67 (s)	7.50 (1)
Ag (s,l,g)	6.09 (s)	7.50 (1)	4.97 (g)
Ca (s,l,g)	6.30 (s)	7.40 (1)	5.22 (g)
Na (s,l,g)	6.74 (s)	4.97 (g)	5.00 (g)
Cd (s,l,g)	6.22 (s)	4.97 (g)	4.97 (g)
Be (s,1)	3.93 (s)	7.74 (s)	7.50 (1)
Al (s,1)	5.82 (s)	7.00 (1)	7.00 (1)
Co (s,1)	5.89 (s)	9.60 (s)	8.30 (1)
Si (s,1)	4.80 (s)	6.83 (s)	7.00 (1)
Mo (s)	5.68 (s)	7.65 (s)	9.36 (s)
W (s)	5.92 (s)	6.91 (s)	7.74 (s)
Pt (s,1)	6.19 (s)	7.75 (s)	8.30 (1)
Sn (s,1)	6.30 (s)	7.30 (1)	7.30 (1)
Ta (s)	6.08 (s)	6.90 (s)	7.32 (s)
Th (s,1)	6.53 (s)	11.99 (s)	11.00 (1)
U (s,1)	6.64 (s)	9.15 (1)	9.15 (1)
V (s,1)	5.91 (s)	8.74 (s)	9.50 (1)
Mn (s,l,g)	6.29 (s)	11.30 (s)	5.04 (g)
Zn (s,l,g)	6.07 (s)	4.97 (g)	4.97 (g)
Hf (s,1)	6.10 (s)	7.54 (s)	8.00 (1)
Sr (s,l,g)	6.30 (s)	7.40 (1)	5.34 (g)
Ba (s,l,g)	6.30 (s)	7.50 (1)	6.95 (g)
Pb (s,l,g)	6.32 (s)	7.00 (1)	7.00 (1)
Au (s,l,g)	6.07 (s)	7.00 (1)	7.00 (1)
Hg (l,g)	6.69 (1)	4.97 (g)	4.97 (g)

#### Thermophysical Properties of Metals and Their Oxides

In Tables 5 and 6, the melting points, boiling points, densities, and heats of fusion and vaporization of metals and their oxides are listed. The vapor pressure of the metals and their oxides are listed in Tables 7 and 8, respectively. The ratio of density of metal to its oxide is of interest in the study of oxide-film mechanism. Vapor pressures are of interest in assessing the behavior of metal skin temperatures at high altitude flight or on reentry of a missile.

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TABLE 5. THERMOPHYSICAL PROPERTIES OF METALS

Metal	Melting Point, K(a)	Boiling Point, K(a)	Density, g/cc(b)	Heat of Fusion, cal/mole at M. P. (c)	Heat of Vaporization, cal/mole at B. P. (c)
Ti	150	3550	4.54	--	--
Zr	2125	4650	6.53 ± 0.01 (calc)	--	--
Fe	1812	3160	7.874 (20 c)	3560	84600
Cu	1356	2855	8.96 (20 c)	3110	72810
Cr	2176(d)	2915	7.18-7.20 (20 c)	3930	--
Ni	1728	3110	8.902 (25 c)	4200	87300
Mg	923	1390	1.738 (20 c)	2160	32520
B	2300	4200	2.34	--	--
Ag	1234.0	2450	10.50 (20 c)	2212	60720
Ca	1123	1765	1.55 (20 c)	2230	36580
Na	370.97	1163	0.9711 (20 c)	630	23120
Cd	594	1038	8.65 (20 c)	1460	23870
Be	1356	2750	1.848 (20 c)	2500	--
Al	932	2720	2.6989 (20 c)	2550	61020
Co	1768	3150	8.9 (20 c)	3660	--
Si	1683	2950	2.33 (25 c)	9470	--
Mo	2890	5100	10.22 (20 c)	[6660]	[128000]
W	3650	5800	19.3 (20 c)	[8400]	[176000]
Pt	2043	4100	21.45 (20 c)	4700	[107000]
Sn	505	2960	5.75 (gray), 7.31 (white)	1720 (Sn <sub>4</sub> )	6800 (Sn <sub>4</sub> )
Ta	3270	5700	16.6	--	--
Th	1960	4500	11.66	4 cal/g(e)	--
U	1406	4200	18.95	20 cal/g(e)	454 1400 K cal/g
V	2190	3650	6.11 (18.75 c)	--	--
Mn	1517	2314	7.21-7.44	3450	55150
Zn	692.7	1181	7.133 (25 c)	1595	27430
Hf	2250	5500	13.29	--	--
Sr	1043	1640	2.54	2190	33610
Ba	983	1910	3.5 (20 c)	[1400]	35670
Pb	600.6	2024	11.35 (20 c)	1224	42060
Au	1336	2980	19.32 (20 c)	3039	81800
Hg	234.29	629.88	13.546 (20 c)	557	13980

(a) Reference 41.  
(b) Reference 43.

(c) Reference 42.  
(d) Reference 39.

(e) Reference 45.

TABLE 6. THERMOCHEMICAL PROPERTIES OF METAL OXIDES

Oxide	Melting Point, C(a)	Boiling Point, C(a)	Density, g/cc(a)	Heat of Fusion, kcal/mole(b)	Heat of Vaporization, kcal/mole(b)
TiO <sub>2</sub> (c)	1830-1850	2500-3000	4.26	(11.4)	--
ZrO <sub>2</sub>	2715	--	5.6	20.8	--
FeO	1420	--	5.7	(7.7)	--
Cu <sub>2</sub> O	1235	-0, 1800	6.0	(13.4)	--
CuO	1326	--	6.3-6.49	28.20	--
Cr <sub>2</sub> O <sub>3</sub>	2435	4000	5.21	--	--
NiO	1990	--	6.65	12.1(d)	--
MgO	2800	3600	3.58	18.5	--
B <sub>2</sub> O <sub>3</sub>	460	ca 1860	2.46 ± 0.01	5.5(d)	--
Ag <sub>2</sub> O	d300	--	7.143	--	--
CaO	2580	2850	3.25-3.38	12.24	--
Na <sub>2</sub> O	subl 1275	--	2.37	11.2(d)	--
CdO	d800	subl 1559	6.95	--	53.820
BeO	2530 ± 30	ca 3900	3.01	14.0	143.5
Al <sub>2</sub> O <sub>3</sub>	2045	2980	3.965	26.0	--
CoO	1935	--	6.45	9.6(d)	--
SiO <sub>2</sub> (quartz)	1610	2230-2590	2.635-2.660	3.4	--
MoO <sub>2</sub>	2607(c)	--	6.47	12.5	--
MoO <sub>3</sub>	795	subl 1155	4.692	--	--
WO <sub>2</sub>	1550-1600 in Na	ca 1430, subl 800	12.11	--	--
WO <sub>3</sub>	1473	--	7.16	15.0(d)	--
PtO	550	--	14.9	--	--
SnO	1080	--	6.446	--	--
Ta <sub>2</sub> O <sub>5</sub>	1800	--	8.2	--	--
ThO <sub>2</sub>	3050	4400	264.04	--	--
UO <sub>2</sub>	2500	--	10.96	--	--
V <sub>2</sub> O <sub>3</sub>	1970	--	4.87	--	--
MnO	2058	--	5.43-5.46	13.0(d)	--
ZnO	1975	--	5.606	4.470	--
HfO <sub>2</sub>	2812	5400	9.68	--	--
SnO	2430	3000	4.7	--	--
BaO	1923	ca 2000	5.72	13.8(d)	--
PbO	888	--	9.53	2.820	51.310
Au <sub>2</sub> O <sub>3</sub>	-0, 160	-30, 250	--	--	--
HgO	d500	--	11.1	--	--

(a) Reference 43.

(b) Reference 42.

(c) Reference 37.

(d) Reference 1.

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TABLE 7. VAPOR PRESSURE OF METALS<sup>(44)</sup>

Metal	Vapor Pressure, atmosphere, K			Metal	Vapor Pressure, atmosphere, K		
	298	1500	2500		298	1500	2500
Ti	$1.37 \cdot 10^{-75}$	$1.29 \cdot 10^{-9}$	$4.57 \cdot 10^{-3}$ (a)	Mo	$4.8 \cdot 10^{-109}$	$4.6 \cdot 10^{-16}$	$5.27 \cdot 10^{-7}$
Zr	$3.21 \cdot 10^{-100}$	$1.22 \cdot 10^{-14}$	$2.38 \cdot 10^{-6}$	W <sub>o</sub>	$9.70 \cdot 10^{-142}$	$1.01 \cdot 10^{-22}$	$9.31 \cdot 10^{-11}$
Fe	$1.1 \cdot 10^{-65}$	$1.40 \cdot 10^{-7}$	$5.69 \cdot 10^{-2}$ (a)	Pt	$8.7 \cdot 10^{-12}$	$1.4 \cdot 10^{-12}$	$1.55 \cdot 10^{-4}$ (a)
Cu	$4.70 \cdot 10^{-53}$	$7.53 \cdot 10^{-6}$	$1.68 \cdot 10^{-1}$	Sn	$1.5 \cdot 10^{-47}$	$1.03 \cdot 10^{-5}$	$0.246$ (a)
Cr	$2.16 \cdot 10^{-62}$	$4.00 \cdot 10^{-6}$ (b)	$8.67 \cdot 10^{-2}$	Ta	$3.22 \cdot 10^{-130}$	$1.37 \cdot 10^{-20}$	$1.03 \cdot 10^{-9}$
Ni	$5.0 \cdot 10^{-68}$	$4.39 \cdot 10^{-9}$ (b)	$4.38 \cdot 10^{-2}$ (a)	Th	$2.3 \cdot 10^{-94}$	$9.1 \cdot 10^{-13}$ (b)	$2.50 \cdot 10^{-6}$
Mg	$1.5 \cdot 10^{-20}$	$1.19$ (c)	--	U	$7.91 \cdot 10^{-87}$	$3.51 \cdot 10^{-12}$	$2.94 \cdot 10^{-5}$
B	--	--	--	V	$5.6 \cdot 10^{-83}$	$1.21 \cdot 10^{-9}$ (b)	$2.06 \cdot 10^{-3}$ (e)
Ag	$7.6 \cdot 10^{-44}$	$3.36 \cdot 10^{-4}$	1.35	Mn	$1.7 \cdot 10^{-12}$ (a)	$1.32 \cdot 10^{-3}$ (f)	$2.22$ (L)
Ca	$7.14 \cdot 10^{-26}$	0.167	--	Zn	$2.12 \cdot 10^{-17}$	1.17(f)	--
Na	$2.64 \cdot 10^{-14}$	5.85(c)	--	Hf	--	--	--
Cd	$2.78 \cdot 10^{-14}$	1.86(d)	--	Sr	$1.14 \cdot 10^{-23}$	0.739(b)	--
Be	$2.59 \cdot 10^{-51}$	$1.52 \cdot 10^{-5}$	0.265	Ba	$1.45 \cdot 10^{-24}$	0.116	--
Al	$2.38 \cdot 10^{-50}$	$9.87 \cdot 10^{-5}$ (b)	$5.64 \cdot 10^{-1}$ (a)	Pb	$4.09 \cdot 10^{-29}$	$6.27 \cdot 10^{-2}$ (b)	$1.52$ (g)
Co	$2.5 \cdot 10^{-67}$	$6.23 \cdot 10^{-8}$	$4.18 \cdot 10^{-2}$ (a)	Au	$8.85 \cdot 10^{-58}$	$8.43 \cdot 10^{-7}$	$4.77 \cdot 10^{-2}$
Si	--	--	--	Hg	$2.550 \cdot 10^{-6}$	6.086(h)	--

(a) 2600 K. (b) 1600 K. (c) 1400 K. (d) 100 K. (e) 2400 K. (f) 1200 K. (g) 2100 K. (h) 700 K.

TABLE 8. VAPOR PRESSURE OF METAL OXIDES

Oxide	Vapor Pressure, atmospheres, K						Reference
	298	1000	1500	2000	2500	3000	
TiO <sub>2</sub>	$1.98 \cdot 10^{-92}$	$4.36 \cdot 10^{-22}$	$4.45 \cdot 10^{-12}$	$4.37 \cdot 10^{-7}$	--	--	(37)
ZrO <sub>2</sub>	--	--	$2.28 \cdot 10^{-17}$	$3.94 \cdot 10^{-11}$	$2.18 \cdot 10^{-7}$	$5.22 \cdot 10^{-5}$	(37)
FeO	--	--	--	--	--	--	--
Cu <sub>2</sub> O	--	--	--	--	--	--	--
CuO	--	$2.5 \cdot 10^{-4}$	1 (1400 K)	--	--	--	(45)
Cr <sub>2</sub> O <sub>3</sub>	--	--	--	--	--	--	--
NiO	--	$8.28 \cdot 10^{-17}$	$1.43 \cdot 10^{-8}$	$1.45 \cdot 10^{-4}$	--	--	(37)
MgO	--	--	--	$<7.5 \cdot 10^{-8}$	--	--	(37)
B <sub>2</sub> O <sub>3</sub>	--	$6.03 \cdot 10^{-11}$	$2.72 \cdot 10^{-5}$	$1.82 \cdot 10^{-2}$	$8.93 \cdot 10^{-1}$	--	(37)
Ag <sub>2</sub> O	--	--	--	--	--	--	--
CaO	$9.18 \cdot 10^{-86}$	$3.09 \cdot 10^{-21}$	$4.19 \cdot 10^{-12}$	$1.55 \cdot 10^{-7}$	$8.51 \cdot 10^{-5}$	--	(38)
Na <sub>2</sub> O	$1.18 \cdot 10^{-72}$	$4.97 \cdot 10^{-16}$	--	--	--	--	(37)
CdO	$8.83 \cdot 10^{-35}$	$3.62 \cdot 10^{-6}$	$4.06 \cdot 10^{-2}$	--	--	--	(37)
BeO	--	--	--	--	$10^{-5}$	$2.5 \cdot 10^{-3}$	(45)
Al <sub>2</sub> O <sub>3</sub>	--	--	--	$2.5 \cdot 10^{-7}$ (2150 K)	$10^{-4}$	--	(45)
CoO	--	--	--	--	--	--	--
SiO <sub>2</sub>	--	--	--	$1.0 \cdot 10^{-7}$	--	--	(37)
MoO <sub>3</sub>	$2.01 \cdot 10^{-45}$	$5.0 \cdot 10^{-4}$	$6.0 \cdot 10^{-1}$	(1350 K)	--	--	(45)
MoO <sub>2</sub>	--	--	--	$1.08 \cdot 10^{-3}$	--	--	(37)
WO <sub>2</sub>	--	--	--	--	--	--	--
WO <sub>3</sub>	$1.19 \cdot 10^{-80}$	$6.28 \cdot 10^{-14}$	$1.82 \cdot 10^{-4}$	--	--	--	(37)
Pt	--	--	--	--	--	--	--
SnO	--	--	--	--	--	--	--
Ta <sub>2</sub> O <sub>5</sub>	--	--	--	--	--	--	--
ThO <sub>2</sub>	--	--	--	$5.0 \cdot 10^{-9}$	$5.0 \cdot 10^{-6}$	$7.5 \cdot 10^{-4}$	(45)
UO <sub>2</sub>	--	--	$10^{-12}$	$10^{-7}$	$2.5 \cdot 10^{-4}$	--	(45)
V <sub>2</sub> O <sub>3</sub>	--	$2.5 \cdot 10^{-6}$ (1875 K)	--	--	--	--	(45)
MnO	--	--	--	--	--	--	--
ZnO	--	--	--	--	--	--	--
HfO <sub>2</sub>	--	--	--	--	--	--	--
SrO	--	--	$2.5 \cdot 10^{-10}$	$7.5 \cdot 10^{-6}$	$3.0 \cdot 10^{-3}$	$1.1 \cdot 10^{-1}$	(45)
BaO	$6.32 \cdot 10^{-68}$	$2.09 \cdot 10^{-15}$	$5.66 \cdot 10^{-8}$	$2.94 \cdot 10^{-4}$	--	--	(37)
PbO	--	$2.63 \cdot 10^{-5}$	$8.13 \cdot 10^{-2}$	--	--	--	--
Al <sub>2</sub> O <sub>3</sub>	--	--	--	--	--	--	--
HgO	--	--	--	--	--	--	--

The thermal conductivity of metals is given in Table 9 and of metal oxides in Table 10. These values are used in calculating the extent of heat losses and energy balances in ignition-temperature calculations.

#### Theoretical Analysis

An extensive amount of experimental work has been reported on the ignition temperature of metals and their alloys in liquid and gaseous oxygen under widely varying conditions. Many observations and conclusions have been reached on the basis of this experimental work. These observations, discussed under the experimental sections of this report, form the basis of a qualitative model of the ignition process.

By contrast, there have been relatively few efforts made to correlate experimental ignition temperatures with those calculated theoretically from the thermophysical properties of metals and kinetic data of low-temperature metal-oxygen reactions. In the theoretical analysis, no claim is made to a quantitative comparison between theory and experiment, but a reasonable enough qualitative comparison is made to justify the postulate

that a direct relation exists between low-temperature oxidation and ignition.

The theoretical analysis can be divided into two groups. The first group considers the massive metal reacting with gaseous oxygen, and the second grouping is gaseous oxygen reacting with metal particles. No attempt has been reported on the theoretical calculation of a metal with liquid oxygen. Several of the theoretical analyses of the massive and particle forms of metal with gaseous oxygen are discussed below. Some of the factors that influence the metal-liquid oxygen reaction are also summarized. The basis of this summary on LOX-metal reaction is taken in part from a dynamic analysis given in Appendix B.

#### Calculation of Ignition Temperatures

##### Reaction of Massive Metal With Gaseous Oxygen

Fassell, et al.,<sup>(5)</sup> investigated the ignition temperature of massive magnesium and magnesium alloys in oxygen from 0.166 to 10 atmospheres pressure. They defined the ignition temperature

TABLE 9. THERMAL CONDUCTIVITY OF METALS

Metal	Material	Thermal Conductivity, Btu/(hr)(ft)(F)						Reference
		100	500	1000	1500	2000	2500	
Ti	99% pure	12.3	10.8	10.0	--	--	--	(45)
Zr	99.9% pure	15.0	14.3	14.4	--	--	--	(45)
Fe	Armco iron	42.0	34.0	24.0	--	17.0	17.0	(45)
Cu	99% pure	232.0	217.0	204.0	192.0	--	--	(45)
Cr	Vacuum melted or electron deposited and annealed >3000 R	52.0	48.0	40.0	36.0	--	--	(45)
Cr	Electron deposited as received	13.0	20.0	38.0	36.0	--	--	(45)
Ni	Grade A	36.6	28.5	29.1	33.5	38.0	42.5	(45)
Mg	99% pure	79.0	77.0	--	--	--	--	--
Ag	99.4% pure	243.0	226.0	200.0	--	--	--	(45)
Ca	0.3 cal/sq cm/cm/sec/C at 20 C	--	--	--	--	--	--	(46)
Na	0.32 cal/sq cm/cm/sec/C at 20 C	--	--	--	--	--	--	(46)
Cd	0.22 cal/sq cm/cm/sec/C at 20 C	--	--	--	--	--	--	(46)
Be	96% pure	104.0	76.0	53.0	44.0	--	--	(45)
Al	99.95% pure	129.0	120.0	107.0	--	--	--	(45)
Co	99% pure	--	--	--	--	--	--	(45)
Si	99.8% pure	70.0	34.0	22.0	17.8	--	--	(45)
Mo	Arc melted, unalloyed	78.8	75.0	70.0	64.0	58.0	51.5	(45)
W	99.94% pure	90.0	80.0	73.0	69.0	65.0	62.0	(45)
Pt	Spectroscopic purity	41.0	40.5	39.7	39.0	38.4	37.6	(45)
Sn	0.150 cal/sq cm/cm/sec/C at 0 C	--	--	--	--	--	--	(46)
Ta	Sintered	36.0	37.5	39.5	41.8	43.0	45.0	(45)
Th	"Probably impure"	17.2	20.0	--	--	--	--	(45)
U	99% pure	14.4	17.8	20.9	24.7	--	--	(45)
V	Unalloyed	21.0	--	--	--	--	--	(45)
Mn	99.9% pure	--	--	--	--	--	--	(45)
Zn	0.27 cal/sq cm/cm/sec/C at 25 C	--	--	--	--	--	--	(46)
Hf	2% Zr	--	12.3	11.8	--	--	--	(45)
Pb	0.083 cal/sq cm/cm/sec/C at 0 C	--	--	--	--	--	--	(46)
Au	99.9% pure	--	--	--	--	--	--	(45)
Hg	0.0196 cal/sq cm/cm/sec/C at 0 C	--	--	--	--	--	--	(46)

23  
TABLE 10. THERMAL CONDUCTIVITY OF METAL OXIDES

Oxide	Material	Thermal Conductivity, Btu/(hr)(ft)(F)						Reference
		100	500	1000	1500	2000	2500	
TiO <sub>2</sub>	94-100% dense	4.0	3.0	2.25	1.80	3.0	--	(13)
ZrO <sub>2</sub>	CaO stabilized	--	0.9	1.0	1.1	1.15	1.2	(13)
ZrO <sub>2</sub>	4-5 wt% CaO stabilized	--	--	0.4	0.45	0.5	--	(13)
ZrO <sub>2</sub>	Unstabilized	--	--	--	--	0.9	0.85	(13)
NiO	100% dense	--	5.5	3.5	2.5	--	--	(13)
MgO	Single crystal	--	19.0	11.0	9.0	5.0	5.5	(13)
MgO	90-100% dense polycrystal	25.0	15.0	8.0	3.0	1.5	2.0	(13)
CaO	Density of $3.36 \pm 0.4$ g/cm <sup>3</sup>	--	6.0	5.0	5.0	--	--	(13)
BeO	Polycrystalline rods, 93-96% dense	175.0	70.0	30.0	20.0	15.0	15.0	(13)
Al <sub>2</sub> O <sub>3</sub>	Single crystal	20.0	11.5	8.0	7.0	6.5	--	(13)
Al <sub>2</sub> O <sub>3</sub>	Polycrystalline, 90-100% dense	20.0	11.5	8.0	4.5	3.0	3.0	(13)
SiO <sub>2</sub>	Parallel to c axis	--	3.6	--	--	--	--	(44)
SiO <sub>2</sub>	Perpendicular to c axis	--	2.1	--	--	--	--	(44)
ThO <sub>2</sub>	Hot pressed, >96% dense	7.0	--	--	--	--	--	(13)
ThO <sub>2</sub>	Slip cast, pressed and sintered, theoretical density	--	4.5	3.0	2.5	2.0	1.9	(13)
ThO <sub>2</sub>	Same as above, only 83% density	--	3.0	2.5	2.0	1.8	1.7	(13)
UO <sub>2</sub>	93-96% dense	--	3.3	2.5	2.25	1.75	1.5	(13)
MnO	Single crystal	5.5	--	--	--	--	--	(13)
ZnO	100% dense	--	9.0	5.0	--	--	--	(13)
HfO <sub>2</sub>	Not given	0.95	0.90	0.85	0.80	--	--	(44)

as the "explosion temperature", where the rate of oxidation suddenly becomes very rapid and a "flame" appears. These authors compared their experimental ignition temperatures with those calculated by Eyring and Zwolinski. (47) A comparison of the experimental ignition temperatures with the calculated values of Eyring and Zwolinski are given in Table 11 from the paper of Fassell, et al. (5) It can be seen that the experimental temperatures are independent of oxide film thickness, contrary to the theory of Eyring and Zwolinski. Although the agreement of ignition temperatures obtained by theory and experiment was not exact, theory does give a result that would be satisfactory for screening a structural material for use in metal-oxygen systems.

Eyring and Zwolinski (47) derived the following quantitative theoretical treatment of ignition temperatures of magnesium and its alloys as presented by Fassell, et al.

According to Fassell, et al, Eyring and Zwolinski concluded that a metal sample will ignite

TABLE 11 EXPERIMENTAL VERSUS CALCULATED IGNITION TEMPERATURES OF MAGNESIUM AND MAGNESIUM ALLOYS

Alloy	Oxide-Film Thickness, cm	Ignition Temperature, C	
		Calculated (47)	Experimental (5)
1.78% Al	$1.35 \cdot 10^{-2}$	551	600(a)
3.81% Al	$1.35 \cdot 10^{-2}$	460	582
Pure Mg	$5 \cdot 10^{-2}$	642	623
Pure Mg	$1 \cdot 10^{-1}$	618	623
Pure Mg	$2 \cdot 10^{-1}$	595	623
Pure Mg	$5 \cdot 10^{-7}$	--	623

(a) Sontis and Rhines obtained a value of 548 C.

if the conduction of heat through the oxide film is insufficient to remove the heat produced at the metal-oxide interface as a result of the oxidation reaction.

Eyring and Zwolinski state that as a result of inadequate loss of heat through the film, the temperature at the metal-oxide boundary will increase accelerating the rate of the reaction. The progressive acceleration of the rate of oxidation will result in the vaporization of magnesium with subsequent ignition of the metal vapor.

The thermal energy lost by conduction from the sample can be equated to the thermal energy produced by the oxidation of the sample. This relationship is expressed by the equation

$$x \frac{(T-T_o)}{d} = \frac{\Delta H}{N} v \quad (1)$$

where  $x$  is the thermal conductivity,  $v$  is the rate of oxidation,  $T$  is the temperature at the metal-oxide interface,  $T_o$  is the temperature at the outer surface of the film,  $d$  is the thickness of the oxide film,  $\Delta H$  is the heat of formation, and  $N$  is Avogadro's number. According to the proposed theory, ignition will occur at the instant the thermal balance represented by Equation (1) is destroyed.

The reaction rate,  $v$ , from the Theory of Absolute Reaction Rates may be written as

$$v = C_s \frac{kT}{h} e^{-E/kT} \quad (2)$$

where  $C_s$  is the number of adsorption sites on metal atoms/sq cm,  $k$  is Boltzmann's constant,  $h$  is Planck's constant,  $T$  is the temperature, °K,  $E$  is the activation energy. On substituting Equation (2) in Equation (1) the following equation is obtained

$$x \frac{(T-T_o)}{d} = C_s \frac{kT}{h} e^{-E/kT\Delta H} \frac{AM}{N AF} \quad (3)$$

where  $AM/AF$  represents a roughness factor. Rewriting Equation (3) in a more convenient form

$$T_o = \left( 1 - C_s \frac{kd\Delta HF}{xhN} e^{-E/RT} \right) T. \quad (4)$$

By using the values given below in Equation (4), Eyring and Zwolinski calculated the values for the ignition temperature of magnesium shown in Table 11.

$$\begin{aligned} C_s &= 1.1 \times 10^{15} \text{ Mg atom/sq cm} \\ k &= 1.38 \times 10^{-16} \text{ ergs/K} \\ \Delta H &\approx 146 \text{ kg-cal/mol} \\ F &= AM/AF = 16 \\ h &= 6.62 \times 10^{-27} \text{ erg sec} \\ x &= 2.8 \times 10^{-4} \text{ cal cm } ^\circ\text{C}^{-1} \text{ cm}^{-2} \text{ sec}^{-1} \\ N &= 6.02 \times 10^{23} \text{ atoms/mol} \end{aligned}$$

$$E = 42.7 \text{ kg-cal/mol for 1.78% Al-Mg alloy from Reference 48}$$

$$E = 50.5 \text{ kg-cal/mol for Mg from Reference 48.}$$

Thus, the theory of Eyring and Zwolinski indicates that the ignition temperature is dependent on the oxide film thickness.

Some of the discrepancy between these calculated and experimental values may be explained by the observation that the time-delay experiments indicate the ignition temperature of magnesium is independent of the nonprotective oxide film thickness.

Fassell, et al, conclude that from the ignition temperatures of magnesium and magnesium alloys, as cited above, it is obvious that none of the experimental values agrees exactly with the calculated values, and that there is some conflict as to the exact definition of the ignition temperature.

Higgins and Schultz<sup>(49)</sup> noted the conflict in the experimental measurements of Fassell, et al, and the theoretically calculated values of Eyring and Zwolinski. They proposed a solution to this paradox by a slight modification in the Eyring-Zwolinski theory. Higgins and Schultz suggested that the terms of  $T$ ,  $T_o$ , and  $d$  be redefined in Equation (1) as follows: for any given microscopic granule,  $T$  is now defined as a mean temperature in the interior of the granule at the metal-oxide interface;  $T_o$  is now defined as a mean

temperature at the external surface of the oxide film that coats each granule; allowance must be made for the probable nonuniformity of thickness of oxide coating on the granule, so that  $d$  is now defined as a mean thickness of the oxide film. It is evident that in an aggregate of small coated granules of approximately the same size,  $T$  for one granule may be nearly identical with  $T$  for adjacent granules. Moreover, in this case,  $T$  for the first granule may be nearly identical with  $T_o$  for adjacent granules and vice versa. In this case, the temperature gradient  $(T-T_o)/d$  across the oxide film becomes vanishingly small, so that the condition of inequality of Equation (1) is easily satisfied, resulting in ignition.

Hill, et al,<sup>(3)</sup> studied the high-temperature oxidation and ignition of metals. Their objective was to assess the possibility of ignition of aircraft construction metals under high-temperature flight conditions. A theory for the spontaneous ignition of metals was derived on the basis of the first law of thermodynamics. They claim that a good correlation of experimental and theoretical spontaneous ignition temperatures was obtained for steel in supersonic air streams. Comparable spontaneous ignition temperatures were obtained by simulation in an atmosphere of oxygen. The comparison of experimental and theoretical ignition temperatures is shown in Figure 5.

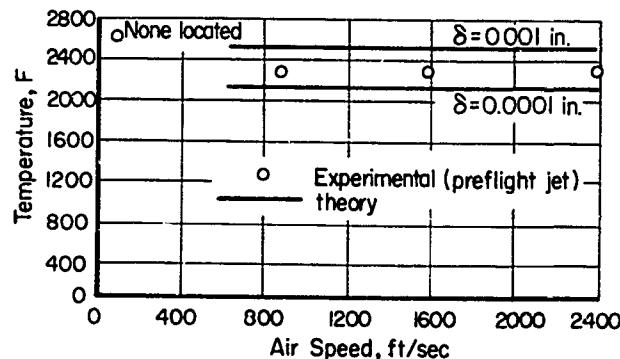


FIGURE 5. SPONTANEOUS IGNITION TEMPERATURE COMPUTATION FOR 1020 STEEL AT A STAGNATION TEMPERATURE OF 600 F AND 1 ATMOSPHERE PRESSURE<sup>(3)</sup>

In this work, Hill, et al, represented the rate of heat generation by oxidation,  $Q_o$ , by the following equation in which  $\delta$  is the oxide thickness

$$Q_o = \frac{134,500}{\delta} e^{-42,170}. \quad (5)$$

In their consideration of oxidation and ignition, they postulated a metallic surface oxidizing at high temperature. When the rate of heat released by oxidation, as shown in Equation (5), is equal to the losses made up of convection, conduction,

and radiation, a critical point is reached. They define this critical point as the spontaneous ignition temperature.

In order to determine whether the spontaneous ignition temperature can be calculated for steel in a supersonic air stream, computations were made for the conditions of the round-nose rods tested in the preflight jet of the Langley Pilotless Aircraft Research Station at Wallops Island, Virginia. The test conditions are stated in Figure 5. The spontaneous ignition temperature equation, which is a form of the first law of thermodynamics, is

$$Q_o = Q_{CONV} + Q_{RAD}, \quad (6)$$

or,

$$\frac{134,500}{\delta} e^{-\frac{42,170}{T}} = 1.32 \frac{k}{d} R^{0.5} N_{Pr}^{0.4} (T_{AW} - T) + 0.000048 e \left( \frac{T}{100} \right)^4. \quad (7)$$

$Q_o$  and  $\delta$  are defined in Equation (5), and  $k$  is the conductivity of air,  $d$  the nose diameter of the specimen,  $R$  the Reynolds number,  $N_{Pr}$  the Prandtl number,  $T_{AW}$  is the adiabatic wall temperature, and  $e$  is the emissivity. Conduction is omitted because the rods were quite uniformly heated. The first term represents oxidation and is taken from Equation (5). The second term is Sibulkin's theory for the heat transfer on a hemispherical nose, which, in this case, had a diameter of 3/8 inch. The last term is the usual expression for radiation. The value of emissivity was taken as 0.88. The unknown quantity  $T$ , the surface temperature for equilibrium conditions, appears in each term. The solutions of this equation for oxide thicknesses of 0.0001 and 0.001 inch are plotted in Figure 5. The theory shows a slight drop in spontaneous ignition temperature with air speed because the convection represents a loss. The measured spontaneous ignition temperatures also show a slight drop with speed at the higher speed range. At 150 ft/sec, no ignition was obtained, although the specimens were heated to or near melting. Insufficient oxygen, together with nitrogen enrichment of the boundary layer, seems to be the most probable cause of the failure to ignite at low air speed, although reduced erosion may possibly affect the result.

Hill, et al, point out that in their analysis, the following limitations and conditions are apparent:

- (1) The method cannot apply at oxide thicknesses approaching zero
- (2) The diffusion equation given should apply to metals over any range of conditions for which their oxidation behavior fits the parabolic equation.

Reynolds defined an ignition temperature through a thermal definition relating rate of oxidation to the heat-transfer parameters of radiation and convection.<sup>(2)</sup> An outline of his derivation follows.

An energy balance is made of a body of arbitrary shape that is being heated spontaneously. Ignition will occur when the exothermic oxidation rate exceeds the cooling rate caused by convection and radiation. Conduction is not considered as a factor in heat loss. The resulting energy balance of an object of arbitrary shape results in a complex partial differential equation, whose solution describes the temperature-time behavior of all points on the object. This equation is shown by Reynolds as

$$\frac{C}{A} \frac{dT}{d\theta} = q''_{ox} - h(T - T_o) - \epsilon(T^4 - T_{\infty}^4) + q''_o = \phi(T). \quad (8)$$

In this equation, the terms are defined as

$q''_{ox}$  = heat input resulting from chemical enthalpy of metal oxidation

$q''_o$  = heat input independent of oxidation or body temperature

$C$  = constant

$A$  = action constant or frequency factor

$T$  = absolute temperature

$T_{\infty}$  = ambient absolute temperature

$\theta$  = time, seconds

$h$  = convective heat-transfer coefficient

$\phi$  = Stefan-Boltzmann constant

$e$  = emissivity.

The parameters used in the equation are assumed to be constant with temperature. The activation energy and the frequency factor of collision that enter  $q''_{ox}$  are probably functions of temperatures. These terms will enter into the integration and application of Equation (8).

The ignition temperature is equivalent to the temperature at which the body temperature begins to increase at an increasing rate. This is expressed mathematically by Reynolds as the temperature at which  $dT/d\theta$  is a minimum, as shown by his sketch (Figure 6). The ignition temperature can be found as a function of the environmental and oxidation parameters by requiring that the derivative of Equation (8) with respect to temperature vanish. The resulting defining equation for the ignition temperature is

$$\left[ \frac{d}{dT} (q''_{ox}) \right]_{T=T_{ig}} - h - 4 ET_{ig}^3 = 0. \quad (9)$$

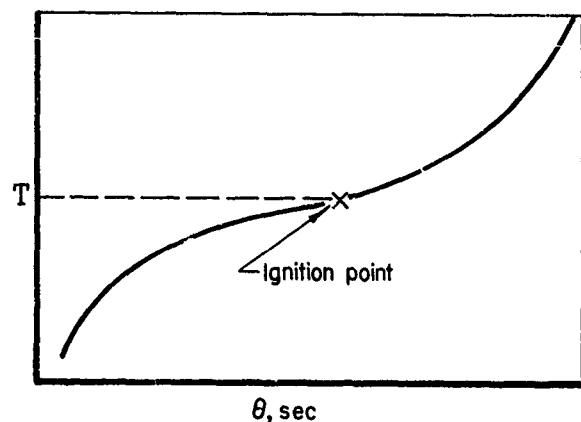


FIGURE 6. TIME-TEMPERATURE DEPENDENCE OF IGNITION OF A MASSIVE METAL IN AN OXIDIZING ATMOSPHERE<sup>(2)</sup>

It should be noted that for ignition to occur,  $dT/d\theta$  must be positive at the ignition temperature,  $T_{ig}$ , and the dependence of the oxidation rate on temperature must be positive and stronger than that of the dominating cooling term. Reynolds states that it is extremely interesting that, unless the oxidation rate depends on ambient temperature, the ignition temperature is independent of ambient temperature.

The oxidation behavior of technically important metals was classified by Reynolds as either linear or parabolic and is expressed by the following equations below. There are, however, other forms of oxidation behavior such as a cubic form. The fundamentals of metal oxidation are discussed in the text on "Oxidation of Metals and Their Alloys", by Kubaschewski and Hopkins.<sup>(50)</sup>

#### Linear Oxidation

$$w = A_1 e^{-E_1/RT} \theta = K_1 \theta \quad (10)$$

#### Parabolic Oxidation

$$w^2 = A_p e^{-E_p/RT} \theta = K_p \theta, \quad (11)$$

where

w = the weight of oxygen that reacts per unit area surface of metal in time,  $\theta$

$A_1$  and  $A_p$  = action constants

$E_1$  and  $E_p$  = activation energy

T = absolute temperature.

Differentiating Equations (10) and (11) with respect to time,  $\theta$ , and multiplying both sides of the equation through by the heat of reaction per gram of oxygen, Q, there follows

$$q''_{ox} = QA_1 \cdot e^{-E_1/RT} \quad (12)$$

for linear oxidation, and

$$q''_{ox} = \frac{QA_p \cdot e^{-E_p/RT}}{2\delta P_{oxide}/\gamma} \quad (13)$$

for parabolic oxidation.

Reynolds, as pointed out by Markstein,<sup>(55)</sup> erroneously shows  $\gamma$  in the denominator. This probably is a typographic error, since deviations in theory from experiment are not a function of  $\gamma$ .

By substituting Equation (12) into (9), collecting terms, and making algebraic operations, an explicit form of ignition temperature,  $T_{ig}$ , for linear oxidation was shown to be

$$e^{-1/T_{ig}} = \frac{T_{ig}}{h_1} + h_1 T_{ig}^2, \quad (14)$$

where

$$T_{ig} = \frac{T_{ig} R}{E_1}, \quad (15)$$

$$n(1) = \frac{A_1 Q}{4\sigma E} \left( \frac{R}{E_1} \right)^4, \quad (16)$$

$$h^*(1) = \frac{h}{A_1 Q} \left( \frac{E_1}{R} \right). \quad (17)$$

Similarly, operations on Equations (13) and (2) give for parabolic oxidation

$$e^{-1/T_{ig}} = \left( \frac{1}{n_p} \right) \left( T_{ig} \right)^5 + h_p \left( T_{ig} \right)^2, \quad (18)$$

where

$$T_{ig} = \frac{T_{ig} R}{E_p}, \quad (19)$$

$$n_p = \frac{ApQ}{8\sigma E_{oxide}} \left( \frac{R}{E_p} \right)^4, \quad (20)$$

$$h_p = \frac{2h\delta P_{oxide}}{ApQ} \left( \frac{E_p}{R} \right), \quad (21)$$

where the symbols have been previously defined except for n which is a pyrophoricity factor.

A high value of  $n_p$  represents a low value for  $T_{ig}$ , the ignition temperature.

Since Equations (14) and (18) are the same form, they can be represented by the same curve. Reynolds assigned arbitrary values to n with a set of values for  $h^*$  as parameters and solved for  $T^*$  in Equations (14) and (15). The solution plotted as

as a curve gives a means of predicting ignition temperatures from oxidation data as shown in Figure 8. Figure 7 shows a curve plotted for a value of  $h^* = 0$ . The assumption that the convective heat transfer is zero can be justified for quiescent atmospheres according to Reynolds. In Figure 8, a comparison is made between calculated and experimental ignition temperatures. The agreement is good for a qualitative correlation. It further justifies the postulated mechanism of slow oxidation and its relation to ignition through environmental parameters.

Reynolds points out the following observations:

- (1) The ignition temperature is essentially independent of ambient temperature and pressure, insofar as these factors influence convective heat transfer
- (2) The dependence of the ignition temperature on convection and radiation heat-transfer rate depend only on the magnitude of transfers and not upon their direction. Higher heating or cooling rates give higher ignition temperatures
- (3) When the ignition temperature depends on the thickness,  $\delta$ , of oxide scale covering the surface, any factors that may reduce scale thickness are important.

A model of the steps in the oxidation are reproduced from Reynolds' paper as given in Figure 9.

Grosse and Conway<sup>(1)</sup> have proposed that the ignition temperature of a metal is a basic property in the same manner as the melting point or boiling point. It was shown, at least to a limited extent, that metal-ignition temperatures vary in a periodic manner similar to other basic properties (Figure 10). This indicates that if a correct definition of ignition temperature was developed, basic relationship could be shown. This would require a method of measurement that would exclude such variables as heat-transfer effects, atmosphere effects, and size and shape effects, or alternatively, a method of correlating these effects.

It has been observed that some metals ignite below their melting points, while others ignite above their melting points. A correlation of these relations with the periodic table also shows that a periodic effect may exist. This is shown in Figure 11. Two complicating factors are involved in the correlation:

- (1) The ignition temperatures that were not obtained under the same conditions are not strictly comparable

- (2) Because of the variations in ignition temperatures, those near the melting point may actually be on either side.

In spite of these limitations, the correlation is reasonably good.

It would be expected that one factor in the above correlation would reduce the probability of ignition under heat-transfer conditions. This factor is the loss of heat from a system to provide the heat of fusion of the metal. Though usually not great, this small additional heat loss may prevent ignition under localized heating conditions such as those produced by shock.

However, it must also be pointed out that some metals that ignite above their melting points are obviously easily ignited because both their melting points and ignition points are low. Conversely, other metals whose ignition temperatures are below their melting points are more difficult to ignite because their melting points are very high.

#### Reaction of Metal Powders With Gaseous Oxygen

The results of metal-powder reaction with gaseous oxygen are not directly applicable to the choice of structural metals for missile design. However, the results are of interest in metal-oxygen mechanisms arising from sharply pointed metal surfaces or from particles arising from fracture. For this reason, several theoretical treatments of the reaction of metal powder-gaseous oxygen are outlined below.

Andersen and Belz developed a semi-quantitative correlation of the combustion of zirconium powder. They showed that ignition temperature is dependent on several variables as given in the qualitative expression:

$$\text{Ignition temperature} = \frac{E}{2R \ln \frac{m^{1/2}}{K_t^{1/2} d}}$$

where

E = activation energy for zirconium oxidation

m = sample mass

d = particle diameter

t = time factor related to oxide film thickness.

The following treatment of zirconium-powder oxidation is taken directly from their work. A general treatment would include a roughness

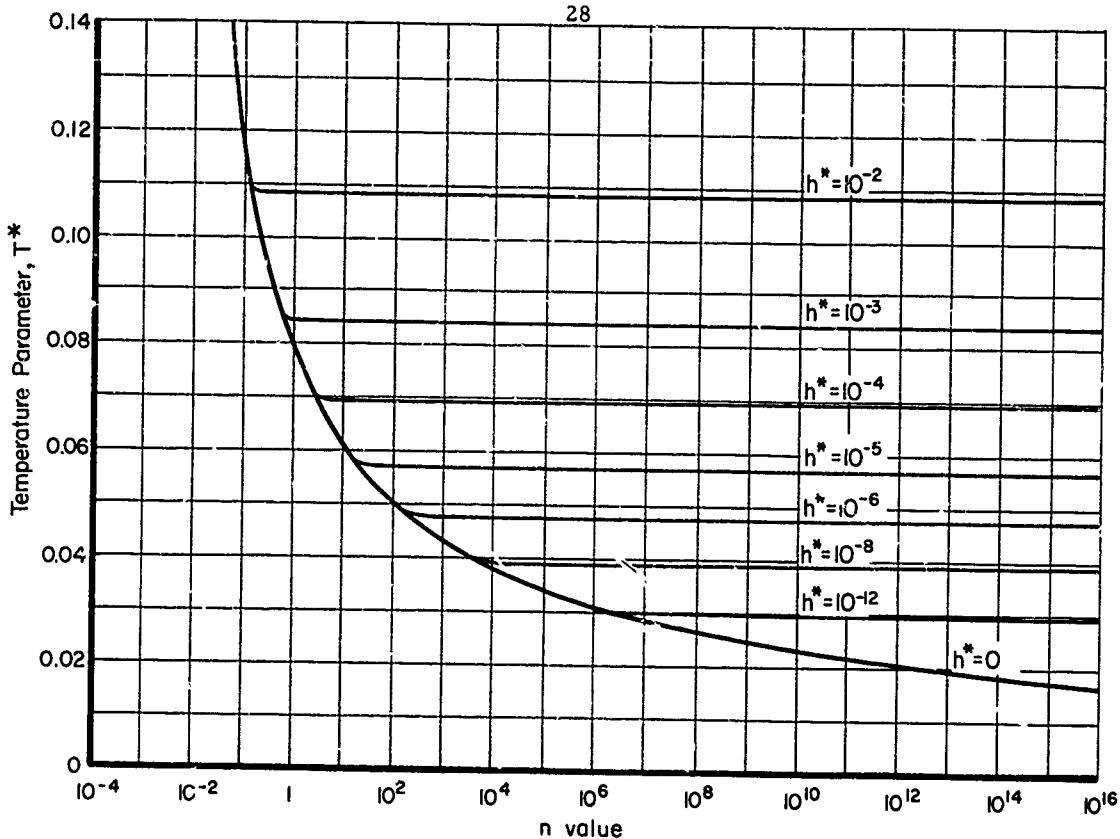


FIGURE 7. CURVES FOR PREDICTION OF IGNITION TEMPERATURES FROM OXIDATION DATA(2)

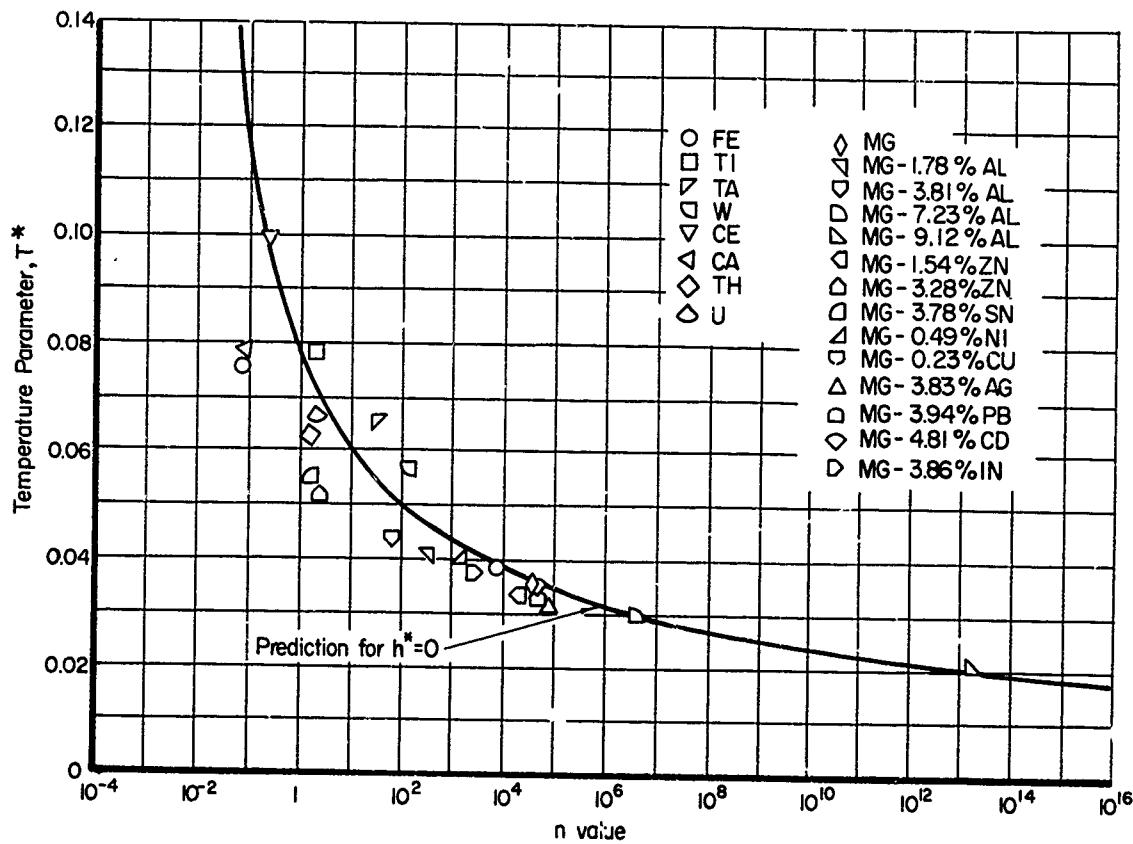


FIGURE 8. COMPARISON OF PREDICTED AND EXPERIMENTAL IGNITION-TEMPERATURE PARAMETERS FOR MASSIVE METALS TESTED IN AIR AT ATMOSPHERIC PRESSURE(2)

factor to account for the fact that the measured surface area is greater than that calculated for smooth spheres. For a given powder lot, however, the necessity for this refinement disappears.

"A semiquantitative explanation of these facts follows. Assume a spherical mass of zirconium powder of radius,  $r$ , in perfect thermal contact at its periphery with an infinite heat reservoir at a controlled temperature,  $T_1$ . Assume further that the mass consists of a small perfect sphere, each of diameter  $d$ . At ordinary

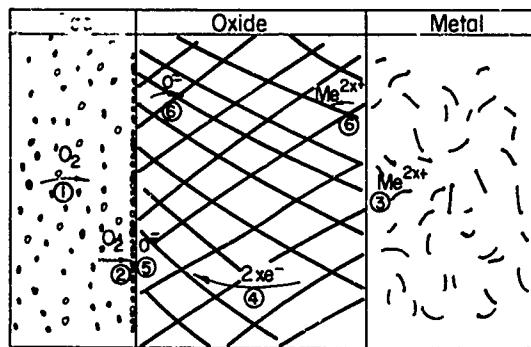


FIGURE 9. OXIDATION MODEL PROPOSED BY REYNOLDS<sup>(2)</sup>

The black dots represent oxygen molecules, and the small circles represent molecules of inert gas present in the gaseous environment. The  $2xe^-$  indicates the number of electrons transferred in the ionization of stoichiometric amounts of metal and oxygen.

The steps that occur in the oxidation reaction are numbered and are as follows:

- (1) Oxygen molecules are transported to the gas-oxide interface by forced or natural diffusion through the inert-gas molecules
- (2) Oxygen molecules whose energy exceeds a certain level are adsorbed by the surface of the oxide
- (3) Metal atoms ionize at the metal-oxide interface
- (4) The electrons given up by the metal atoms diffuse through the oxide lattice to the gas-oxide interface
- (5) The oxygen molecules dissociate, and oxygen atoms are ionized by the electrons
- (6) The oxygen and metal ions diffuse in the oxide lattice, meeting and falling into place in the crystal structure.

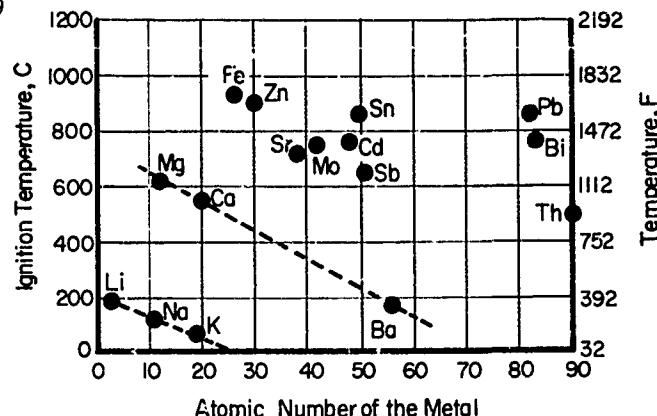


FIGURE 10. RELATIONSHIP OF IGNITION TEMPERATURE AND ATOMIC PERIODICITY OF METALS<sup>(55)</sup>

temperatures, oxidation occurs so slowly that the infinitesimal amount of heat developed is easily dissipated to the surroundings. As the temperature is raised, and the oxidation rate increases, the exothermic heat becomes appreciable and causes further temperature increase of a segment of the powder which is thermally isolated. If the rate of heat development at the center of the mass is greater than the rate at which the heat can be transported to the container, ignition eventually occurs. Then, the following condition is necessary to ignition: rate of exothermic heat development  $>$  rate of heat loss.

"It has been shown that zirconium reacts with oxygen in the temperature range of  $200^\circ - 425^\circ\text{C}$  according to a modified parabolic law:

$$W^2 = Kt + C$$

where  $W$  is the weight gain of a sample of known geometric area,  $t$  is the time, and  $K$  a reaction rate constant with Arrhenius temperature dependence. The constant  $C$  expresses a slight deviation from the simple parabolic law in the initial stages of reaction, and can be omitted as negligibly small for reactions in advanced stages or metal with appreciable oxide film thickness. The reaction rate per unit area is then

$$\frac{dW}{dt} = \frac{K^{1/2}}{2t^{1/2}} = \frac{K'e^{-E/2RT}}{t^{1/2}},$$

where  $E$  is the activation energy, reported to have a value of 18.2 kcal.

"For a small mass of fixed weight at the center of the hypothetical spherical sample, the rate of heat development is obtained by multiplying the reaction rate per unit area by the total surface area and the heat of reaction,  $\Delta H$ . The total area per gram of a system of uniformly sized spheres is  $6/pd^2$ , where  $p$  is the density and  $d$  the sphere diameter. A general treatment would include a roughness factor to account for the fact that the measured surface area is greater than

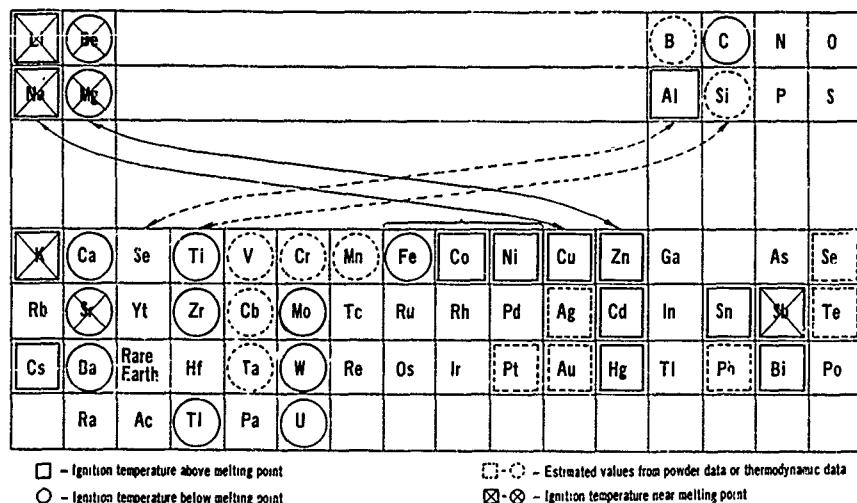


FIGURE 11. PERIODIC RELATION BETWEEN IGNITION TEMPERATURES IN OXYGEN OF MASSIVE METALS AND MELTING POINTS OF THE METALS

that calculated for smooth spheres. For a given powder lot, however, the necessity for this refinement disappears. The rate of heat generation by center element is thus

$$K'' \frac{\Delta He^{-E/2RT_2}}{t^{1/2}d},$$

where  $T_2$  is the temperature of the central mass, and  $K''$  includes all previous constants. Assuming that the rate of heat transport from the center element to the reservoir is of the form

$$k'''(T_2 - T_1)/r,$$

the fundamental condition for ignition becomes

$$K''' \frac{\Delta He^{-E/2RT_2}}{t^{1/2}d} \frac{k'''(T_2 - T_1)}{r}.$$

The expression cannot be solved for  $T_1$ , the ignition temperature, in terms independent of  $T_2$ , the internal temperature. On the assumption that ignition is possible when  $T_2$  exceeds  $T_1$  by some small constant value, two simplifications are possible. Thus,  $(T_2 - T_1)$  in the heat-loss term can be taken as constant, and  $T_2$  can be taken as roughly equal to  $T_1$  in the exponential. The inequality then simplifies to

$$e^{-E/2RT_1} > \frac{Kt^{1/2}d}{r},$$

or eventually,

$$T_1 > \frac{E}{2R \ln\left(\frac{r}{Kt^{1/2}d}\right)}; T_1 > \frac{E}{2R \ln\left(\frac{m^{1/2}}{Kt^{1/2}d}\right)}$$

where  $m$  is the sample mass.

"Various interpretations of the time factor in this expression are possible. If it is interpreted as an inverse function of the external heating rate, then the expression predicts a decrease in ignition temperature with heating rate. This is the experimental case for small samples. In the case of

larger samples, the increase of ignition temperature with heating rate is attributed to increased lag of internal temperature with respect to external temperature. The predicted increase of ignition temperature with time is in qualitative agreement with the observations that the ignition temperature can be greatly raised by keeping powder below the usual ignition point for some time. For a system of fixed particle size and shape distribution, and constant time, i.e., heating rate, the expression indicates a relationship between sample mass and ignition temperature as shown in Figure 12. The form of this theoretical curve is very similar to those found experimentally. Likewise, the expression is in qualitative agreement with the data, as regards particle size."

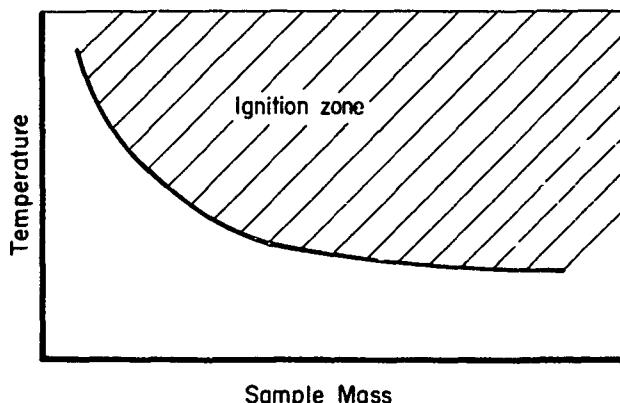


FIGURE 12. THEORETICAL CURVE OF IGNITION TEMPERATURE VERSUS MASS, FOR ANY GIVEN POWDER (HEATING-RATE CONSTANT)

Friedman and Macek found that experimental results of the ignition of aluminum particles were consistent with an ignition theory that they developed. (8) In their theory, they assumed a

substantial change in the rate of surface reaction at the melting point of aluminum. When ignition occurs, the delay time, which varies with the square of the particle diameter, is in excellent agreement with simple heat-transfer calculations. This agreement requires that the initial lag of the particle velocity relative to the gas to be taken into account.

Talley compared the ignition temperature of boron rods with a theoretically calculated ignition temperature.<sup>(51)</sup> He found good agreement between theory and experiment. Talley obtained his limiting reaction rate data from experimental evaporation of B<sub>2</sub>O<sub>3</sub> from a burning surface. He assumed heat loss by radiation only.

Tetenbaum, et al,<sup>(9)</sup> studied the ignition of uranium powder. The ignition behavior was found to be dependent on specific areas of powder fraction, rate of heating, and geometry of sample. On the basis of the Frank-Kamenetskii theory of thermal explosions, when used in a restricted manner, limiting ignition temperature values can be estimated. These calculated ignition temperatures are in reasonable agreement with experimental values obtained by Tetenbaum and co-workers. The theory of Frank-Kamenetskii was originally applied to gas mixtures in containers.

Cassel and Liebinan studied the ignition of dust dispersions and magnesium particles.<sup>(6,7)</sup> In agreement with theoretical predictions, the ignition temperature of single particles greatly increases with decreasing size.

The rather high ignition temperatures of fine metal particles preclude a low oxidation rate as the mechanism of ignition of metals in liquid or gaseous oxygen at cryogenic temperatures. Therefore, another energy input must be sought as the cause of the failure of the LOX-metal systems. Impact or a shock-wave mechanism was suggested as a probable cause.

#### Reactions in Massive Metal-Liquid Oxygen Systems

As discussed in the experimental section, many investigations on the reaction of metal-liquid oxygen (LOX) reactions have been carried out. A number of significant observations have been made with logical interpretations of the cause of the metal-LOX reaction below 100 K, but there are no theoretical calculations available in the literature for ignition of metal-LOX systems. It becomes obvious that the low reaction rate of metal-LOX as predicted from the Arrhenius rate equation cannot account for a sustained reaction. The dissipation of heat in this reaction would prevent the system from ever reaching the ignition temperature. Therefore, there must be an energy input, such as impact, that gives very high local temperatures. For this reason, an analysis was made on the effect of shock-loading that could lead

to ignition in metal-LOX systems. This is given in Appendix B. From this analysis, the following conclusions can be drawn:

- (1) Compressibility of metals at low-level impact can have an energy change smaller than that required to start ignition
- (2) Local plastic deformation of metals due to impulsive loading offers a possible mechanism for local high temperatures in a cryogenic system
- (3) Reflected stress waves very probably will denude the surface of oxide. Fresh metal surface is a factor in promoting ignition
- (4) Plane stress waves transmitted into liquid oxygen from metal surfaces do not appear to give a large enough thermal gradient to cause ignition
- (5) Multiple reflection in liquid oxygen entrapped at crevices, such as formed by oxide cracks or mechanically formed metal surface cracks, will produce a temperature rise that could cause ignition. A LOX-metal particle interface and small particles could produce multiple reflection
- (6) Cavitation in liquid oxygen caused by a reflected wave is likely. Cavitation can give rise to gaseous oxygen adjacent to metal surface in a LOX system
- (7) Increase in adsorption of oxygen by metals may occur due to stress waves
- (8) Internal friction of metals does not seem to be a likely mechanism to generate heat in short-time dynamic effects
- (9) Piezoelectric effects should be examined in a theoretical derivation of ignition temperatures in LOX-metal reactions.

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APPENDIX A

SUMMARY OF EXPERIMENTAL IGNITION TEMPERATURES  
OF METALS AND ALLOYS IN OXYGEN SYSTEMS

TABLE A-1. SUMMARY OF EXPERIMENTAL IGNITION TEMPERATURES OF MASSIVE METALS AND ALLOYS IN OXYGEN SYSTEMS

TABLE A-1. (CONTINUED)

TABLE A-1 (CONTINUED)

Metal or Alloy	In Oxygen, psi				In Air, psi				High Flow Rates	In Mixtures More Dilute Than Air, psi	
	15-50	50-200	200-400	400-700	Above 700	15-50	50-200	400-700			
Titanium	1315(4)	1580-1630(2)	870(4)	1100(3)	--	1580-1630(2)	--	--	1580-1630(2)	--	815(4)
RS-110A	--	1570-1600(2)	--	--	--	>MP(2)	--	--	>MP(2)	--	--
RS-110BX	--	1570-1600(2)	--	--	--	>MP(2)	--	--	1530-1660(2)	--	--
Ti, Cu coated	--	--	--	--	--	--	--	--	--	--	--
Ti-8Al-2.5Sn-3.5Fe-1Cu	--	--	--	--	--	--	--	--	--	--	--
Ti-2.8H <sub>2</sub>	--	--	--	--	--	--	--	--	--	--	--
Ti-3.8H <sub>2</sub>	--	--	--	--	--	--	--	--	--	--	--
Ti-70Fe-7.0C	--	--	--	--	--	--	--	--	--	--	--
Ti-74Fe-9.06C Ti(broken by stress rupture)	>1200(22)	300-1200(22)	RT-300(22)	--	--	--	--	--	--	--	--
Tungsten	--	--	--	--	--	--	--	--	1240-1290(2)	1240-1290(2)	--
Zinc	900(1)	--	--	--	--	--	--	--	--	--	--
Zn-2Pb	--	--	--	--	--	--	--	--	--	--	--

A-3

## A-4

TABLE A-2. SUMMARY OF EXPERIMENTAL IGNITION TEMPERATURES OF SMALL PARTICLES OF METALS AND ALLOYS IN OXYGEN SYSTEMS  
Ignition Temperature, C

Metal or Alloy	In Oxygen, psi			In Air, psi			In Mixtures More Dilute Than Air, psi	
	Single Particles	Clouds	Single Particles	Clouds	Layers	Single Particles	Clouds	
Aluminum	--	--	--	650(21)	760(21)	1950-2080(8)	--	--
Aluminum	--	--	--	--	--	--	--	--
Antimony	--	--	--	420(21)	330(21)	--	--	--
Barium	--	--	--	--	--	--	--	--
Beryllium	--	--	--	910->1000(21)	540(21)	--	--	--
Berylico 10	--	--	--	--	--	--	--	--
Berylico 25	--	--	--	--	--	--	--	--
Bismuth	--	--	--	--	--	--	--	--
Boron	--	--	--	470(21)	400(21)	--	--	--
Cadmium	--	--	--	570(21)	250(21)	--	--	--
Calcium	--	--	--	--	--	--	--	--
Cesium	--	--	--	--	--	--	--	--
Chromium	--	--	--	580->1000(21)	400-670(21)	--	--	--
Cr-Fe	--	--	--	790(21)	670(21)	--	--	--
Cobalt	--	--	--	760(21)	370(21)	--	--	--
Multimet	--	--	--	--	--	--	--	--
Co-60Al	--	--	--	950->1000(21)	570->1000(21)	--	--	--
Haynes 25	--	--	--	--	--	--	--	--
Copper	--	--	--	700(21)	--	--	--	--
Berylico 25	--	--	--	>1000(21)	>1000(21)	--	--	--
Cu-29Zn	--	--	--	370(21)	190(21)	--	--	--
Mn-Bronze	--	--	--	>1000(21)	910(21)	--	--	--
Cu-50Al	--	--	--	930->1000(21)	830(21)	--	--	--
Berylico 10	--	--	--	--	--	--	--	--
Iron	--	--	--	320(21)	310(21)	--	--	--
Carbon steel	--	--	--	--	--	--	--	--
Mild steel	--	--	--	--	--	--	--	--
4130	--	--	--	--	--	--	--	--
Tool steel	--	--	--	--	--	--	--	--
Fe-2Si	--	--	--	780-900(21)	--	--	--	--
Fe-Cr	--	--	--	790(21)	670(21)	--	--	--
Fe-V	--	--	--	440(21)	400(21)	--	--	--
Fe-Mn	--	--	--	450-700(21)	--	--	--	--
Fe-Si	--	--	--	860(21)	--	--	--	--
Fe-Ti	--	--	--	360-580(21)	--	--	--	--
Fe-50Al	--	--	--	>1000(21)	--	--	--	--
Fe-30Al	--	--	--	560(21)	--	--	--	--
Stainless steel (18-8)	--	--	--	>1000(21)	>1000(21)	--	--	--
Type 302	--	--	--	--	--	--	--	--
Type 304	--	--	--	--	--	--	--	--
Type 310	--	--	--	--	--	--	--	--
Type 321	--	--	--	--	--	--	--	--
Type 347	--	--	--	--	--	--	--	--
Type 410	--	--	--	--	--	--	--	--
Type 430	--	--	--	--	--	--	--	--
17-7PH	--	--	--	--	--	--	--	--
AM-350	--	--	--	--	--	--	--	--
Lead	--	--	--	710(21)	270(21)	--	--	--
Pb-5Sn	--	--	--	750(21)	300(21)	--	--	--

A-5  
TABLE A-2. (CONTINUED)

Metal or Alloy	In Oxygen, psi		In Air, psi			In Mixtures More Dilute Than Air, psi	
	Single Particles	Clouds	Single Particles	Clouds	Layers	Single Particles	Clouds
Lithium	--	--	--	--	--	--	--
Magnesium	640-715(7)	--	636-742(6)	620(21)	490(21)	627-732(6)	--
Magnesium	--	--	645-695(7)	590-800(7)	--	--	--
Magnesium	--	--	(Less dense clouds - higher temperature)(7)			--	--
Mg-50Al	675(7)	--	685-845(7)	430(21)	480(21)	--	--
Mg-6 to 63 Al	--	--	--	--	--	--	--
Mg-80 to 94 Al	--	--	--	--	--	--	--
Mg-5 to 20 Ni	--	--	--	--	--	--	--
Mg-1.2 to 29 Sb	--	--	--	--	--	--	--
Mg-5 to 14 Ag	--	--	--	--	--	--	--
Mg-10 to 20 Pt	--	--	--	--	--	--	--
Mg-7 to 91 Cd	--	--	--	--	--	--	--
Mg-1 to 5 Co	--	--	--	--	--	--	--
Mg-10 to 31 Cu	--	--	--	--	--	--	--
Mg-1 to 5 Ca	--	--	--	--	--	--	--
Mg-10 to 30 In	--	--	--	--	--	--	--
Mg-0.3 to 11 Li	--	--	--	--	--	--	--
Mg-1 to 3 Mn	--	--	--	--	--	--	--
Mg-1.8 to 3.1 Si	--	--	--	--	--	--	--
Mg-10 to 26 Sn	--	--	--	--	--	--	--
Mg-16 to 58 Pb	--	--	--	--	--	--	--
Mg-3 to 89 Zn	--	--	--	--	--	--	--
Mg-1 to 11 Al, 1 to 14 Zn	--	--	--	--	--	--	--
Mg-10 to 15 Al, 5 to 11 Cd	--	--	--	--	--	--	--
Mg-22 to 27 Cd, 0.3 to 2.3 Ag	--	--	--	--	--	--	--
Mg-20Cd-3Zn	--	--	--	--	--	--	--
Mg in contact with Ni	--	--	--	--	--	--	--
Mg in contact with Ag	--	--	--	--	--	--	--
Mg in contact with 70-30 brass	--	--	--	--	--	--	--
Mg in contact with steel	--	--	--	--	--	--	--
Mg in contact with Al	--	--	--	--	--	--	--
Manganese	--	--	--	460(21)	240(21)	--	--
Molybdenum	--	--	--	720(21)	360(21)	--	--
Nickel	--	--	--	>1000(21)	>1000(21)	--	--
Inconel	--	--	--	--	--	--	--
Inconel X	--	--	--	--	--	--	--
Monel	--	--	--	--	--	--	--
Ni-50Al	--	--	--	>1000(21)	650(21)	--	--
Ni-58Al	--	--	--	940(21)	550(21)	--	--
Hastelloy C	--	--	--	--	--	--	--
Hastelloy R	--	--	--	--	--	--	--
Hastelloy X	--	--	--	--	--	--	--
Potassium	--	--	--	--	--	--	--
Selenium	--	--	--	>1000(21)	--	--	--
Silicon	--	--	--	780(21)	760(21)	--	--
Si-50Fe	--	--	--	>1000(21)	>1000(21)	--	--
Si-25Fe	--	--	--	>1000(21)	>1000(21)	--	--
Si-15 to 20 Fe	--	--	--	>1000(21)	800(21)	--	--
Si-10 to 15 Fe	--	--	--	>1000(21)	920(21)	--	--
Si-5 to 10 Fe	--	--	--	>1000(21)	980(21)	--	--
Sodium	--	--	--	--	--	--	--
Strontium	--	--	--	--	--	--	--

A-6

TABLE A-2. (CONTINUED)

Metal or Alloy	In Oxygen, psi			In Air, psi			In Mixtures More Dilute Than Air, psi	
	Single Particles	Clouds	Single Particles	Clouds	Layers	Single Particles	Clouds	
Tantalum	--	--	--	630(21)	300(21)	--	--	--
Tellurium	--	--	--	550(21)	340(21)	--	--	--
Thorium	--	--	--	270(21)	280(21)	--	--	--
Tin	--	--	--	660(21)	520(21)	--	--	--
Sn-2Pb	--	--	--	630(21)	430(21)	--	--	--
Titanium	--	--	--	330(21)	510(21)	--	--	--
RS-110A	--	--	--	--	--	--	--	--
RS-110BX	--	--	--	460-590(21)	380-430(21)	--	--	--
Ti, Cu coated	--	--	--	530(21)	470(21)	--	--	--
Ti-8Al-2.5Sn-3.5Fe-1Cu	--	--	--	440(21)	500(21)	--	--	--
Ti-2.8H <sub>2</sub>	--	--	--	480(21)	540(21)	--	--	--
Ti-3.8H <sub>2</sub>	--	--	--	580(21)	330(21)	--	--	--
Ti-70Fe-7.0C	--	--	--	370(21)	400(21)	--	--	--
Ti-74Fe-6.06C	--	--	--	--	--	--	--	--
Ti (broken by stress rupture)	--	--	--	--	--	--	--	--
Tungsten	--	--	--	730(21)	470(21)	--	--	--
50% W (bearing)	--	--	--	>1000(21)	500(21)	--	--	--
40% W (bearing)	--	--	--	>1000(21)	550(21)	--	--	--
Uranium	--	--	--	20(21)	100(21)	--	--	--
Vanadium	--	--	--	500(21)	490(21)	--	--	--
V-56Fe	--	--	--	490(21)	400(21)	--	--	--
V-46Fe	--	--	--	330(21)	380(21)	--	--	--
Zinc	--	--	--	64(21)	460(21)	--	--	--
Zn-2Pb	--	--	--	600-680(21)	460-540(26)	--	--	--
Zirconium	--	--	--	--	199-378 (Smaller particles, lower temps)			
Zirconium	--	--	--	20(21)	190(21)	--	--	--
Zircaloy 2	--	--	--	420(21)	340(21)	--	--	--
Zr-2.1H <sub>2</sub>	--	--	--	350(21)	270(21)	--	--	--
Ti-22 to 45 Zr	--	--	--	--	228-279(54)	--	--	--
Ti-8 to 12 Zr	--	--	--	--	>400(54)	--	--	--
Ni-79 to 87 Zr	--	--	--	--	176-200(54)	--	--	--
Ni-35 to 65 Zr	--	--	--	--	>400(54)	--	--	--
Cu-49 to 85 Zr	--	--	--	--	194-212(54)	--	--	--
Fe-82 to 87 Zr	--	--	--	--	132-162(54)	--	--	--
Zr-89Co	--	--	--	--	188(54)	--	--	--
Zr-10 to 11.4 H <sub>2</sub>	--	--	--	--	200-260(54)	--	--	--
Zr-11.5H <sub>2</sub>	--	--	--	--	>400(54)	--	--	--

APPENDIX B

THERMODYNAMICS OF SHOCK LOADING IN METALS CONDITIONS THAT MAY  
LEAD TO METAL-LOX IGNITION

E. G. Bodine

B-1  
APPENDIX B

THERMODYNAMICS OF SHOCK LOADING IN METALS CONDITIONS THAT MAY LEAD TO METAL-LOX IGNITION

E. G. Bodine

Experiments have shown that metals, especially titanium, that are in contact with liquid oxygen (LOX) are often ignited by impact. As a portion of this review, therefore, it was felt appropriate to make a brief examination of the thermodynamics of shock loading in metals and to explore those conditions that could lead to ignition. No attempt has been made to include all possible shock-loading effects, but those that are recognized and that might contribute to ignition at a LOX-metal boundary are mentioned. When enough information was available to permit a rough calculation of the temperature or energy that might be expected in a particular circumstance, this calculation was made and the results are given.

It should be mentioned that the effects of shock loading should not necessarily be considered as an independent mechanism by which burning is initiated, but as one of a combination of thermodynamic effects that may ultimately lead to ignition.

Stress-Wave Effects

During impulsive loading, the stresses - initially set up at the surface - move about through the body as highly transient localized wave disturbances capable of affecting one part of the body quite independently of what happens in another part. In general, the effects of these stress disturbances and their magnitude cannot be arrived at from clear-cut theoretical considerations. Interactions with reflecting surfaces, reinforcement of waves due to multiple reflections at corners or inclusions, stress concentration at crack edges, all produce local effects apart from those easily described by the theory of wave propagation. Therefore, in order to approach the problem with any hope of solution, a simplification of the localized stress state will be made that seems reasonable in lieu of the myriad possibilities. It is assumed, first, that the local stresses can be like the yield stress or the tensile stress of the material. From this, it will be shown that the energy change in most metals due to low-level impulsive loading will be smaller than that required to significantly raise the temperature, and that some other additional mechanism must be sought.

The description of the behavior of materials during shock loading has developed on the basis of the conservation of mass, momentum, and energy by the three Rankine-Hugoniot equations. For solid materials, it is generally assumed that an equation of state can be written in the form of the equation of state of an ideal gas. It is justified on the basis that shock loading produces stresses far beyond the yield strength of the solid and, therefore, the solid behaves according to its thermo-

dynamic properties without much regard to its mechanical properties, per se. The equation of state of a solid material can thus be derived from purely thermodynamic considerations.

The energy conservation equation for a material subjected to shock loading is given by the Rankine-Hugoniot relation

$$\theta_1 - \theta_0 = 1/2(V_0 - V_1)(p_1 + p_0) \quad (B-1)$$

where

$\theta$  is internal energy  
 $V$  is volume  
 $p$  is pressure,

and the subscripts 0 and 1, respectively, refer to conditions ahead of and behind the shock wave.

When a material is shocked from an initial state  $\theta_0$ ,  $p_0$ , and  $V_0$  to a final state  $\theta_1$ ,  $p_1$ , and  $V_1$ , the change in internal energy is given by Equation (B-1). Part of this energy goes into compressional energy - work necessary to move the atoms closer together, and the remainder of the energy goes into thermal motions. Similarly, the pressure is the sum of a compressional and a thermal pressure. The compressional energy and pressure are the values of the total energy and pressure at  $0^{\circ}\text{K}$  and are consequently dependent on volume only. The thermodynamic parameter that characterizes the relationship between the thermal pressure and thermal energy of a system is the Gruneisen ratio,  $\gamma$ . The Mie-Gruneisen equation of state is

$$p - p_k = (\gamma/V)(\theta - \theta_k)$$

where the subscript K refers to the  $0^{\circ}\text{K}$  isotherm. Another form of the above equation is

$$p - p_H = (\gamma/V)(\theta - \theta_H),$$

where the subscript H refers to the Hugoniot shock-state curves. By assuming constancy of  $(\delta\theta/\delta p)_V$  in the vicinity of the Hugoniot and differentiating the last form of the Mie-Gruneisen equation, the Gruneisen ratio can be found from

$$\gamma = V/(\delta\theta/\delta p)_V - \frac{[V(\delta p/\delta V)_S(\delta V/\delta T)_p]}{C_p}.$$

The use of experimental data at zero pressure for the bulk modulus, thermal-expansion coefficient, and specific heat gives a "thermodynamic" gamma at zero pressure. Adiabats may now be calculated and temperatures can be calculated along the adiabats using

$$\text{or } \Delta\theta = 0.75 \times 10^{-4} E,$$

where  $\mu$  is taken to be 0.25. Typical values for  $E$  of metals range from  $10 \times 10^6$  psi to  $30 \times 10^6$  psi, so that the energy change due to a high intensity elastic wave is from  $600 \text{ ft-lb/in.}^3$  to  $2000 \text{ ft-lb/in.}^3$ . The recoverable elastic energy is estimated by

$$\theta_e = 1/2 \frac{\sigma_0^2}{E}, \quad (\text{B-4})$$

where  $\sigma_0$  is the yield stress. Therefore, only about  $1/3$  of the change in energy from Equation (B-3) is available to produce heat.

Using the equation of state in the Meißneisen form, temperatures and entropies of typical materials shocked to various densities are given in Table B-1. It is apparent from Equation (B-1) and Table B-1 that changes in energy level are a function of the intensity of the shock,  $p$ , and the compressibility of material ( $V_1 - V_0$ ). For most solids, the compressibility does not become significant until pressure is very large - perhaps many times the yield strength of the material under uniaxial stress. For this reason, it would not appear likely that any low intensity shock stimuli would create energy changes sufficient to heat a metal to its ignition temperature, especially from LOX temperature. For example, for a pressure level that is like the yield stress, the modulus of volume expansion,  $K$ , for a material is given by

$$K = \frac{E}{3(1 - 2\mu)}, \quad (\text{B-2})$$

where

$$E = \text{modulus of elasticity}, \\ \mu = \text{Poisson's ratio},$$

which relates the change in hydrostatic pressure with volume compression. Assuming  $p_1 \approx E/100$  = yield strength, and combining Equations (B-1) and (B-2), the change in internal energy caused by the maximum intensity elastic pressure wave would be

$$\Delta\theta = 1/2 \left[ \frac{3(1 - 2\mu)E/100}{E} \right] \frac{E}{100} \quad (\text{B-3})$$

TABLE B-1. TEMPERATURES AND ENTROPIES OF TYPICAL MATERIALS EXPLOSIVELY SHOCKED FROM 20 C

Material	Density Ratio, $d/d_0$ , or Volume Ratio, $V_0/V$											
	1.1			1.3			1.5			1.7		
	$P$ , K bar	T, C	$\Delta S$ cal/g deg	p	T	$\Delta S$	p	T	$\Delta S$	p	T	$\Delta S$
Water(a)	4	32	0.004	18	86	0.051	55	277	0.247	120	120	0.543
Aluminum(b)	90	75	0.008	374	545	0.157	861	2367	0.386	1650	6520	0.588
Copper(b)	167	87	0.005	755	877	0.089	1858	4080	0.197	3880	12000	0.292
Lead(b)	53	91	0.001	250	770	0.025	655	3280	0.062	1330	8200	0.095

(a) Rice and Walsh (1957), above values determined by interpolation.

(b) Altshuler, et al (1960),  $S$  computed from  $p$ ,  $V$ ,  $T$ , values.

In a recent report on the plastic behavior of metals at cryogenic temperatures,\* a phenomenon called serrated yielding is identified in many metals

\*Kula, E. B., and De Sisto, T. S., "Plastic Behavior of Metals at Cryogenic Temperatures", paper presented at the 68th Annual Meeting of ASTM, Lafayette, Indiana, June 13-18, 1965.

(including titanium) tested at low temperatures. It is attributed to adiabatic heating and can occur, according to the authors, independently of deformation mechanisms. The production of heat due to plastic deformation is, of course, a well known phenomenon and is attributable to the conversion of work to heat along inclined shear zones. Metals may become hot enough to soften locally, which, in turn, enhances the possibility of further deformation and further heat generation. The faster the deformation, the more likely the occurrence of adiabatic softening. The localized yielding of small volumes of metal near a free boundary can be used to calculate the adiabatic temperature rise in an assumed uniaxially stressed region, e.g., the tip of a crack. The energy for plastic deformation is

$$\Theta = \sigma_0 \epsilon, \quad (B-5)$$

where  $\sigma_0$  = yield stress (ideally plastic) and  $\epsilon$  = localized plastic strain. If, for example,  $\sigma_0$  is assumed to be 75,000 psi and  $\epsilon$  about 0.5 in./in. the temperature rise in a metal having a density of 0.2 lb/in.<sup>3</sup> and a specific heat of 0.05 Btu/lb F would be 500 F. The necessary externally supplied energy could come from a stress wave or from residual stresses already present in the metal.

Still another interesting mechanical effect can result in the formation of free metal surface. If a compressive shock wave impinges on an interface that leads into a medium of lower acoustic impedance than the medium in which it is traveling, a reflection of the compressive pulse as a tensile wave occurs. The reflected stress, if the initial compression was large enough, can cause a tensile failure in the material. This phenomenon is called scabbing and is well known in the explosive working of metals. The ingredients for scabbing to occur are manifested at a metal-LOX interface. The thin oxide layer that protects the metal has generally poor tensile strength. The acoustic impedance of LOX is several times less than that in most metals, and, therefore, the reflection of a sharp-fronted compressive pulse could conceivably denude areas of the metal of its oxide. The conditions under which this occurrence would be most favorable would be for a compressive pulse width of  $2t/C_0$  where  $t$  is the thickness of oxide coating and  $C_0$  is the sound speed in the oxide. The stress amplitude in compression would be equal to the tensile strength of the oxide.

Stress pulses and durations that are reasonable with respect to the conditions that have just been suggested are possible and can be easily seen from the following illustration.

Consider a small particle of approximately spherical geometry traveling with a velocity,  $v$ . Detailed calculations show that the time of contact will be

$$t_0 \approx 5 \frac{r}{C_0} \left( \frac{C_0}{v} \right)^{1/5}, \quad (B-6)$$

where  $r$  is the sphere radius. Thus, a steel ball, 0.5 cm in radius and 4 grams in mass, dropped from a height of only 0.5 cm onto a steel plate would exert an average stress of 150,000 psi for 35  $\mu$ sec, conditions that appear sufficient to scab off the underlying oxide in a thin pressure vessel.

While the effects of stress waves just discussed have been confined to those that exist in the metal, those that are transmitted into, or originate in, the LOX are also important.

#### Stress Waves in Liquid Oxygen

As was previously mentioned, stress waves reflect and transmit portions of their energy at boundaries between materials of different acoustic impedance. The acoustic impedance of a material is defined as the product of its density and its speed of sound,  $C_d$ , and the portion of the stress wave that is transmitted from Material 1 into Material 2 is given by Rinehart and Pearson\*

$$\frac{\sigma_T}{\sigma_I} = \frac{2d_2C_2}{d_1C_1 + d_2C_2}, \quad (B-7)$$

where  $\sigma_T$  is the transmitted wave and  $\sigma_I$  the incident wave. Likewise, the reflected wave can be found from

$$\frac{\sigma_R}{\sigma_I} = \frac{d_2C_2 - d_1C_1}{d_1C_1 + d_2C_2}, \quad (B-8)$$

where  $\sigma_R$  is the reflected wave.

For LOX, the speed of sound at -297 F is about 3100 ft/sec and the density about 0.036 lb/in.<sup>3</sup> Metals have a speed of sound near 15,000 ft/sec and densities near 0.2 lb/in.<sup>3</sup> A transmitted wave from the metal into the LOX would thus be about 1/30 of the incident wave amplitude. Returning to the third Rankin-Hugoniot relation of Equation (B-1), the change in internal energy in the LOX for an incident wave of 150,000 psi in the metal would be

$$\Delta\Theta = 1/2(\Delta V)\Delta p. \quad (B-9)$$

Substituting 150,000/30 psi = 5,000 psi for  $\Delta p$  and using the known compressibility of liquid oxygen of  $72.4 \times 10^{-7}$  in.<sup>2</sup>/lb at -297 F to find the change in volume, the energy change becomes

$$\Delta\Theta \approx 7.5 \text{ ft-lb/in.}^3 \quad (B-10)$$

The specific heat of LOX is approximately 0.406 Btu/lb F and the density is 0.036 lb/in.<sup>3</sup> The temperature rise is, therefore, no greater than about 1 or 2 degrees F. It would appear that a transmitted wave into the LOX from the metal is not capable of generating a significant change in temperatures.

\*Rinehart, J. S., and Pearson, J., Explosive Working of Metals, The Macmillan Company, New York, New York (1936) p. 114.

If, however, a small reentrant crack or void is present at the surface of the metal, an entirely different situation could exist. Consider a small crack or imperfection with its length 3 or 4 times its average width (one can visualize, for example, a reentrant pocket at a weld or seam) that is subjected to a compressive stress wave. Due to multiple reflection and due to the inertia of the long (with respect to width) column of entrapped liquid, the pressure in the trapped LOX would soon approach that of the incident wave. In other words, at such a stress concentration, the energy change in the LOX would be orders of magnitude larger than for a nonrestricted transmission. Now, the temperature rise for the same stress wave (150,000 psi) could conceivably become 600 F. Coupled with the likelihood of the formation of a clean surface as the tip of the crack grows, ignition becomes probable. A possible mechanism for ignition on the basis of stress waves of relatively low amplitude is, therefore, available.

A further consideration of stress waves in liquids shows that after reflection at a metal-LOX interface, a rarefaction (tensile) wave may follow the incident compressive wave. Dynamic experiments in which sharp pulses of tensile stress are produced in the liquid by, for example, intense sound waves have demonstrated the considerable tensile strength of cold liquids (~500 atm). The liquid fails under these circumstances by cavitation, i. e., by the formation of small vapor bubbles inside it. These bubbles often collapse violently, emitting strong pressure waves. Repeated mechanical blows by the collapse of these bubbles have been known to tear small fragments out of metallic surfaces, e.g., cavitation damage in propellers.

An estimate of the tensile strength of a liquid is obtained from van der Waal's reduced equation of state,

$$P = \frac{8T}{3V-1} - \frac{3}{v^2}, \quad (B-11)$$

in which the critical quantities  $v_c$ ,  $p_c$ , and  $T_c$  are used as limits of volume, pressure, and temperature. For liquid oxygen

$$\begin{aligned} v_c &= 78 \text{ cm}^3/\text{mole} \\ p_c &= 50.1 \text{ atm} \\ T_c &= 154.8 \text{ K.} \end{aligned}$$

Since  $dp/dV = 0$  for tensile fracture,

$$(3V_m-1)^2 = 4V_m^3T, \quad (B-12)$$

which gives the volume,  $V_m$ , at failure. The tensile strength,  $p_m$ , would be

$$p_m = \frac{3V_m-2}{V_m^3}. \quad (B-13)$$

Since  $p_m = 0$  when  $V_m = 2/3$ , a van der Waal's liquid has tensile strength only at temperatures below that for which  $V_m = 2/3$ . It can be seen that

the conditions for cavitation exist in LOX due to transmitted waves,  $T \leq (27/32)T_c$ . The implication as far as an increase in the possibility of ignition cannot be quantitatively defined without further definition of a specific situation, but a mechanism for the formation of gaseous oxygen even at liquid-oxygen temperatures is seen to exist.

#### Other Possible Dynamic Effects

Further possible effects of dynamic loading are: (1) change in adsorption at metal-LOX interface, (2) generation of heat from mechanical vibration due to internal friction, and (3) a possible piezoelectric effect. These possibilities will be briefly discussed in the following paragraphs.

According to thermodynamics, the change of surface tension,  $\gamma$ , with pressure is a function of the area of the interface and the total volume. For a one-component system in equilibrium with its vapor, a change in surface tension with pressure at constant temperature appears meaningless. However, if a second material acts as a pressure transmitting medium, the result will be a solution in the liquid component and adsorption at the interface of the second component.\* Apparently, the effect can occur at relatively low pressures (~1000 atm). The ability of the oxide layer to inhibit oxygen adsorption by the metal under these circumstances may be subject to further question.

The possibility of producing a significant temperature rise by internal friction has been briefly examined. It does not appear possible that conditions could exist that would allow the internal damping of a metal to produce the high temperatures required for ignition, at least under short-duration impulsive loadings.

One other possibility that has not been mentioned previously is the generation of electrical energy by piezo-electric behavior in either the metal or the metal oxide. No evidence of this effect has, as far as is known, been reported.

\*Bradley, R. S., High Pressure Physics and Chemistry 2, Academic Press, London and New York (1963) p 334.

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	ROLE	WT	ROLE	WT	ROLE	WT
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Ignition temperature	7,8	3				
Metals	9	3				
Titanium alloys	1,2,9	3				
Aluminum alloys	1,2,9	3				
Copper alloys	1,2,9	3				
Nickel alloys	1,2,9	3				
Iron alloys	1,2,9	3				
Cobalt alloys	1,2,9	3				
Magnesium alloys	1,2,9	3				
Tin alloys	1,2,9	3				
Lead alloys	1,2,9	3				
Stainless steel	1,2,9	3				
Silver	1,2,9	3				
Silver solder	1,2,9	3				
Gaseous oxygen	5	3				
Liquid oxygen	5	3				
Heat sources	6	3				
Electrical-energy sources	6	3				
Mechanical-energy sources	6	3				
Atmospheres	5	3				
Oxygen-containing atmospheres	5	3				

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