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Standard Guide for Evaluating Metals for Oxygen Service¹

This standard is issued under the fixed designation G94; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide applies to metallic materials under consideration for oxygen or oxygen-enriched fluid service, direct or indirect, as defined in Section 3. It is concerned primarily with the properties of a metallic material associated with its relative susceptibility to ignition and propagation of combustion. It does not involve mechanical properties, potential toxicity, outgassing, reactions between various materials in the system, functional reliability, or performance characteristics such as aging, shredding, or sloughing of particles, except when these might contribute to an ignition.

1.2 This document applies only to metals; nonmetals are covered in Guide G63.

NOTE 1—The American Society for Testing and Materials takes no position respecting the validity of any evaluation methods asserted in connection with any item mentioned in this guide. Users of this guide are expressly advised that determination of the validity of any such evaluation methods and data and the risk of use of such evaluation methods and data are entirely their own responsibility.

NOTE 2—In evaluating materials, any mixture with oxygen exceeding atmospheric concentration at pressures higher than atmospheric should be evaluated from the hazard point of view for possible significant increase in material combustibility.

1.3 Units—The values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

- D2512 Test Method for Compatibility of Materials with Liquid Oxygen (Impact Sensitivity Threshold and Pass-Fail Techniques)
- D2863 Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)
- D4809 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method)
- G63 Guide for Evaluating Nonmetallic Materials for Oxygen Service
- G72 Test Method for Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen-Enriched Environment

¹ This guide is under the jurisdiction of ASTM Committee G04 on Compatibility and Sensitivity of Materials in Oxygen Enriched Atmospheres and is the direct responsibility of Subcommittee G04.02 on Recommended Practices.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- G86 Test Method for Determining Ignition Sensitivity of Materials to Mechanical Impact in Ambient Liquid Oxygen and Pressurized Liquid and Gaseous Oxygen Environments
- G88 Guide for Designing Systems for Oxygen Service
- G93 Guide for Cleanliness Levels and Cleaning Methods for Materials and Equipment Used in Oxygen-Enriched Environments
- G124 Test Method for Determining the Combustion Behavior of Metallic Materials in Oxygen-Enriched Atmospheres
- G126 Terminology Relating to the Compatibility and Sensitivity of Materials in Oxygen Enriched Atmospheres
- G128 Guide for Control of Hazards and Risks in Oxygen Enriched Systems

2.2 *ASTM Special Technical Publications (STPs) on the Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres:*

ASTM STPs in this category are listed as: 812, 910, 986, 1040, 1111, 1167, 1197, 1319, 1395, and 1454

2.3 *Compressed Gas Association—CGA Documents:*³

~~Pamphlet G-4.4-2003-G-4.4 (EIGA Doc. 13/02)13~~ Oxygen Pipeline and Piping Systems

~~Pamphlet G-4.8~~ Safe Use of Aluminum Structured Packing for Oxygen Distillation

~~Pamphlet G-4.9~~ Safe Use of Brazed Aluminum Heat Exchangers for Producing Pressurized Oxygen

~~Pamphlet P-8.4 (EIGA Doc. 65/99)65~~ Safe Operation of Reboilers—~~Condensers~~ Reboilers/Condensers in Air Separation Plants

2.4 *ASTM Adjuncts:*

Test Program Report on the Ignition and Combustion of Materials in High-Pressure Oxygen⁴

3. Terminology

3.1 *Definitions:*

3.1.1 *autoignition temperature*—*temperature, n*—the lowest temperature at which a material will spontaneously ignite in oxygen under specific test conditions (see Guide Terminology G126).

3.1.2 *direct oxygen service*—*service, n*—in contact with oxygen during normal operations. Examples: oxygen compressor piston rings, control valve seats (see Guide Terminology G126).

3.1.3 *exemption pressure*—*pressure, n*—the maximum pressure for an engineering alloy at which there are no oxygen velocity restrictions (from CGA 4.4 and EIGA doc 13/02).

3.1.4 *impact-ignition resistance*—*resistance, n*—the resistance of a material to ignition when struck by an object in an oxygen atmosphere under a specific test procedure (see Guide Terminology G126).

3.1.5 *indirect oxygen service*—*service, n*—not normally in contact with oxygen, but which might be as a result of a reasonably foreseeable malfunction, operator error, or process upset. Examples: liquid oxygen tank insulation, liquid oxygen pump motor bearings (see Guide Terminology G126).

3.1.6 *maximum use pressure*—*pressure, n*—the maximum pressure to which a material can be subjected due to a reasonably foreseeable malfunction, operator error, or process upset (see Guide G63).

3.1.7 *maximum use temperature*—*temperature, n*—the maximum temperature to which a material can be subjected due to a reasonably foreseeable malfunction, operator error, or process upset (see Guide Terminology G126).

3.1.8 *nonmetallic*—*nonmetallic, adj*—applies to any material, other than a metal, or any composite in which the metal is not the most easily ignited component and for which the individual constituents cannot be evaluated independently (see Guide Terminology G126).

3.1.9 *operating pressure*—*pressure, n*—the pressure expected under normal operating conditions (see Guide Terminology G126).

3.1.10 *operating temperature*—*temperature, n*—the temperature expected under normal operating conditions (see Guide Terminology G126).

³ Available from Compressed Gas Association (CGA), 4221 Walney Rd., 5th Floor, Chantilly, VA 20151-2923; 8484 Westpark Drive, Suite 220, McLean, VA 22102, <http://www.cganet.com>.

⁴ Available from ASTM International Headquarters. Order Adjunct No. ADJG0094. Original adjunct produced in 1986.

3.1.11 *oxygen-enriched—oxygen-enriched, adj*—applies to a fluid (gas or liquid) that contains more than 25 mol % oxygen (see [Guide Terminology G126](#)).

3.1.12 *qualified technical personnel—personnel, n*—persons such as engineers and chemists who, by virtue of education, training, or experience, know how to apply physical and chemical principles involved in the reactions between oxygen and other materials (see [Guide Terminology G126](#)).

3.1.13 *reaction effect—effect, n*—the personnel injury, facility damage, product loss, downtime, or mission loss that could occur as the result of an ignition (see [Guide Terminology G126](#)).

3.1.14 *threshold pressure—pressure, n*—there are several different definitions of threshold pressure that are pertinent to the technical literature. It is important that the user of the technical literature fully understand those definitions of threshold pressure which apply to specific investigations being reviewed. Two definitions for threshold pressure, based on interpretations of the bulk of the current literature, appear below.

3.1.14.1 *threshold pressure—pressure, n—in a promoted ignition-combustion test series conducted over a range of pressures*, this is the maximum pressure at which no burns, per the test criteria, were observed and above which burns were experienced or tests were not conducted.

3.1.14.2 *threshold pressure—pressure, n—the minimum gas pressure (at a specified oxygen concentration and ambient temperature) that supports self-sustained combustion of the entire standard sample* (see [Guide Test Method G124](#)).

4. Significance and Use

4.1 The purpose of this guide is to furnish qualified technical personnel with pertinent information for use in selecting metals for oxygen service in order to minimize the probability of ignition and the risk of explosion or fire. It is intended for use in selecting materials for applications in connection with the production, storage, transportation, distribution, or use of oxygen. *It is not intended as a specification for approving materials for oxygen service.*

5. Factors Affecting Selection of Materials

5.1 General:

5.1.1 The selection of a material for use with oxygen or oxygen-enriched atmospheres is primarily a matter of understanding the circumstances that cause oxygen to react with the material. Most materials in contact with oxygen will not ignite without a source of ignition energy. When an energy-input exceeds the configuration-dependent threshold, then ignition and combustion may occur. Thus, the material's flammability properties and the ignition energy sources within a system must be considered. These should be viewed in the context of the entire system design so that the specific factors listed in this guide will assume the proper relative significance. In summary, it depends on the application.

5.2 Relative Amount of Data Available for Metals and Nonmetals:

5.2.1 Studies of the flammability of gaseous fuels were begun more than 150 years ago. A wide variety of applications have been studied and documented, including a wide range of important subtleties such as quenching phenomena, turbulence, cool flames, influence of initial temperature, etc., all of which have been used effectively for safety and loss prevention. A smaller, yet still substantial, background exists for nonmetallic solids. In contrast to this, the study of the flammability of metals dates only to the 1950s, and even though it has accelerated rapidly, the uncovering and understanding of subtleties have not yet matured. In addition, the heterogeneity of the metal and oxidizer systems and the heat transfer properties of metals, as well as the known, complex ignition energy and ignition/burning mechanisms, clearly dictate that caution is required when applying laboratory findings to actual applications. In many cases, laboratory metals burning tests are designed on what is believed to be a worst-case basis, but could the particular actual application be worse? Further, because so many subtleties exist, accumulation of favorable experience (no metal fires) in some particular application may not be as fully relevant to another application as might be the case for gaseous or nonmetallic solids where the relevance may be more thoroughly understood.

5.2.1.1 ASTM Symposia and Special Technical Publications on these symposia have contributed significantly to the study of the flammability and sensitivity of materials in oxygen-enriched atmospheres. See section 2.2 for listing of STP numbers and the References Section for key papers.

5.3 Relationship of Guide G94 with Guides G63, G88, and G93:

5.3.1 This guide addresses the evaluation of metals for use in oxygen systems and especially in major structural portions of a system. Guide G63 addresses the evaluation of nonmetals. Guide G88 presents design and operational maxims for all systems. In general, however, Guides G63 and G88 focus on physically small portions of an oxygen system that represent the critical sites most likely to encounter ignition. Guide G93 covers a key issue pertinent to actual operating oxygen systems; cleaning for the service.

5.3.2 The nonmetals in an oxygen system (valve seats and packing, piston rings, gaskets, o-rings) are small; therefore, the use of the most fire-resistant materials is usually a realistic, practical option with regard to cost and availability. In comparison, the choice of material for the major structural members of a system is much more limited, and the use of special alloys may have to be avoided to achieve realistic costs and delivery times. Indeed, with the exception of ceramic materials, which have relatively few practical uses, most nonmetals have less fire resistance than virtually all metals. Nonmetals are typically introduced into a system to provide a physical property not achievable from metals. Nonmetals may serve as “links” in a kindling chain (see 5.6.5), and since the locations of use are typically mechanically severe, the primary thrust in achieving compatible oxygen systems rests with the minor components as addressed by Guides G63 and G88 that explain the emphasis on using the most fire-resistant materials and Guide G93 which deals with the importance of system cleanliness.

5.3.3 Since metals are typically more fire-resistant and are used in typically less fire-prone functions, they represent a second tier of interest. However, because metal components are relatively so large, a fire of a metal component is a very important event, and should a nonmetal ignite, any consequential reaction of the metal can aggravate the severity of an ignition many times over. Hence, while the selection of nonmetals by Guide G63 and the careful design of components by Guide G88 are the first line of defense, optimum metal selection is an important second-line of defense.

5.3.4 Contaminants and residues that are left in oxygen systems may contribute to incidents via ignition mechanisms such as particle impact and promoted ignition-combustion (kindling chain). Therefore, oxygen system cleanliness is essential. Guide G93 describes in detail the essential elements for cleaning oxygen systems.

5.4 Differences in Oxygen Compatibility of Metals and Nonmetals:

5.4.1 There are several fundamental differences between the oxygen compatibility of metals and nonceramic nonmetals. These principal differences are summarized in Table 1.

5.4.2 Common-use metals are harder to ignite. They have high autoignition temperatures in the range 900 to 2000 °C (1650 to 3600 °F). In comparison, most combustible nonmetals have autoignition temperatures in the range 150 to 500 °C (300 to 1000 °F). Metals have high thermal conductivities that help dissipate local heat inputs that might easily ignite nonmetals. Many metals also grow protective oxide coatings (see 5.5) that interfere with ignition and propagation.

5.4.3 Once ignited, however, metal combustion can be highly destructive. Adiabatic flame temperatures for metals are much higher than for most polymers (Table X1.7). The greater density of most metals provides greater heat release potential from components of comparable size. Since many metal oxides do not exist as oxide vapors (they largely dissociate upon vaporization), combustion of these metals inherently yields coalescing liquid metal oxide of high heat capacity in the flame zone at the oxide boiling point (there may be very little gaseous metal oxide). In comparison, combustion of polymers yields gaseous combustion products (typically carbon dioxide and steam) that tend to dissipate the heat release.

5.4.4 Contact with a mixture of liquid metal and oxide at high temperature results in a massive heat transfer relative to that

TABLE 1 Comparison of Metals and Nonmetals Flammability

	Metals	Nonmetals
Combustion products	molten metal oxide	hot gases
Autoignition temperatures	900–2000 °C	150–500 °C
Autoignition temperatures	900–2000 °C	150–500 °C
Thermal conductivities	higher	lower
Flame temperature	higher	lower
Heat release	higher due to density	lower
Surface oxide	can be protective	negligible

possible upon contact with hot, low-heat-capacity, gaseous combustion products of polymers. As a result, metal combustion can be very destructive. Indeed, certain metal combustion flames are an effective scarfing agent for hard-to-cut materials like concrete **(1)**.⁵

5.4.5 Finally, because most polymers produce largely inert gas combustion products, there is a substantial dilution of the oxygen in the flame that inhibits combustion and if in a stagnant system, may even extinguish a fire. For many metals, combustion produces the molten oxide of negligible volume condensing in the flame front and, hence, oxygen dilution is much less.

5.5 Protective Oxide Coatings:

5.5.1 Oxides that grow on the surfaces of metals can play a role in the metal's flammability. Those films that interfere with ignition and combustion are known as protective oxides. Typically, an oxide will tend to be protective if it fully covers the exposed metal, if it is tenaciously adherent, and if it has a high melting point. Designers have very limited control over the integrity of an oxide layer; however, since oxide can have significant influence on metal's test data, an understanding of its influence is useful.

5.5.2 A protective oxide provides a barrier between the metal and the oxygen. Hence, ignition and combustion can be inhibited in those cases where the oxide barrier is preserved. For example, in some cases, an oxide will prevent autogenous ignition of a metal up to the temperature at which the metal melts and produces geometry changes that breach the film. In other cases (such as anodized aluminum wires), the oxide may be sufficiently sturdy as either a structure or a flexible skin to contain and support the molten base metal at temperatures up to the melting point of the oxide itself. In either of these cases, autogenous ignition may occur at much lower temperatures if the metal experiences mechanisms that damage the oxide coating. Oxide damaging mechanisms may include mechanical stresses, frictional rubs and abrasion, or chemical oxide attack (amalgamation, etc.). Depending upon the application, a high metal autoignition temperature, therefore, may be misleading relative to the metal's flammability.

5.5.3 One criterion for estimating whether an oxide is protective is based upon whether the oxide that grows on a metal occupies a volume greater or less than the volume of the metal it replaces. Pilling and Bedworth **(2)** formulated an equation for predicting the transition between protective and nonprotective oxides in 1923. Two forms of the Pilling and Bedworth (P&B) equation appear in the literature and can yield different results. ASTM Committee G04 has concluded that the most meaningful formulation for the P&B ratio in oxide evaluations for flammability situations is:

$$\text{P\&B Ratio} = Wd/awD \quad (1)$$

where the metal, M, forms the oxide M_aO_b , a and b are the oxide stoichiometry coefficients, W is the formula weight of the oxide, d is the density of the metal, w is the formula weight of the metal, and D is the density of the oxide. The other form of the equation treats the stoichiometry coefficient as unity and thus for those oxides that have a single metal atom in the formula, the two equations yield the same results. Pilling and Bedworth ratios should always reference an oxide rather than the metal of oxide origin, because for many metals, several different oxides can form each having a different P&B ratio. For example, normal atmospheric corrosion of iron tends to produce the oxide, Fe_2O_3 , whereas the oxide that forms for iron at the elevated temperatures of combustion is Fe_3O_4 . In cases where a mixture of oxides forms, the stoichiometry coefficients, a and b, may be weighted to reflect this fact. **Table 2** presents numerous P&B ratios for a number of metal oxides. The P&B ratio suggests whether a grown metal oxide is sufficient in volume to thoroughly cover a metal surface, but it does not provide insight into the tenacity of the coating or whether it does indeed grow in a conformal fashion. The ratios in **Table 2** have been segregated into those oxides that one would suspect to be nonprotective ($P\&B < 1$) and those that might more likely be protective ($P\&B \geq 1$). Note also that if the P&B ratio $\gg 1$ (as in the case of Fe_2O_3), the volume of the oxide can increase so dramatically that chipping, cracking, or breaking can occur that may reduce its "protection." The effect of protective oxides on alloys is a still more complex aspect of a metal's flammability.

5.6 Operational Hazard Thresholds:

5.6.1 Most practical oxygen systems are capable of ignition and combustion to some extent under at least some conditions of pressure, temperature, flow, etc. The key to specifying oxygen-compatible systems is avoiding the circumstances in which ignition is likely and in which consequential combustion may be extensive. This often involves avoiding the crossing of hazard thresholds. Guide **G128** is very useful in assessing hazards and risks in oxygen systems.

5.6.2 For example, many materials exhibit a bulk system-related ignition temperature that represents a hazard threshold. When a

⁵ The boldface numbers in parentheses refer to the list of references at the end of this guide.

TABLE 2 Pilling and Bedworth Ratios^A of Metal Oxides

Nonprotective Oxides		Potentially Protective Oxides	
Oxide	P&B < 1	Oxide	P&B ≥ 1
BaO	0.685	Al ₂ O ₃	1.29
CaO	0.663–0.637	CuO	1.71–1.77
MgO	0.806	Cu ₂ O	1.68
		Cr ₂ O ₃	2.02
		FeO	1.78
		Fe ₂ O ₃	2.15
		Fe ₃ O ₄	2.09
		CoO	1.76
		MoO ₂	2.10
		NiO	1.70
		PbO	1.28–1.52
		SnO	1.15–1.28
		SnO ₂	1.19–1.33
		TiO ₂	1.76–1.95
		ZnO	1.59

^A The Pilling and Bedworth (P&B) ratio is the ratio of the volume of a metal oxide compared to the volume of metal from which it was grown. A P&B ratio ≥ 1 suggests the potential for an oxide to be protective if it is also conformal and tenaciously adherent. All data are calculated and do not always agree with P&B ratios in the literature (1-5).

region of a system is exposed to a temperature greater than its bulk in-situ autoignition temperature, the likelihood of an ignition increases greatly; a hazard threshold has been crossed.

5.6.3 Hazard thresholds can be of many types. Ignition may depend upon a minimum heat energy input, and the threshold may be different for heat inputs due to heat transfer, friction, arc/spark, etc. Propagation may require the presence of a minimum oxygen concentration (the oxygen index is one such flammability limit) or it may require a minimum oxygen pressure (a threshold pressure below which propagation does not even occur in pure oxygen). It may also require a specific geometry.

5.6.4 For a fire to occur, it may be necessary to cross several thresholds of hazard simultaneously. For example, brief local exposure to high temperature above the ignition temperature might not produce ignition unless the heat transferred also exceeds the minimum energy threshold. And even if a local ignition results, the fire may self-extinguish without propagation if the pressure, oxidant concentration, or other conditions, are not simultaneously in excess of their related hazard threshold. It is desirable to operate on the conservative side of as many hazard thresholds as possible.

5.6.5 *Kindling Chains*—A kindling chain reaction can lead to the crossing of a hazard threshold. In a kindling chain, ignition of an easily ignited material (such as a contaminant by adiabatic compression) may not release enough heat to, in turn, ignite a valve body, but may be sufficient to ignite a valve seat, which, in turn, may release sufficient heat to ignite the larger, harder-to-ignite valve body.

5.7 *Practical Metal Systems: Systems Considerations:*

5.7.1 It is not always possible to use the most fire-resistant metals in practical systems. As a result, operation below every hazard threshold may not always be used to minimize the chance of a fire. ~~Guide G128 is very useful in assessing hazards and risks in oxygen systems.~~ Additional conservatism is often used to increase the safety margins where possible. For example, if the pressure and temperature of an application are such that particle impact may cause an ignition, the remedy has been to limit the severity of particle impacts by limiting gas velocity and filtering or screening of particles. This, in effect, limits the application severity by constraining the operation conditions; ~~CGA Pamphlet G-4.4-2003 (EIGA Doc. 13/02) details an industry practice using this approach.~~ conditions.

5.7.1.1 A joint CGA-EIGA Task Force recently issued a “harmonized” document CGA G-4.4-2003 (EIGA Doc. 13/02) which has produced a unified view on velocity limitation guidance and other mitigating approaches. The Compressed Gas Association (CGA) and the European Industrial Gas Association (EIGA) have published a “harmonized” document, CGA G-4.4 (EIGA Doc. 13), which provides a prescriptive metal selection method considering flammability (based on pressure and thickness limits) and ignition risk (based on gas pressure-velocity limits).

The harmonized CGA G-4.4/EIGA Doc 13 document includes design and installation requirements and recommendations for the use of metal alloys in oxygen pipelines and equipment for gaseous oxygen with a temperature range between –30 °C and 200 °C (–22 °F and 400 °F), and pressures up to 21 MPa (3000 psi). This publication includes guidance for selection of metals based on exemption pressures (EP), minimum application thickness, and pressure-velocity curves. The prescribed EP is defined

as the maximum pressure at which a metal is not subject to oxygen gas velocity limitations. Thus, at pressures below an alloy's EP, an alloy may be used for gaseous oxygen applications regardless of gas velocity, as long as the application meets the minimum thickness criteria. At pressures above an alloy's EP, the alloy is limited to pressure-velocity (PV) combinations as dictated by corresponding PV curves, which include impingement and non-impingement versions, depending on the application. The PV curves evolved over time based on the experience of the industrial gas community and experts. The EPs were more recently established based on Test Method G124 test data and guidance of industry experts. If an alloy is desired for use above its EP and corresponding PV curve, CGA G-4.4/EIGA Doc. 13 allows for an oxygen hazard analysis to be performed to evaluate the risk of fire.

5.8 Properties of the Metal:

5.8.1 *Ease of Ignition*—Although metals are typically harder to ignite than nonmetals, there is a wide range of ignition properties exhibited among potential structural materials, and, indeed, some metals are difficult to ignite in some ways while being relatively easy to ignite in others. The principal recognized sources of metal ignition include:

5.8.1.1 Contaminant promotion where the contaminant itself may be ignited by mechanical impact, adiabatic compression, sparks, or resonance.

5.8.1.2 Particle impact ignition in which a particle may ignite and promote ignition of the metal.

5.8.1.3 Friction ignition where the friction results from mechanical failure, cavitation, rubs, etc.

5.8.1.4 Bulk heating to ignition.

5.8.2 Ignition may also result from the following mechanisms, though these are not thoroughly studied nor understood for metals, nor have they been implicated in significant numbers of incidents relative to those in 5.8.1.

5.8.2.1 Mechanical impact.

5.8.2.2 Resonance.

5.8.2.3 Fresh metal exposure.

5.8.2.4 Crack propagation.

5.8.2.5 Electric arc or spark.

5.8.2.6 Puncture.

5.8.2.7 Trapped volume pressurization.

5.8.2.8 *Autoignition*—In the preceding mechanisms, heating to the autoignition temperature can result. For some of them, the achievement of ignition also can result from the material self heating as the freshly exposed metal oxidizes.

5.8.3 Ignition can result from bulk heating to the autoignition temperature, but this is rare in oxygen systems unless an environmental fire is present or unless electrical heaters experience runaways. Autoignition temperatures are often used to compare metals, but they can yield rankings that disagree with observed experience. This is because ignition is a very complex process. For example, where a metal grows a protective oxide, the autoignition temperature can vary widely depending upon such things as the adherence of the oxide, its degree of protection (as indicated in part by its Pilling and Bedworth number), and its melting point. A more likely effect of temperature on the ignition of a metal is via a promoted ignition-combustion mechanism.

5.8.4 *Properties and Conditions Affecting Potential Resultant Damage*—A material's heat of combustion, its mass, its geometry (thick versus thin), the oxygen concentration and pressure, the presence of gaseous versus liquid oxygen, the flow conditions before and after ignition, and the flame propagation characteristics affect the potential damage if ignition should occur. They should be taken into account in estimating the reaction effect in 8.5. Since so much damage in metal fires is attributable to direct contact with the molten oxide and from radiation due to its extremely high temperature, the probable flow path or trajectory of the molten oxide should be considered in predicting the zones of greatest damage.

5.9 Extenuating Factors:

5.9.1 In choosing major structural members of a system, practicality becomes a critical factor. Frequently, the more fire-resistant materials are simply impractical or uneconomical. For example, their strength-to-weight ratios may not meet minimum mechanical standards for turbine wheels. The cost or availability of an alloy may also preclude its use in a long pipeline. Corrosive environments may preclude still other materials. In contrast, there may be a base of experience with traditional metals in oxygen service, such as carbon steel pipelines, that clearly demonstrates suitability for continued service with appropriate safeguards. As a result, where these extenuating factors are present, less than optimum metals are frequently selected in conjunction with operational controls (such as operating valves only during zero-flow), established past practice (such as CGA Pamphlet G-4.4 for steel piping), or measures to mitigate the risk (such as use with a shield or removal of personnel from the vicinity).

5.10 Operating Conditions:

5.10.1 Conditions that affect the suitability of a material include the other materials of construction and their arrangement and geometry in the equipment and also the pressure, temperature, concentration, flow, and velocity of the oxygen. For metals, pressure, concentration or purity, and oxygen flow rate are usually the most significant factors. Temperature is a much less significant factor than is the case for nonmetals because ignition temperatures of metals are all significantly higher than those of nonmetals. The effects of these factors show up in the estimate of ignition potential (8.2) and reaction effect assessment (8.5), as explained in Section 8.

5.10.2 *Pressure*—The oxygen pressure is important, because it generally affects the generation of potential ignition mechanisms, and because it affects the destructive effects if ignition should occur. While generalizations are difficult, rough scales would be as given in Table 3.

NOTE 3—While the pressure generally affects the reaction as given in Table 3, data indicate that it has varying effects on individual flammability properties. For example, for many metals, increasing pressure results in the following:

- (a) A reduction in the oxygen concentration required to enable propagation;
- (a) A reduction in the oxygen concentration required to enable propagation;
- (b) Differing effects on autoignition temperature, with many metals having invariant autoignition temperatures, many metals having decreasing autoignition temperatures, and some metals having increasing autoignition temperatures;
- (c) An increase in sensitivity to mechanical impact;
- (d) A negligible change in heat of combustion;
- (e) An increase in the difficulty of friction ignition, apparently due to increased convective heat dissipation;
- (f) An increase in the likelihood of adiabatic compression ignition, however, adiabatic compression is an unlikely direct ignition mechanism for metals except at pressures in excess of 20 000 kPa (3 000 psi); and
- (g) An increase in the rate of combustion.
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- (e) An increase in the difficulty of friction ignition, apparently due to increased convective heat dissipation;
- (f) An increase in the likelihood of adiabatic compression ignition, however, adiabatic compression is an unlikely direct ignition mechanism for metals except at pressures in excess of 20 000 kPa (3 000 psi); and
- (g) An increase in the rate of combustion.

5.10.3 *Concentration*—As oxygen concentration decreases from 100 %, the likelihood and intensity of a potential fire also decrease. Therefore, greater latitude may be exercised in the selection of materials. For all metals, there is an oxygen concentration (a flammability limit analogous to the oxygen index), below which (in the specific metal combustion tests undertaken) propagating combustion will not occur, even in the presence of an assured (very high energy) ignition. This concentration decreases with

TABLE 3 Effect of Pressure on Typical Metal Burning Reactions

kPa	kPa	psi	psi	Pressure Effect Assessment ^A
0–70		0–10		relatively mild
70–700		10–100		moderate
700–7000		100–1000		intermediate
7000–20 000		1000–3000		severe
Over 20 000		Over 3000		extremely severe

^A See 5.10.2.

increasing pressure above a threshold pressure (below which the metal will not burn even in pure oxygen). The concentration may approach an asymptote at high pressures, [Fig. X1.2](#), [Fig. X2.1](#), and [Fig. X2.3](#).

NOTE 4—Some metals are extremely sensitive to oxygen purity. Since many metal oxides do not exist as gases, the combustion products of some metals do not interfere with the combustion as is the case with polymers. Therefore, small amounts of inert gases in the oxygen can accumulate and control the combustion. In a research project, Benning et al. (6) found that as little as 0.2 % argon could increase the minimum pressure at which ~~6.4 mm~~ (0.25 in.) 6.4 mm (0.25 in.) diameter aluminum rods sustained combustion from 210 kPa (30 psi absolute) to 830 kPa (120 psi absolute). This effect is believed to be most significant for “vapor-burning” metals such as aluminum and less significant for “liquid-burning” metals such as iron. Theory is found in Benning (6) and Glassman (7-9).

5.10.4 *Flow and Oxygen Inventory*—The quantity of oxygen present and the rate at which it can flow to an ignition site affects the intensity and scale of a metal fire. Since many metals do not form gaseous combustion products, self extinguishment through accumulation of combustion products cannot occur as it does with polymers. However, accumulation of inert gases in the oxygen may cause extinguishment. Since the density of oxygen gas is much lower than the metal density, the quantity of metal that can burn is often limited by the quantity of oxygen present or the rate at which it can be supplied.

5.10.5 *Temperature*—Increasing temperature obviously increases the risk of ignition, as well as the prospect for sustained combustion. Indeed, an increase in temperature may enable combustion in cases where propagation would not be possible at lower temperature. The influence of environmental temperature on metals is much less significant than for nonmetals; this is because the autoignition temperature of the most sensitive bulk metal (perhaps carbon steel at ~~(~900°C (~1650°F))~~ (~900 °C (~1650 °F))) is significantly greater than for the most resistant polymers (for example PTFE at ~~(~480°C (~900°F))~~ (~480 °C (~900 °F))).

5.10.5.1 Although autoignition temperatures of metals in oxygen atmospheres have been cited as a means of ranking materials for service in high temperature oxygen, promoted ignition-combustion of metals in high temperature oxygen may be more appropriate. Zawierucha et al. (10) have reported on elevated temperature promoted ignition-combustion resistance.

5.10.6 *LOX versus GOX*—Combustion of aluminum in LOX has led to extremely serious combustion events known as Violent Energy Releases (VERs) in both operating systems and experiments. In GOX, aluminum will experience rapid combustion but not VERs. The destruction caused by a VER is more typical of an explosion than simple combustion. Numerous investigators have duplicated this phenomenon (11-24). Key Aluminum-LOX incidents are referenced (25-27). Mitigating approaches are described in CGA pamphlets G4.8, ~~G4.9~~ G4.9, and P-8.4 for aluminum air separation plant components.

5.10.7 *Geometry*—The geometry of the component can have a striking effect on the flammability of metals. Generally, thin components or high-surface-area-to-volume components will tend to be more flammable. For example, both Stoltzfus et al. (28) and Dunbobbin et al. (29) have shown that materials such as thin wire mesh and thin layered sheets can become much more flammable than might be expected on the basis of tests of rods. In these works, copper and brass alloys that typically resist propagation in bulkier systems were capable of complete combustion. Zabrenski et al. (30) have found that thin-wall tubes of ~~6.4 mm (0.25 in.)~~ 6.4 mm (0.25 in.) diameter stainless steel would propagate combustion at atmospheric pressure while solid rods required pressures of 5.0 MPa [740 psi absolute]. Samant et al. (31) in promoted ignition-combustion studies of Nickel 200, Monel 400, Hastelloy C-276, Copper, and Stainless Steels at pressures up to 34.6 MPa show that Nickel 200 was the most combustion resistant in thin cross sections while 316/316L stainless steel was the least.

5.11 *Ignition Mechanisms*—For combustion to occur, it is necessary to have three elements present: oxidizer, fuel, and ignition energy. The oxygen environment is obviously the oxidizer, and the system itself is the fuel. Several potential sources of ignition energy are listed below. The list is not all-inclusive or in order of importance or in frequency of occurrence.

5.11.1 *Promoted Ignition*—A source of heat input occurs (perhaps due to a kindling chain) that acts to start the metal burning. Examples: the ignition of contamination (oil or alien debris) which combusts and its own heat release starts a metal fire.

5.11.2 *Friction Ignition*—The rubbing of two solid materials results in the generation of heat and removal of protective oxide. Example: the rub of a centrifugal compressor rotor against its casing.

5.11.3 *Heat from Particle Impact*—Heat is generated from the transfer of kinetic, thermal, or chemical energy when small particles (sometimes incandescent, sometimes igniting on impact), moving at high velocity, strike a material. Example: high velocity particles from a dirty pipeline striking a valve plunger.

5.11.4 *Fresh Metal Exposure*—Heat is generated when a metal with a protective surface oxide is scratched or abraded, and a fresh surface oxide forms. Titanium has demonstrated ignition from this effect, but there are no known cases of similar ignition of other

common metals. Nonetheless, fresh metal exposure may be a synergistic contributor to ignition by friction, particle impact, etc. Example: the breaking of a titanium wire in oxygen.

5.11.5 *Mechanical Impact*—Heat is generated from the transfer of kinetic energy when an object having a large mass or momentum strikes a material. Aluminum and titanium have been experimentally ignited this way, but stainless steels and carbon steels have not. Examples: a backhoe rooting-up an oxygen line; a fork truck penetrating an oxygen cylinder.

5.11.6 *Heat of Compression*—Heat is generated from the conversion of mechanical work when a gas is compressed from a low to a high pressure. This can occur when high-pressure oxygen is released into a dead-ended tube or pipe, quickly compressing the residual oxygen that was in the tube ahead of it. An effective ignition mechanism with polymers, the much higher heat capacity and thermal conductivity of significantly sized metals greatly attenuates high temperature produced this way. Example: a downstream valve or flexible lined pigtail in a dead-ended high-pressure oxygen manifold.

5.11.7 *Electrical Arc*—Electrical arcing can occur from motor brushes, electrical control instrumentation, other instrumentation, electrical power supplies, lightning, etc. Electrical arcing can be a very effective metal igniter, because current flow between metals is easily sustained, electron beam heating occurs, and metal vaporizes under the influence of the plasma. All of these are conducive to combustion. Example: an insulated electric heater element in oxygen experiences a short circuit and arcs through to the oxygen gas.

5.11.8 *Resonance*—Acoustic oscillations within resonant cavities are associated with rapid gas temperature rise. This rise is more rapid and achieves higher values where particulates are present or where there are high gas velocities. Ignition can result if the heat transferred is not rapidly dissipated, and fires of aluminum have been induced experimentally by resonance. Example: a gas flow into a tee and out of a side port such that the remaining closed port forms a resonance.

5.11.9 *Other*—Since little is known about the actual cause of some oxygen fires or explosions, other mechanisms, not readily apparent, may be factors in, or causes of, such incidents. These might include external sources, such as welding spatter, or internal sources, such as fracture or thermite reactions of iron oxide with aluminum.

5.12 *Reaction Effect*—The effect of an ignition (and subsequent propagation, if it should occur) has a strong bearing on the selection of a material. While reaction effect assessment is an obviously imprecise and strongly subjective judgment, it must be balanced against extenuating factors such as those given in 5.9. Suggested criteria for rating the reaction effect severity have been developed in Guide G63 and are shown in Table 4, and a method of applying the rating in a material selection process is given in Section 8. Note that, in some cases, the reaction effect severity rating for a particular application can be lowered by changing other materials that may be present in the system, changing component locations, varying operating procedures, or using shields and the like (see Guide G88). The combustion of aluminum in LOX has generated combustion phenomena, VERs, that are explosive on systems and test facilities.

5.12.1 *Heat of Combustion*—The combustion of a metal releases heat, and the quantity has a direct effect on the destructive nature of the fire. On a mass basis, numerous metals and polymers release about the same amount of heat. However, because of its much larger mass in most systems, combustion of many metals has the potential for release of the major amount of heat in a fire. Combustion of aluminum in LOX is an example of an explosive phenomenon.

5.12.2 *Rate of Combustion*—The intensity of a fire is related to both the heat of combustion of the materials and the rate at which

TABLE 4 Reaction Effect Assessment for Oxygen Applications

Rating		Effect on Personnel Safety	Effect on System Objectives	Effect on Functional Capability
Code	Severity Level			
A	negligible	No injury to personnel.	No unacceptable effect on production, storage, transportation, distribution, or use as applicable.	No unacceptable damage to the system.
B	marginal	Personnel-injuring factors can be controlled by automatic devices, warning devices, or special operating procedures.	Production, storage, transportation, distribution, or use as applicable is possible by utilizing available redundant operational options.	No more than one component or subsystem damaged. This condition is either repairable or replaceable on site within an acceptable time frame.
C	critical	Personnel injured: (1) operating the system; (2) maintaining the system; or (3) being in vicinity of the system.	Production, storage, transportation, distribution, or use as applicable impaired seriously.	Two or more major subsystems are damaged; this condition requires extensive maintenance.
D	catastrophic	Personnel suffer death or multiple injuries.	Production, storage, transportation, distribution, or use as applicable rendered impossible; major unit is lost.	No portion of system can be salvaged; total loss.

the combustion occurs. The rates of combustion of various metals can vary more than an order of magnitude, and for some metals can be so rapid as to be considered explosive.

6. Test Methods

6.1 Promoted Combustion Test—A metal specimen is deliberately exposed to the combustion of a promoter (easily ignited material) or other ignition source. Metal specimens reported in the literature have varied in length and thickness. The promoter may be standardized, in which case the test ranks those materials that resisted ignition as being superior to those that burned; varying the oxygen pressure, oxygen purity or specimen temperature allows further ranking control. The promoter mass may also be varied, in which case, the metals are ranked according to the quantity of promoter required to bring about combustion. In yet another variation, ignition of the test specimen is ensured and the velocity of propagation or the specimen regression rate is measured. The regression rate is the velocity at which the combustion zone moves along the metal; the molten material that drains away may not be completely combusted. A low propagation rate ranks a metal higher (more desirable).—

NOTE 5—ASTM Committee G04 has sponsored a series of metal-promoted combustion tests at the NASA White Sands Test Facility using the methodology reported by Benz et al. (32). These data, along with similar data generated by NASA, are included in Table X1.1. This table ranks metals according to (1) the highest pressure at which combustion was resisted, (2) for metals that ranked comparably above, according to the average propagation rate, and (3) for metals that ranked comparably by both (1) and (2), above, according to the average burn length below the threshold. Test Method G124 has been developed for determining the combustion behavior of metallic materials in oxygen enriched atmospheres.

6.2 Frictional Heating Test—One metal is rotated against another in an oxygen atmosphere. Test variables include oxygen pressure, specimen loads, and linear velocity. At constant test conditions, a material is ranked higher if it exhibits a higher Pv product at ignition (where P is the force divided by the initial cross-sectional area, and v is the linear velocity).

NOTE 6—ASTM Committee G04 has sponsored a series of metals friction ignition tests at the NASA White Sands test facility using the methodology reported by Benz and Stoltzfus (33). Due to the high cost of the apparatus and tests, round robin testing is not realistic and this procedure is not being developed into an ASTM standard; however, these data, along with similar data generated by NASA, are included in Table X1.2 (see Adjunct Par 2.3). Friction ignition is a very complex phenomenon. Test data suggest there is significance to the Pv product at the time of ignition (where P is the mechanical loading in force per apparent area, and v is the linear velocity), and this is the ranking criterion used in Table X1.2. Pressure affects friction ignition in that it has been harder to ignite metals at higher pressures above a minimum Pv value. In addition, in limited testing to date, the relative rankings of metals may change at different linear velocities.

6.3 Particle Impact Test—An oxidant stream with one or more entrained particles is impinged on a candidate metal target. The particles may be incandescent from preheating (likely for smaller particles) due to earlier impacts. The particles may be capable of ignition themselves upon impact (in this case, the test resembles a promoted ignition test under flowing conditions with the burning particle being the promoter). Test variables include pressure, particle and gas temperature, nature of particle, size and number of particles, and gas velocity.

NOTE 7—ASTM Committee G04 has sponsored a series of industry-funded particle impact tests at the NASA White Sands Test Facility using the methodology reported by Benz et al. (34) in ASTM STP 910. Due to high cost of the apparatus and test, round robin testing is not realistic, and this procedure is not being developed into an ASTM standard. Because of the scatter in these data, they are portrayed graphically and qualitatively ranked in Fig. 1. The results are qualitatively similar to those from the promoted combustion test (6.1), but with several significant exceptions. For example, aluminum bronze resisted particle impact ignition much better than aluminum; in the promoted combustion test, the results were more comparable.

6.4 Limiting Oxygen Index Test—This is a determination of the minimum concentration of oxygen in a flowing mixture of oxygen and a diluent that will just support propagation of combustion. There is a test method (see Test Method D2863) that applies to nonmetals at atmospheric pressure. While no standard ASTM Oxygen Index Test method has specifically been designated for metals, oxygen index data can be obtained using Test Method G124 and prepared oxygen gas mixtures of various purities.

NOTE 8—The existence of an oxygen index for metals is established. The index of carbon steel decreases with increasing pressure. Data on the oxygen index of carbon steel was first reported by Benning and Werley (36), and the data are included in Table X1.4 and Fig. X1.2.

6.5 Autoignition Temperature Test—A measurement of the minimum sample temperature at which a metal will spontaneously ignite when heated in an oxygen or oxygen-enriched atmosphere. Autoignition temperatures of nonmetals are commonly measured by methods such as Test Method G72. Metals autoignite at much higher temperature than nonmetals (37-39). These temperatures are much higher than would occur in actual systems. Further, the experimental problems of containing the specimens, effects of variable specimen sizes and shapes, effects of protective oxides that may be removed in actual systems, difficulty in measuring the temperature, and problems in deciding when ignition has occurred have prevented development of a reliable standard test procedure to yield meaningful data.

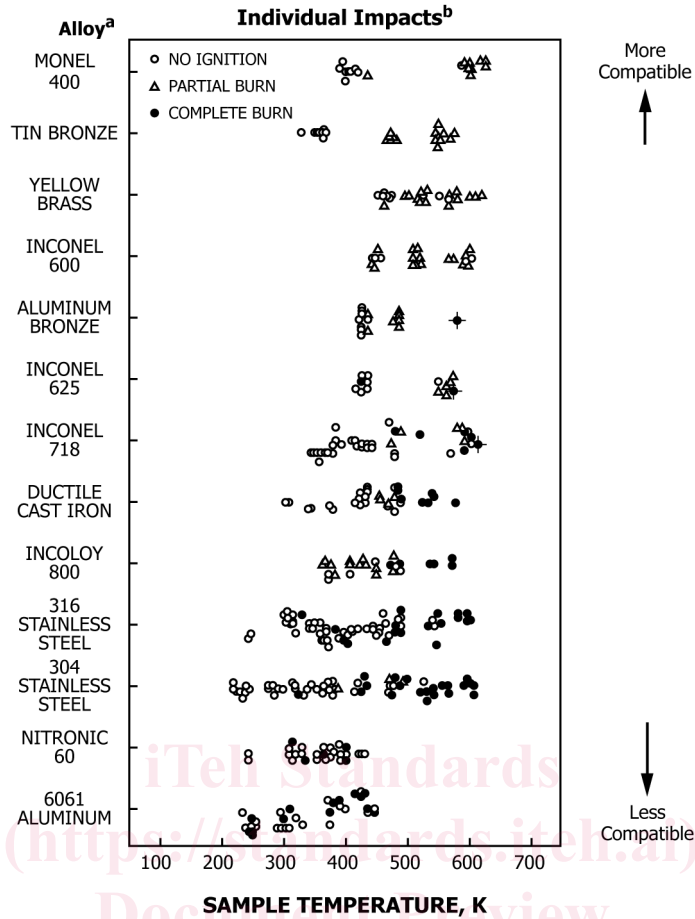


FIG. 1 Particle Impact Test Results

NOTE 1—0.2 cm. (0.5 in.) diameter by 0.24 cm. (0.60 in.) thick specimens impacted with 1600- μm aluminum particles in 1000 psig oxygen, velocity ~1360 m/s.

NOTE 2—See Adjunct, Par. 2.3.

^A See Table X1.9 for alloy compositions.

^B From Benz et al. (34), Stoltzfus (35).

6.6 *Mechanical Impact Test*—A known mass is dropped from a known height and impacts a test specimen immersed in oxidant. Two procedures, Test Methods D2512 and G86 have been used with nonmetals and are discussed in Guide G63. Mechanical impact ignitions of metals are much less likely than for nonmetals; occasional ignitions have occurred during impact of zirconium, titanium, magnesium, and aluminum; however, ranking of other metals has not been achieved.

6.7 *Calorimeter Test*—A measurement of the heat evolved per unit mass (the heat of combustion) when a material is completely burned in 25 to 35 atm (2.5 to 3.5 MPa) of oxygen at constant volume. Several procedures such as Test Methods D4809, D2382 (discontinued), and D2015 (discontinued) have been used in the past. The results are reported in calories per gram (or megajoules per kilogram). For many fire-resistant materials of interest to oxygen systems, measured amounts of combustion promoter must be added to ensure complete combustion.

NOTE 9—Heats of combustion for metallic elements and alloys have been reported by Lowrie (40) and are given in Table X1.5. In practice, it is usually not necessary to measure an alloy’s heat of combustion, since it may be calculated from these data using the formula

$$\Delta H = \sum C_i \Delta H_i \tag{2}$$

where:

C_i = fractional weight concentration of the alloying element, and
 ΔH_i = heat of combustion of the alloying element (in consistent units).

Heat of combustion per unit volume of metal can be calculated by the product of ΔH and density, ρ .

7. Pertinent Literature

7.1 *Periodic Chart of the Elements*—The periodic chart can provide insight into the oxygen compatibility of elemental metals. Grosse and Conway (1) and McKinley (41) have elaborated on this correlation. For example, Fig. 2 depicts the cyclic nature of heats of formation, and Fig. 3 shows the periodic chart with selected similar metals highlighted. Observe that the periodic chart shows how elements of demonstrated combustion resistance (such as the vertical columns Cu, Ag, Au, and Ni, Pd, Pt) are clustered together, as are elements of known flammability (such as Be, Mg, Ca, etc., and Ti, Zr, Hf, etc.).

NOTE 10—Behavior of metallic alloys containing these elements can be drastically different from that of pure elements. For example, alloys containing small quantities of beryllium or titanium can be acceptable.

7.2 *Burn Ratios*—A number of attempts have been made in the literature to relate the physicochemical properties of metals to their oxygen compatibility. Monroe et al. (42, 43) have proposed two “burn ratios” for understanding metals combustion: the melting-point burn ratio, BR_{mp} , and the boiling-point burn ratio, BR_{bp} . Although these factors lend insight into the burning of metallic elements, their application to alloys is complicated by imprecise melting and boiling points, vapor pressure enhancements and suppressions, potential preferential combustion of flammable constituents, and an importance of system heat losses that can alter the alloys rankings by these parameters.

7.2.1 *Melting Point Burn Ratio*—Numerous metals burn essentially in the molten state. Therefore, combustion of the metal must be able to produce melting of the metal itself. The BR_{mp} is a ratio of the heat released during combustion of a metal to the heat required to both warm the metal to its melting point and provide the latent heat of fusion. It is defined by:

$$BR_{mp} = \Delta H_{\text{combustion}} / (\Delta H_{rt-mp} + \Delta H_{\text{fusion}}) \quad (3)$$

where:

ΔH = heat of combustion,

ΔH_{rt-mp} = heat required to warm the metal from room temperature, rt, to the melting point, mp, and

ΔH_{fusion} = latent heat of fusion.

Clearly, a metal that does not contain sufficient heat to melt itself (that is, one that has a $BR_{mp} < 1$) is severely impeded from burning in the molten state. Monroe et al. (42, 43) have calculated numerous BR_{mp,s_2} and they are given in Table X1.6.

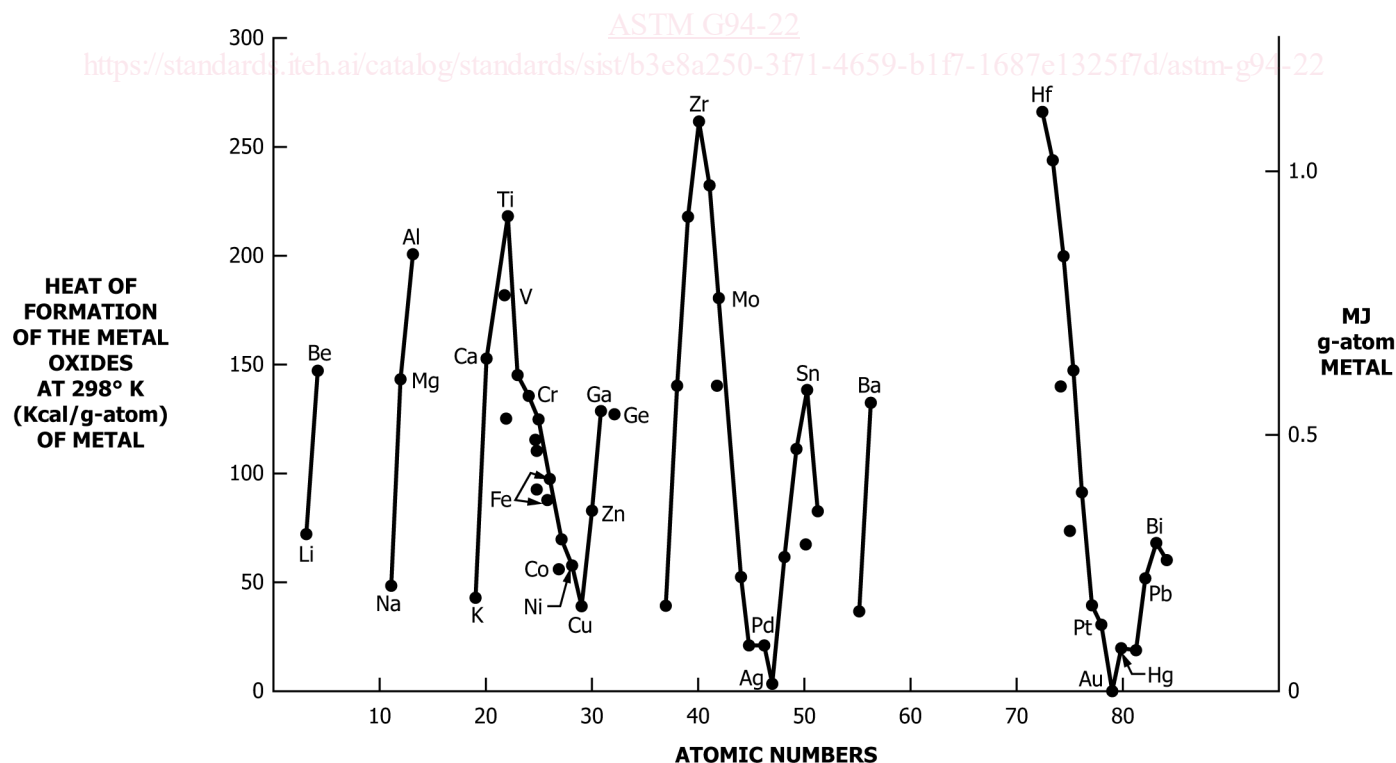


FIG. 2 Heat of Formation of the Metal Oxides Versus Atomic Numbers