

TECHNICAL REPORT

ANSI/ISA-TR12.13.02-1999 (R2013)

ANSI Technical Report prepared by ISA

**Investigation of Fire and Explosion
Accidents in the Fuel-Related Industries –
A Manual by Kuchta**

Reaffirmed

ANSI/ISA–TR12.13.02–1999 (R2013)
Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries
— A Manual by Kuchta

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FOREWORD

Publication of this Technical Report that has been registered with ANSI has been approved by the Accredited Standards Developer ISA, 67 Alexander Drive, Research Triangle Park, NC 27709. This document is registered as a Technical Report according to the Procedures for the Registration of Technical Reports with ANSI. This document is not an American National Standard and the material contained herein is not normative in nature. Comments on the content of this document should be sent to the Secretary, Standards and Practices Board; ISA; 67 Alexander Drive; P. O. Box 12277; Research Triangle Park, NC 27709.

As a service to industry, the accompanying document, Bureau of Mines Bulletin 680 - Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries - A Manual, by Kuchta, 1985, is hereby reprinted in its entirety.

This compendium, formerly available from the U.S. Bureau of Mines, contains information essential to an understanding of detection, measurement, and handling of flammable gases and vapors.

For further information, refer to ANSI/ISA-TR12.13.01.

ABSTRACT

This technical report includes theoretical and practical work carried out and collected by the U.S. Bureau of Mines relating to ignitability, flammability and physicochemical properties of flammable gas mixtures, liquids, and solids. While emphasis of this document is on investigation of fires and explosions, a significant amount of theoretical & practical data related to flammability limits, under varying conditions of proportion, temperature and pressure is included.

KEY WORDS

Fire
Explosion
Flammability limits
Flammable
Combustible
LEL, UEL
LFL, UFL
Gas

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Appendix I

The following document, *Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries - A Manual by Kuchta*, is reprinted in its entirety by permission of the publisher, the Bureau of Mines, U.S. Department of the Interior.

Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries— A Manual

By Joseph M. Kuchta



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INVESTIGATION OF FIRE AND EXPLOSION ACCIDENTS IN THE CHEMICAL, MINING, AND FUEL-RELATED INDUSTRIES—A MANUAL

By Joseph M. Kuchta¹

ABSTRACT

This Bureau of Mines manual is oriented to the technical needs of an investigation of fire or explosion accidents and includes various practical and theoretical information that is needed in analyzing accidents or evaluating conditions that might lead to an accident. It is applicable to accidents in the chemical, mining, transportation, and other fuel-related industries. Specific procedures for conducting an accident investigation are outlined, and various guidelines are given for developing the fire or explosion evidence. Ignitability, flammability, and physicochemical data are presented for over 500 combustible gases, liquids, and solids; empirical and theoretical expressions are also given for extrapolating the behavior of combustible-oxidant-diluent systems to various environmental conditions. In addition, various data pertinent to damage analysis are summarized to facilitate the task of the investigator in developing plausible accident scenarios.

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INTRODUCTION

Accidental fires and explosions generally occur when combustibles are produced, transported, or utilized in a hostile environment or under unsafe conditions. Proper investigation of such accidents is essential for determining their cause and assessing life or property loss and for preventing their recurrence. This requires a methodical and thorough investigation, knowledge of the basic properties of pertinent materials, understanding of the ignitability and flammability characteristics of the combustible-oxidant system, and understanding of combustion or explosion principles. The main purpose of this manual is to summarize useful guidelines and provide data that are frequently needed for investigating fires and explosions or evaluating conditions that may be conducive to such events. It is applicable to flammable liquids, gases, and solids that may be encountered in the chemical, mining, transportation, or other mineral-fuel-related industries.

Among the most widely used publications on the flammability characteristics of combustibles are the Bureau's bulletins by Zabetakis (110)² and Coward (11). However, these bulletins are limited to liquid and gaseous combustibles, and reference must be made to other publications for similar information on combustible solids. Furthermore, other combustion and physicochemical data that may be required in a hazard analysis are even more widely scattered throughout the literature. Some safety handbooks, such as that of the National Fire Protection Association (NFPA) (72), provide various data on many combustibles, but the information is not sufficiently comprehensive for the analysis of an accident; also, the data are rather meager for mining applications. This manual attempts to overcome the scope limitations of the earlier Bureau bulletins and brings together many other essential data for characterizing the reactivity and damage potential of various classes of combustibles.

Ignitability, flammability, and thermochemical data are presented for over 500 combustible gases, liquids, and solids. The main groups of combustibles include hydrocarbons and substituted hydrocarbons, gasolines and lubricating fluids, coals and other mine-related combustibles, and various agricultural, chemical, plastic, metallic, and carbonaceous solids; explosives are beyond the scope of this report, although certain data are included for comparison. Most of the ignitability and flammability data are taken from Bureau publications, but other authoritative sources were also relied upon to complete the data. Generally, the various data represent the most acceptable or conservative values from the standpoint of safety, unless otherwise specified.

This manual is organized to facilitate the task of finding the particular data or information of interest. The initial section outlines specific procedures for accident investigations; the second section presents pertinent definitions and basic concepts for understanding combustion data; the next sections discuss the large compilation of combustion data presented for various combustible classes; and the final section deals with the damage analyses of fire and explosion accidents. The main data compilations are given in summary tables which provide easy access to many useful properties of the combustibles; additional data in the text expand on this data base. Limitations of the experimental data are discussed, and both empirical and theoretical guidelines are given for extrapolating the data to other environmental conditions and for estimating the energy or damage potential of a combustible-oxidant system. Other publications can be referred to for more fundamental knowledge of the combustion processes discussed in this report (21, 24, 66, 93, 98).

ACKNOWLEDGMENTS

The Bureau of Mines data in this manual represent selected contributions of various research groups of the Pittsburgh Research Center over at least four decades. Particular acknowledgment is given to the members of the fire or explosion groups with whom the author was associated in advancing the art of safety technology. The author is especially indebted to Drs. Michael G. Zabetakis, presently with the University of Pittsburgh, Pittsburgh, PA, and David S. Burgess, retired, who provided practical and

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PROCEDURES FOR ACCIDENT INVESTIGATION

INITIAL ACTIONS

A formal investigation of an accidental fire or explosion is ordinarily conducted by a cadre of technical specialists and responsible officials. In industrial cases, this typically includes plant representatives, safety officers, fire department officials, and experts in combustion and engineering

technologies. Where military or civilian Government agencies have jurisdiction, as in mining and aircraft disasters, the makeup and procedures of the investigating team will necessarily be determined by the requirements of the proper agency. In all cases, the team members should meet as soon as possible to obtain a briefing of the accident, decide upon the plan(s) of action, and establish task groups to accomplish various specific objectives. The head of the investigating team must organize and coordinate these actions to ensure that all aspects of the accident are

²Italicized numbers in parentheses refer to items in the list of references preceding the appendix.

properly covered. Initial actions that should be taken are—

1. Isolation of accident site.
2. Protection of evidence.
3. Recovery of material evidence.
4. Photographic documentation of evidence.
5. Documentation of witness accounts.

Isolation of the accident site is important to ensure recovery and protection of all available evidence and also to minimize unnecessary human exposure to any hazards that may still exist. Confined areas should be entered with caution since flammable or toxic gases may be present even after a fire. Before removal of any fire or explosion debris, the accident area should be photographed, including detailed color exposures of suspect items; also, tagging and mapping of damaged materials is common practice to avoid subsequent confusion. Where materials are fragmented by an explosion, areas beyond the accident site may have to be searched to recover the items. Those involved in these early actions must protect the evidence from being inadvertently tampered with, destroyed, or lost.

Equally important are the accounts of all available witnesses, including those present in the immediate or remote vicinity of the accident and those who arrive later on the scene, such as firemen and medical personnel. Such accounts should be obtained as soon as possible after the accident with the witness calm and at ease. Of particular interest is what the witness saw, heard, or sensed before and after the accident, as well as the proximity and activity of the witness during the course of events. All witness accounts are recorded in writing, and further interrogations are made when necessary in developing the evidence.

INVESTIGATIVE PROCEDURES

The procedures for investigating accidents will vary from one case to another, but all involve the basic elements of factfinding and problem solving to develop a credible accident scenario. Frequently, the cause of an accident is difficult to pinpoint because the available evidence is incomplete, inconsistent, or only circumstantial. Therefore, it is necessary to have a methodical plan for accumulating and developing evidence, both direct and indirect, that will be needed to fully explain an accident. A recommended plan of investigation is summarized herein, including—

1. Accumulation of background information.
2. Inspection of accident site.
3. Interrogation of witnesses.
4. Development and analysis of evidence.
5. Conclusions and report.

Background Information

At the outset, the investigator should obtain all available background information pertaining to the accident. This includes a description of the accident site and systems or operations involved, conditions and events that led to the accident, performance histories of any suspect systems, and all the available evidence accumulated from any initial actions. Particularly important are what combustibles and oxidants were present and what abnormal or hazardous conditions existed that might account for the accident. A close examination should be made of witness accounts, maintenance records, operational logs and manuals, weather reports, previous accident reports, and other records that may be helpful in developing the evidence. Recent changes in equipment, procedures, or operating

conditions can be especially significant. The investigator must be open-minded and reserve any judgment until all human and material factors have been fully considered.

Site Inspection

Inspection of the accident site is one of the most important steps in obtaining physical evidence. Initially, an examination is made of the overall operation involved and damage sustained by the immediate and remote surroundings. The investigator should prepare an areal map on which the damage patterns, including fragments from any explosion, can be spatially defined. Subsequently, a detailed examination is made to obtain evidence on the apparent origin, propagation, and localized damage of the fire or explosion. This should include examination of all electrical and mechanical systems as possible problem sources. The area with the greatest damage is generally given the most initial attention because it is normally the source of the combustible. The following items are typical of the evidence which an investigator must uncover or consider:

1. Combustible quantity, distribution, and consumption.
2. Combustible leakage or spillage.
3. Open flame heat sources.
4. Electrical and mechanical heat sources.
5. Chemical-type heat sources.
6. Fire condition, propagation, and damage.
7. Explosion condition, propagation, and damage.
8. Material and system failures.
9. Operator or human error.

Witness Interrogation

After inspection of the accident site, the investigator should review the witness accounts for consistency with the physical evidence and interrogate any witnesses, as may be necessary, to help clarify any inconsistencies. It is important to recognize that witness accounts of accidents are subject to sight and hearing limitations in resolving a rapid series of events. For example, it is not unusual for a witness to claim hearing two explosions when only one actually occurred, or to give poor estimates of distances to an object or between two moving objects because of confusion during an accident; similarly, the size and velocity of moving objects are frequently exaggerated. Therefore, witnesses should be requested to qualify their observations relative to known landmarks and events to help establish their evidence spatially and temporally. Interrogation of maintenance personnel on any equipment involved should always be included as a standard practice. At this time, the investigator needs to decide what facts are known and what evidence must be substantiated or developed.

Evidence Development and Analysis

Ideally, sufficient evidence should be accumulated to explain all phases of an accident, including the specific cause. The required physical evidence will vary with the type of accident. In fires or explosions, it is particularly important to account for the combustible source, probable ignition source, resultant propagation, and observed damage. The available evidence is analyzed by developing and testing hypotheses that may explain the sequence of events; any assumptions must be consistent with the fully established evidence and basic scientific principles. Some

important considerations in developing the evidence are reviewed in the following paragraphs.

1. Combustible Source.—In a fire situation, various combustible classes can be consumed as the fire spreads. These include ordinary combustible solids or dusts (class A), combustible liquids and gases (class B), combustibles of electrical equipment (class C), combustible metals (class D), or other miscellaneous materials; combustible fire classification is that of NFPA (72). Fires that spread rapidly are usually attributable to combustible gases, vapors of highly volatile liquid or solid combustibles, or finely divided solids that are highly flammable. Those that can be initiated without an external heat source are likely to involve pyrophoric, hypergolic, water-reactive, or self-heating combustibles. Soot formation is evidence of hydrocarbon or organic fuel fires, and extremely high temperatures can be indicative of combustion with high-energy fuels or high-strength oxidizers. Any widespread fire will always be accompanied by a wide distribution or dispersion of combustible.

In gaseous or dust explosions, the combustible sources are only those that can form flammable gas, vapor, or dust concentrations in the particular oxidant atmosphere and temperature environment; this implies some degree of confinement. Prime combustible suspects are fuel gases, low-flash-point liquids, gassy solids, and dispersed flammable dusts. The ignitability and flammability characteristics of the suspect combustible-oxidant system should be examined for supporting evidence. When possible, samples of the combustible system are taken for analysis to verify compositions. A likely combustible source also has to be present in sufficient concentration to account for the observed explosion pressure damage. The investigator must realize that relatively low combustible concentrations can be hazardous and that even an "empty" fuel tank may contain sufficient combustible vapor to account for the explosion. Where damage is unusually severe, combustible systems capable of detonation are to be suspected.

2. Ignition Source.—The possible sources of ignition can include electrical, mechanical, chemical, or nuclear forms of energy. Some of the specific types are (1) electrical arcs or sparks from lightning, static electricity, and defective electrical equipment; (2) hot surfaces from mechanical friction, electrical resistance heating, aerodynamic heating, and any vessel or reactor heating; (3) hot gases or flames from pilot burners, combustor exhaust systems, and gaseous compressor systems; and (4) chemical heating from pyrophoric, hypergolic, and spontaneous or self-heating reactions. Most fires or explosions are initiated by electrical sources. The static electricity source should be especially suspected as possible in the pumping of liquids or dusts and similar operations where triboelectrification can occur; this hazard will be greatest in the presence of plastic or nonconductive materials. The most common type of chemical self-heating involves slow oxidation and may be encountered with many combustibles of animal or vegetable oil origin and such ordinary combustibles as coal and charcoal. Self-heating, pyrophoric, and hypergolic ignitions require no external heat source.

In some accidents, the ignition source may be evident from localized heat damage such as weldlike fusion of metals from electrical arcing, discoloration or wear of metals from mechanical friction, and melting of metal materials due to abnormal process temperatures. The heat source in other cases, including electrostatic, self-heating, and hot

gas ignitions, is not usually identifiable from the fire or explosion damage; therefore, the investigator must rely upon circumstantial evidence in such cases.

Both the nature of the available heat source and the physical state of the suspect combustible must be considered in determining the ignition source. For example, a flammable gas (such as hydrogen) may have a very low ignition energy but a relatively high ignition temperature; or a flammable liquid spray can have a high ignition energy compared to that possible with homogeneous vapor-air mixtures. Similarly the ignition energy requirements for a solid (such as coal dust) can be excessive for large particles, in which case the ignition temperature can be of greater significance. A proper assessment requires reference to ignition property data.

3. Propagation.—Propagation of a fire or explosion is deduced from the available physical evidence and known flammability properties of the combustible-oxidant system. Gas or dust explosions will propagate only into areas where flammable combustible-oxidant mixtures have accumulated but may then initiate fires of other combustibles. In comparison, fires do not require uniform combustible-oxidant mixtures and can propagate into areas where any concentration of combustible exists; also, the gaseous fire products may be flammable and produce an explosion in a confined environment, as in some coal mine disasters.

To fully characterize the propagation of fires or explosions, the investigator needs to define the consumption rates (burning rates) of the reactants and their flame propagation rates (flame speeds or flame spread rates). Such information may be available in the literature but is necessarily limited to certain temperature, pressure, and combustible-oxidant conditions. Therefore, it is often necessary to extrapolate laboratory data to conditions of interest by the prudent use of empirical rules or laws.

Typically, flame propagation rates of common hydrocarbon gas-air explosions are of the order of several meters per second, or about eight times the burning velocity of the particular mixture composition. In comparison, fires are usually associated with much lower spatial propagation rates, especially in the burning of bulk liquids and solids. However, all fires or flame propagation can accelerate by increased ventilation, turbulence, or wind effects, as in flight vehicles, ventilation ducts, or mine tunnels. The flame spread can be even greater when the fires are supported by strong buoyant forces, such as in a building stairwell or an elevator shaft. Highest propagation rates with liquids and solids will occur when they are finely dispersed or flash vaporized.

Very high propagation rates of the order of a 1,000 m/s or more are possible when deflagrations develop into detonations. Detonations are most likely to be encountered in combustion involving high pressures, high oxygen concentrations, or high-energy fuels. Even ordinary fuel-air systems are capable of detonation, but these require stronger ignition sources or longer flame runup distances.

4. Fire Damage.—Fire damage is largely attributable to the exposure of materials to excessive temperatures or heat. Fire temperatures of ordinary combustibles in air will generally be 1,000° to 2,000° C, but temperatures can be much higher in oxygen or with more exotic combustibles. An investigator's analysis of the fire damage should include consideration of such factors as—

1. Combustible loading and ventilation.
2. Size, shape, and distribution of materials.

3. Proximity and exposure duration of materials.
4. Fire temperatures, burning rates, and heat release.
5. Fire resistance properties of damaged materials.

Maximum fire temperatures will normally be evident where the air or oxygen ventilation is optimum for combustion, whereas the heat flux or heat release will depend additionally upon the combustible loading and burning rate. Most constructional materials cannot withstand the fire temperatures and heat loading from a fully developed hydrocarbon or carbonaceous fuel-air fire. Materials of low fire resistance, such as those having low melting points or ignition temperatures, will be consumed or largely destroyed; this will be especially the case for fine wires, sheet materials, or finely divided substances. However, one should also expect highly fire-resistant materials to fail when the fires are of severe intensity. On the other hand, even paper will not ignite if its exposure time to flame is too short or if its proximity to the heat source is too remote.

Ordinarily, material failures will be severest in fires involving large combustible loadings (as in fuel storage facilities), high ventilation or turbulence levels (as in aircraft flight applications), high oxidant concentrations (as in hyperbaric chambers), or high-energy combustibles (as in space rocket applications). Few materials will survive a torchlike fire, particularly one in oxygen; such intense fires are often evidenced by the erosion and fusion of metals. Similar metal damage can also occur in electrical fires, although any metal fusion due to electrical arcing will be more localized and display beadlike welds. Damage to powered equipment (motor, pumps, compressors, etc.) is often attributed to electrical or mechanical malfunctions but can be a result of the fire itself. Temperature limitations of materials and the extent of their fire exposure should be considered in making the fire damage assessment.

5. *Explosion Damage.*—Explosion damage is caused by the high pressures and winds that are generated by the sudden release of chemical or physical energy. Although the damage analyses may vary with the complexity of the explosions, they should at least include consideration of the following important items:

1. Combustible loading and confinement.
2. Explosion pressures, propagation rates, and energy release.
3. Pressure limitations of containment materials.
4. Nature of containment failure.
5. Blast wave or far-field effects.
6. TNT energy equivalence.

The most common explosions will involve the ignition of flammable vapor-air mixtures in a confined environment. If near-stoichiometric mixtures are present, the explosion pressure in a fully confined system can be approximately eight times the initial pressure ($P_2/P_1 = 8$). Such internal pressure loading will be evidenced by the rupture of the container unless it can sustain the explosion pressure. Similar damage can result in the absence of combustion, as in the failure of an overpressurized steam boiler, compressed gas cylinder, or cryogenic liquid receiver; the rupture of an evacuated chamber (implosion) or a decompressed aircraft compartment also falls into this category. Other explosions may produce damage from a combination of physical and chemical energy release. These include fuel tank explosions under high-impact conditions, furnace explosions of molten metal and water or combustible liquids, and boiling liquid-expanding vapor explosions

(Bleves). In all cases, the explosion damage will be more severe when combustion involves high oxygen concentrations, elevated pressures, or highly turbulent environments. Detonations are more likely to occur in these situations, in which case the explosion pressure rise ratio (P_2/P_1) can be of the order of 18 to 1 for gaseous systems, or several orders of magnitude greater for condensed explosive systems.

Containment material failure or near-field damage is largely determined by the nature of the pressure loading, the degree of confinement, and the pressure or mechanical limitations of the container, fasteners, and adjacent materials. Explosions in highly confined systems have high damage potential because near-theoretical pressures can develop before any containment failure. In comparison, even an ordinary oven or building can sustain an explosion if it is adequately protected with large pressure relief panels or vent areas. Explosion venting guidelines are available for predicting the safe pressure limits of containments as a function of vent area. The containment failures in ordinary explosions will be evidenced by material stretching or thinning out (tension failure), whereas those in detonations will tend to be more severe and cleaner breaks (shear failure); an implosion will be characterized by a compression-type failure. The pressure limitations of a container can be estimated from a knowledge of the elastic limit or ultimate strength of the container material. However, one must allow for the fact that the dynamic stress is about two to three times the static stress for plastic deformation; pressure ratings of commercial vessels are usually specified for static-type loadings. Any container fragmentation should be expected to be greater for brittle materials than for highly ductile types.

Far-field effects are associated with the explosion damage that results from air blast waves and flying fragments. These effects will be especially evident where strong containments fail owing to detonations or highly energetic deflagrations. Here, the investigator should estimate the TNT energy equivalent of the exploding system from the available chemical energy or potential useful work (gas expansion); apply the cube-root scaling law for predicting blast pressures at any distance from any mass equivalent of TNT; and correlate the estimated blast pressures to published damage thresholds for structural and biological targets. Generally, one can expect a peak overpressure of 1 to 2 psi to cause the failure of most light structural materials, such as nonreinforced wood siding, corrugated steel paneling, or masonry block walls. In comparison, much higher overpressures can be tolerated when the structural design is reinforced, particularly for materials of good ductility. As a rule, pressure thresholds for far-field damage (external loading) will be greater than those for near-field damage, such as a containment failure (internal loading). Where condensed-phase detonable systems are involved, crater formation will also be possible besides far-field damage.

Conclusions and Report

All the available direct and indirect evidence is finally reviewed for accuracy and reliability to define the most likely sequence of events and probable cause(s) of the accident. Any hypotheses proposed to explain the accident should be logically and technically consistent with the

established evidence. A proper analysis will include consideration of both material and human factors. To complete the investigation, the investigator should prepare a summary report on the accident. This should include a description of the accident, accounts of witnesses, evidence from field inspection, analysis of evidence, and development of

accident scenario to explain the cause of the accident. Most importantly, system malfunctions and hazardous conditions should be identified, and specific recommendations should be made to prevent recurrence of the accident, including both operative and protective measures.

THEORY AND DEFINITIONS

PHYSICAL GAS LAWS

Pressure-volume-temperature (PVT) relationships are important in determining material balances for a gaseous system. In most cases, one can assume *ideal gas behavior* and define the initial (1) and final (2) states of a gas as follows:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (1)$$

where T_1 and T_2 refer to absolute temperature, such as in kelvins (K). The general form of the ideal gas law is given by

$$PV = nRT = \frac{W}{M} RT \quad (2)$$

$$\text{or } P = \frac{W}{V} \frac{RT}{M} = \rho \frac{RT}{M}, \quad (3)$$

where n , W , M , and ρ are the moles, weight, molecular weight, and density of the gas, respectively; R is a universal gas constant equal to 1.987 cal/(K·mol), 0.08205 L·atm/(K·mol), or 8.314 J/(K·mol) depending upon the P-V units. Thus, the volume of gas will vary directly with absolute temperature and inversely with total pressure. In calculating the moles of gas, it is useful to know that the *molar volume* of any ideal gas will occupy 22.414 L at 1 atm and 273 K (0° C).

For mixtures of ideal gases, the total pressure (P_t) is equal to the sum of the component partial pressures ($P_t = p_1 + p_2 + \dots$) and proportional to the total number of moles ($N_t = n_1 + n_2 + \dots$). Hence, the mole fraction (X) of a gaseous component (i) is

$$X_i = n_i/N_t = p_i/P_t, \quad (4)$$

and $100 X_i$ gives the mole or volume percent. For the vapors of ideal liquids, one uses Raoult's law:

$$X_i (\text{liquid}) = n_i/N_t (\text{liquid}) = p_i/p_i^\circ (\text{vapor}), \quad (5)$$

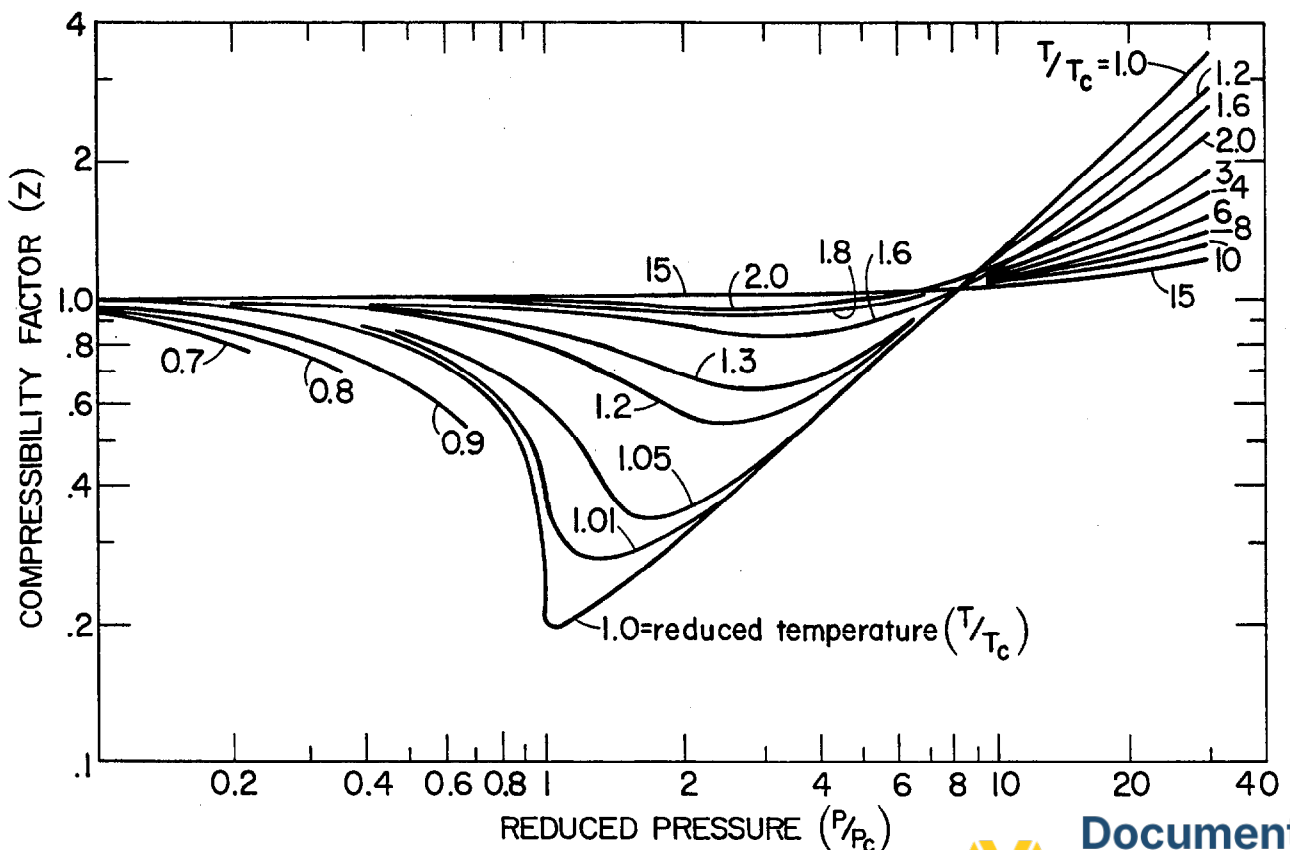


Figure 1.—Compressibility factor as a function of reduced pressure and reduced temperature.

where p_i is partial pressure of the i^{th} component in solution, p_i° is the vapor pressure of the pure component, and X_i is its mole fraction in solution.

Real gases deviate from ideal behavior, particularly when subjected to high pressures or cryogenic temperatures. In such cases, other equations must be used to determine the P-V-T relationships, such as the equation

$$PV = nZRT, \quad (6)$$

where Z is a compressibility factor and depends upon the critical properties of the gas (P_c , T_c , and V_c). A fair approximation of the Z factor can be obtained for most gases from the generalized compressibility curves (34, p. 479) shown in figure 1 in terms of reduced pressure ($\pi = P/P_c$) and reduced temperature ($\Theta = T/T_c$); gases difficult to liquefy, such as hydrogen, give a more complex behavior. Critical states and vaporization properties are given in table 1 for a number of common gases and liquids (27, p. 502).

Table 1. — Critical states and vaporization properties of common gases or liquids (27, p. 502)

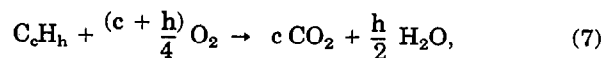
Substance	Boiling point (T_b), K	Heat of vaporization at T_b , kcal/mol	Critical temperature (T_c), K	Critical pressure (P_c), atm
Acetylene	184.7	NA	309.1	61.7
Ammonia	239.8	5.56	405.5	111.5
Benzene	353.3	7.40	561.6	47.7
n-Butane	272.6	5.30	426.0	36.0
i-Butane	263.0	5.08	407.1	37.0
Carbon dioxide	NA	NA	304.1	72.9
Carbon monoxide	81.1	1.41	134.4	34.6
Chlorine	239.5	4.80	417.0	76.0
Ethane	185.9	3.80	305.2	48.8
Ethylene	169.3	NA	282.8	50.7
Ethyl alcohol	351.6	9.40	516.2	63.1
Hydrogen	20.3	.216	33.2	12.8
Hydrogen bromide	206.2	3.95	363.0	84.0
Hydrogen chloride	189.5	3.60	324.5	81.6
Hydrogen cyanide	299.2	5.70	458.6	56.9
Hydrogen sulfide	213.4	4.49	373.5	88.9
Methane	111.7	1.95	191.1	45.8
Methyl alcohol	337.8	8.41	513.2	98.7
Nitrogen	77.3	1.36	126.0	33.5
Nitrogen oxide	121.4	NA	179.0	65.0
Nitrogen dioxide	NA	NA	431.0	99.0
Oxygen	90.2	1.61	154.3	49.7
Propane	231.0	4.50	369.9	42.0
Propylene	226.2	NA	364.8	45.0
Sulfur dioxide	263.2	6.08	430.3	77.7
Water	373.2	9.717	647.3	218.2

NA Not available.

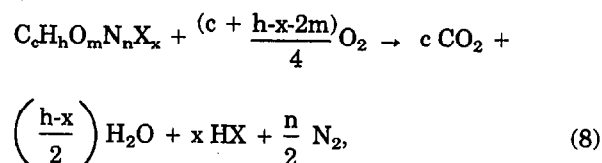
STOICHIOMETRY

Combustion material balances will vary with the composition and concentration of the reactants and the nature of the products at the reaction conditions. Theoretically, the maximum heat release should occur at the *stoichiometric concentration* (C_{st}) that defines the optimum molar

concentration of combustible for complete reaction with the particular oxidant; fuel-lean mixtures suffer from oxidant dilution and fuel-rich mixtures from incomplete reaction. The stoichiometry for complete combustion of a simple hydrocarbon in oxygen is given by the expression



and for substituted hydrocarbons by the general expression



where X is any halogen atom. Thus, the C_{st} of methane (CH_4) in oxygen ($\frac{100}{1+c+h/4}$) is 33.3 mol pct. For combustion in air,

$$C_{st} \text{ (in air)} = \frac{100}{1 + 4.773(c + \frac{h-x-2m}{4})} \text{ mol pct}, \quad (9)$$

where 4.773 is the reciprocal of the molar oxygen concentration in air (0.2095). By this equation, one obtains a C_{st} of 9.48 mol pct for methane in air. Similar expressions may be derived for incomplete or other combustion reactions in which H_2 , CO , NO_2 , or other possible products are assumed. For example, if NO_2 instead of N_2 is an assumed product, the oxygen term in equations 8 and 9 would be

$$(c + n + \frac{h-x-2m}{4}).$$

The volume percentages can be converted to a weight basis from a knowledge of the densities or molecular weights of the mixture components. As an example, the fuel-air weight ratio (F/A) of a stoichiometric mixture is given by

$$(F/A)_{st} = \frac{M [C_{st}(\text{vol pct})]}{28.97 [100 - C_{st}(\text{vol pct})]}, \quad (10)$$

where M is the fuel molecular weight and 28.97 is the air molecular weight. Pertinent properties of air are summarized in tables 2 and 3.

Table 2. — Major components of dry air (43, 105)

Constituent	Molecular weight	Density (0° C), g/L	Specific heat (20° C), cal/(g° C)	vol pct
Nitrogen	28.01	1.251	0.249	78.09
Oxygen	32.00	1.429	.219	20.95
Argon	39.94	1.784	.124	.93
Carbon dioxide	44.01	1.977	.200	.033
Air	28.97	{ 1.293 (0° C) 1.205 (20° C) }	.240	100.0

Table 3. — Standard air atmosphere (43)

Altitude ft	Temperature, °C	Pressure, bars	Density, kg/m ³
0	15	1.013	1.225
1,000	13	.977	1.190
5,000	5	.842	1.056
10,000	-5	.696	.905
15,000	-15	.571	.771
20,000	-24	.465	.654
30,000	-44	.301	.458
40,000	-55	.188	.300
50,000	-55	.116	.186
60,000	-55	.072	.115

THERMODYNAMIC RELATIONSHIPS

A knowledge of thermodynamic properties is essential in calculating the energy balance of a given system. The energy change may be in the form of work performed or heat transferred relative to the system surroundings. By the first law of thermodynamics (energy conservation), the energy change (ΔE) is

$$\Delta E = Q - W, \quad (11)$$

where Q is the heat absorbed (positive) and W is the work done by the system (positive); heat evolved or work on the system would be negative. For an *isothermal process* ($\Delta E = 0$), the total mechanical work ($W = \int P dV$) of expansion or compression of an ideal gas is

$$W = n RT \ln V_2/V_1 = n RT \ln P_1/P_2; \quad (12)$$

$$P_1 V_1 = P_2 V_2.$$

For an *adiabatic process* ($Q = 0$), the total work ($W = - \int C_v dT$) is

$$W = n C_v T_1 [1 - (P_2/P_1)^{R/C_p}]; P_1 V_1^\gamma = P_2 V_2^\gamma, \quad (13)$$

where C_v and C_p are molar heat capacities, γ is C_p/C_v ratio, and their subscripts refer to constant volume (v) or constant pressure (p). Figure 2 shows how much greater the volume change of an ideal gas can be in an isothermal compression as compared to an adiabatic compression at various pressure ratios. In the adiabatic process, the temperature change is

$$T_2/T_1 = (V_1/V_2)^{R/C_v} = (P_2/P_1)^{R/C_p}. \quad (14)$$

Reactions may occur at constant volume or constant pressure. Under constant volume, where no mechanical work is performed ($W = 0$), the heat change by equation 11 would be $Q_v = \Delta E$; at constant pressure, the heat change

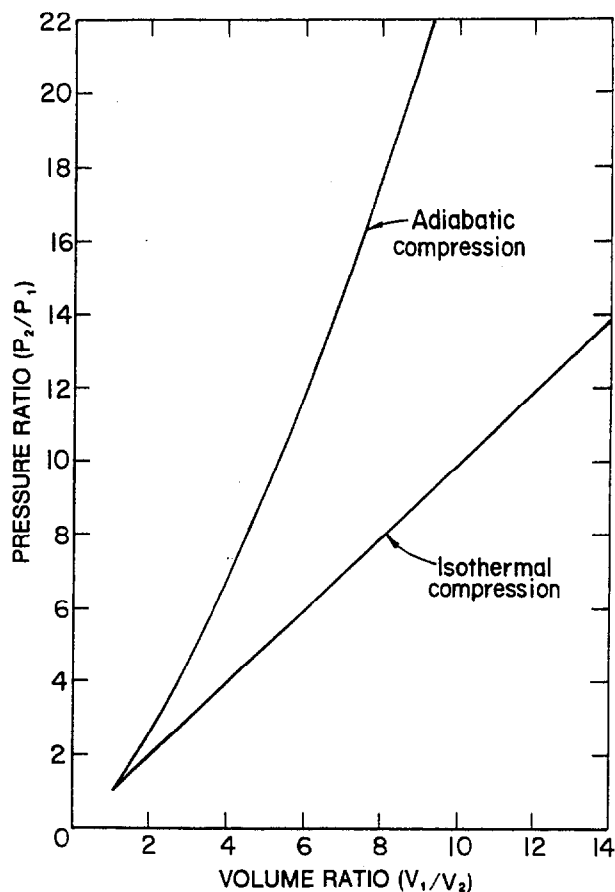


Figure 2.—Variation of pressure ratio with volume ratio in adiabatic and isothermal compression of an ideal gas.

is $Q_p = \Delta E + P\Delta V$. Since the heat content or enthalpy (H) of a system is

$$H = E + PV \quad (15)$$

and $\Delta H = H_2 - H_1 = Q_p$, the heat change at constant pressure becomes

$$\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n RT, \quad (16)$$

where Δn is the change in the moles of gas after reaction of the system. Equations 15 and 16 are very useful because most standard thermodynamic properties are at constant pressure. The molar heat content of a number of common product gases is given at various temperatures in table 4;

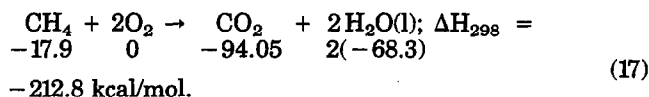
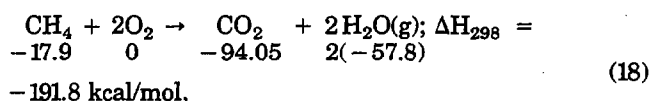
Table 4. — Heat content (enthalpy) of combustion product gases at various temperatures¹

Temperature, K	Heat content, kcal/mol						
	H ₂	O ₂	N ₂	CO	CO ₂	H ₂ O	NO
298.16	0	0	0	0	0	0	0
400	.71	.72	.71	.71	.94	.82	.73
600	2.10	2.21	2.13	2.14	3.09	2.51	2.19
800	3.51	3.78	3.60	3.63	5.45	4.30	3.72
1,000	4.94	5.43	5.13	5.18	7.98	6.21	5.31
1,200	6.40	7.11	6.72	6.79	10.63	8.24	6.96
1,400	7.91	8.83	8.35	8.45	13.36	10.38	8.64
1,600	9.45	10.58	10.01	10.13	16.15	12.63	10.36
1,800	11.04	12.35	11.71	11.84	18.99	14.96	12.09
2,000	12.66	14.15	13.42	13.56	21.86	17.37	13.84
2,200	14.31	15.97	15.14	15.30	24.75	19.84	15.60
2,400	16.00	17.80	16.88	17.05	27.67	22.37	17.37
2,600	17.71	19.66	18.63	18.81	30.61	24.91	19.14
2,800	19.45	21.54	20.39	20.58	33.56	27.45	20.91
3,000	21.21	23.45	22.16	22.36	36.53	30.20	22.72

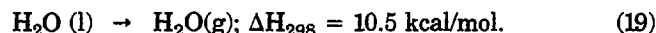
¹Data from reference 28 rounded off to 2 decimal places.

298.16 is the reference zero enthalpy state. These data are derived from the heat capacity relationship at constant pressure, $C_p = dH/dT$; the corresponding relation at constant volume is $C_v = dE/dT$; C_v is usually obtained from the approximation $C_p - C_v = R$. The constant-pressure heat capacity data are particularly important in calculating the final temperature of a reacting system, as discussed in a later section.

In a chemically reactive system, the reaction may evolve heat (exothermic) or absorb heat (endothermic). The heat of reaction (ΔH) is indicated by the enthalpy change of the reactants from their initial state to the final or product state. Here, the enthalpy change can be calculated by use of the heats of formation (ΔH_f - kcal/mol) of each specie; the standard values are defined at 25° C (298 K) and 1 atm. This is illustrated below for the complete combustion of methane at constant pressure with water formed as a liquid (l) or vapor (g):



ΔH_f values are given below each specie, and ΔH is equal to the sum difference of ΔH_f (products) - ΔH_f (reactants); negative ΔH indicates heat is evolved. The variation between the ΔH values (-212.8 versus -191.8) is equal to the latent heat of vaporization of water, i.e.,



Essentially, the larger ΔH represents the gross heat of combustion (ΔH_c), and the smaller ΔH is a net ΔH_c that is most meaningful when one is concerned with the product state at flame temperatures. Standard ΔH_f and ΔH_c (net) values are compiled in the summary data tables that are presented for each class of combustibles; the ΔH_f values can be used to calculate the ΔH_c values for other reactions of interest.

If the reactions occur under constant volume (closed system), the heats of reaction would not include any PV work ($\Delta V = 0$) and would be defined by

$$\Delta E = \Delta H - \Delta n RT. \quad (20)$$

For example, the change in gaseous moles in equation 18 is zero and, therefore, $\Delta E = \Delta H$. However, in the case of equation 17 where $\Delta n = -2$,

$$\begin{aligned} \Delta E &= -212.8 + 2 \times 1.987 \times 10^{-3} \times 298 \\ &= -211.6 \text{ kcal/mol.} \end{aligned} \quad (21)$$

It is evident that unless Δn is large, differences between heats of reaction at constant volume and constant pressure will be small.

IGNITION PROCESSES

General Concepts

Ignition is usually considered to be a vapor-phase combustion reaction with the evolution of heat and emission of light that may or may not be visible to the naked eye. Such reactions are most often associated with the rapid

oxidation of a combustible in air or oxygen. They may also occur with other oxidants, such as the halogens and nitrogen oxides, as well as without any oxidant when the combustible is capable of highly exothermic decomposition. The potential heat release for any reacting system can be calculated from thermodynamic considerations, but the combustion rate or intensity will depend upon the chemical kinetics at the reaction conditions. For example, in the constant-pressure reaction of hydrogen and oxygen,



the theoretical heat release is 28.9 kcal per gram of hydrogen. If this heat is produced rapidly and results in a branching chain reaction, high temperatures and flaming combustion are possible. However, if the heat is generated at a slow rate, as in a low-temperature oxidation process, flaming combustion is unlikely to occur unless the slow oxidation can initiate a self-accelerating reaction.

Most combustible-oxidant systems are not capable of sufficient self-reaction at ambient temperature to produce ignition. Generally, they require heating to some critical level by an external temperature or energy source. It is useful to consider the sources in terms of their spatial and temporal characteristics, as illustrated in figure 3. At one extreme (electrical sparks), the source is infinitesimally small and very high in temperature and heating rate; here, one is primarily concerned with energy density and the ignition energy. At the other extreme (heated vessels), the source is large, heating rate is very low, and temperature is also relatively low; here, one is mostly concerned with the concept of an ignition temperature. Thus, it is most meaningful to define ignition requirements in terms of energy for a highly concentrated heat source and in terms of temperature for a distributed heat source; an exception

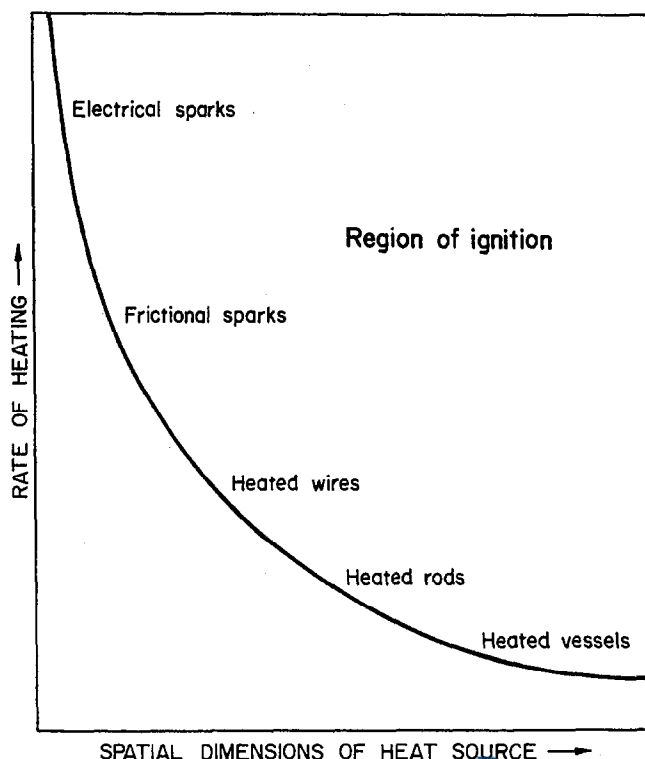


Figure 3.—Temporal and spatial characterization of various ignition sources.

is a large radiative heat source, which is usually defined in terms of energy.

Basically, ignition sources can be classified as either thermal or chemical types, the former being by far the most predominant type. In practice, electrical ignitions are treated as a separate category, although they are of a thermal nature; also, some ignitions are considered as thermal (self-heating) or chemical (pyrophoricity or hypergolicity) but are unique in that they do not require any external heat source. With this in mind, the various ignition sources may be categorized as follows:

Electrical ignitions:

1. High-voltage sparks or arcs.
2. Low-voltage sparks or arcs.

Thermal ignitions:

1. Hot surfaces:
 - a. Heated vessels or walls.
 - b. Heated wires or rods.
 - c. Heated particles or frictional sparks.
2. Self-heating (spontaneous combustion).
3. Hot gases:
 - a. Heated gas jets or pilot flames.
 - b. Adiabatic or shock compression.
4. Thermal radiation.

Chemical ignitions:

1. Catalytic materials.
2. Pyrophoric and hypergolic mixtures.

Electrical Ignition

The simplest form of electrical ignition is a thermal process in which excessive surface heating is produced by the resistance to current flow in an electrical circuit. This resistance heating can be calculated from

$$E = VI t = I^2 R t, \quad (23)$$

where E is heat (J), V is potential difference (V), I is current (A), R is resistance (Ω), and t is time (s); Ohm's law ($V = IR$) is applied here. Ignitions by such heating may occur within a second or more and fall in the hot surface temperature category that is discussed later.

Other electrical ignitions involve sparks or arcs in which the energy approximates a point source and the heating duration may be as little as a fraction of a microsecond. These can be classified as a high-voltage or electrostatic type and low-voltage or break spark type. In the case of *electrostatic sparks*, they are formed when the electrical charge of a conductor is sufficient to bridge ("jump") the gap to another conductor or nonconductor. The energy of electrostatic discharge is given by

$$E = \frac{1}{2} C V^2, \quad (24)$$

where E is the stored energy (J), C is capacitance of the charged conductor (F), and V is the potential difference (V); the capacitance is related to the electrical charge (Q) by $C = Q/V$, where Q is in coulombs. In the case of *break sparks*, they are formed when current-carrying conductors are abruptly separated to result in a collapsing field, such as when an electrical switch is opened. The energy of break sparks or arcs is given by

$$E = \frac{1}{2} L I^2, \quad (25)$$

where L is the inductance (H). Although such energies can be orders of magnitude greater than those associated with capacitive spark discharges, the differences are not so

noticeable when the breaking circuit involves a short gap length, as in the rapid separation of very fine wires.

Capacitive spark-type discharges are generally relied upon to determine the *minimum ignition energy* (MIE) of a combustible vapor-oxidant system. The MIE value occurs at an optimum spark gap length (electrode separation) and varies with temperature, pressure, and combustible-oxidant concentration; the optimum gap is referred to as the *minimum ignition quenching distance*. Figure 4 shows how the spark ignition energy can vary with the fuel-air weight ratio (F/A) for the butane-air system (41). Although stoichiometric butane combustion occurs at an F/A of 0.065 (3.12 vol pct), the MIE falls on the rich side of stoichiometric for this fuel. This figure also shows that whereas the minimum spark energy for ignition may be only a few tenths of a millijoule, it tends to be infinitely large as the mixture ratio approaches the limits of flammability.

The minimum ignition quenching distances in this context imply an optimum electrode design that maximizes

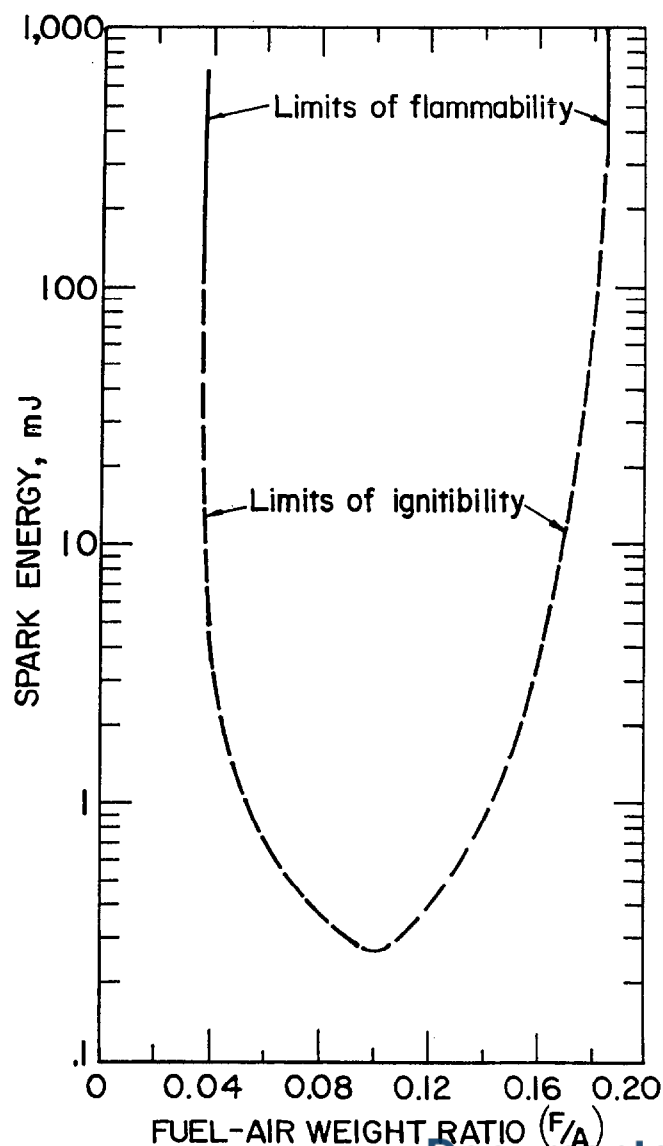


Figure 4.—Spark energy versus fuel-air ratio for ignition of n-butane-air mixtures at 25°C and 1 atm.

the spark energy efficiency in a quiescent mixture. They should not be confused with *minimum ignition quenching diameters* since these involve flowing mixtures and larger quenching surfaces; quenching diameters are roughly 1-1/2 times greater than corresponding quenching distances for many ordinary fuels, largely because of greater heat losses. In contrast, the so-called *maximum experimental safe gaps* involve much more severe combustion conditions, including both elevated pressures and large flame runup distances, which result in high turbulence, high flame speeds, and pressure piling (71). Thus, safe gap values tend to be much smaller than the ignition quenching distances that involve combustion at low flame propagation rates.

Generation of *static electricity* is commonly known to occur by triboelectrification, i.e., from the frictional action of two electrically unlike materials. The materials can be liquids, solids, and/or gases, one of which needs to be a relatively poor conductor for the charge to accumulate. This frequently occurs in the pumping of fluids, pneumatic transport of solids, and processes involving plastics. Even a human body can accumulate hazardous static charges (101). For example, by equation 24, an average human with a capacitance of 300×10^{-12} F and charge of 10,000 V could conceivably produce a static discharge of 0.015 J (15 mJ), which is much greater than the MIE of most combustible-air systems. The ability of a nonconductor (or conductor) to accumulate a static charge will depend upon

its resistivity $\left(\frac{\text{resistance} \times \text{area}}{\text{length}} \right)$ as well as that of the

surrounding medium. Obviously, charge dissipation will be greater in a liquid than in a dry gaseous medium, indicating the importance of humidity.

Thermal Ignition

Most thermal sources other than sparks or arcs tend to be much less localized spatially and temporally. These are discussed below, together with the concept of an ignition temperature or critical heating, which is basic to thermal ignition theory.

1. *Hot Surfaces*.—In the simplest terms, thermal ignition is a combustion reaction in which the limiting condition is determined primarily by the rate of chemical heat release versus the rate of heat loss to the surroundings. The rate of chemical heat release (q_1) by the Semenov theory (93), which assumes a uniform temperature distribution, is given by

$$q_1 = VQZ a^n e^{-E/RT}, \quad (26)$$

where V is vessel volume, Q is heat reaction, Z is rate frequency factor, a is reactant concentration, n is order of reaction, E is activation energy, R is universal gas constant, and T is the reactant absolute temperature. Also, the rate of heat loss (q_2) is defined by

$$q_2 = \alpha S (T - T_0), \quad (27)$$

where α is heat transfer coefficient, S is wall surface area, and T_0 is wall temperature. The critical heating condition for ignition is that temperature and pressure at which $q_1 = q_2$. Based on this theory, ignition temperature will be a function of the S/V ratio of the vessel, or roughly its reciprocal diameter ($S/V \propto d^2/d^3 = 1/d$). The variation of

the *time delay to ignition* (τ) with temperature is given by the following useful expression:

$$\tau P^n = A e^{E/RT}, \quad (28)$$

which at constant pressure (P) yields

$$\log \tau = \frac{0.22 E}{T} + A', \quad (29)$$

where A and A' are system constants and E is the apparent activation energy of the global processes controlling τ , i.e., the temperature coefficient of ignition delay. The lowest temperature that can accelerate the reaction to ignition occurs when the ignition delay (or induction period) is maximized and the vessel S/V ratio is minimized; this temperature is commonly referred to as the *minimum autoignition temperature* (AIT).

Figure 5 illustrates typical AIT data obtained for the n-decane-air system by injecting various quantities of liquid fuel in an open heated vessel; a plot of $\log \tau$ versus $1/T$ is more useful to define E and A in equation 29. Corresponding data under flowing conditions, where the contact time with the heated surface is shorter (<1 s), would be characterized by smaller τ and greater AIT values. In all such ignitions, the AIT's will be sensitive to fuel composition, fuel-oxygen ratio, pressure, and nature of the container surface. Generally, hot surface ignition temperatures increase with decreasing diameter or area of the heat source, although this dependence may not be uniform over a wide temperature range.

2. *Self-heating*.—A more rigorous thermal theory is one developed by Frank-Kamenetskii (21, p. 209) in which a nonuniform temperature distribution is assumed. It is particularly suitable for predicting the size of the reactant mass that may undergo self-heating at various ambient temperatures. Here, time delay to ignition can be of the order of hours or days in the case of adiabatic self-heating, as opposed to only minutes or seconds in the case of isothermal heating by an external source. The *self-heating*

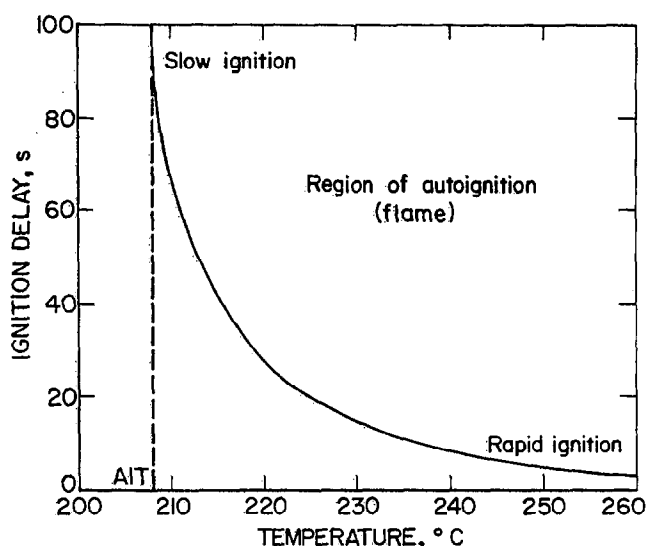


Figure 5.—Ignition delay versus temperature for autoignition of n-decane in air at atmospheric pressure.

rate (q) is defined as the sum of the chemical heat release rate (q_1) and the conductive heat loss rate (q_2):

$$\rho C \frac{\partial T}{\partial t} = \rho Q Z e^{-E/RT} + \lambda \nabla^2 T \quad (30)$$

(q) (q₁) (q₂)

where ρ is density, C is specific heat, λ is thermal conductivity, ∇^2 is a differential operator, and other quantities have the same meaning as above. For steady state conditions ($\partial T/\partial t = 0$), $q_1 = q_2$ and the critical mass radius (r_c) that will self-heat is

$$r_c = \left[\frac{\delta_c \lambda R T^2}{\rho E Q Z e^{-E/RT}} \right]^{1/2}, \quad (31)$$

where δ_c is a shape factor that is equal to 3.33 for a sphere, 2.0 for a cylinder, and 0.88 for plane-parallel slabs. For adiabatic conditions ($\partial T/\partial x = 0$), $q = q_1$ and the critical temperature rise rate for self-heating is

$$dT/dt = \frac{QZ}{C} e^{-E/RT} \quad (32)$$

Thus, autoignition by self-heating is strongly dependent upon the dimensions of the reactant mass, whereas auto-ignition by external heating depends more upon the dimensions of the heat source (heated vessels, wires, rods, etc.). In real self-heating situations, convective heat transport cannot be fully neglected as done in equation 30. For example, the self-heating of conical coal piles is due in part to the favorable "chimney effect" that can occur during the weathering of coal; furthermore, the *heat of wetting* itself can be greater than the heat of oxidation at ambient temperature. In all ignitions of combustible solids, the reactions will be particularly sensitive to particle size, bed porosity, moisture conditions, and the air ventilation rate.

3. *Hot Gases*.—As with heated surfaces, ignitions by hot gas sources also differ in their temporal and spatial characteristics. *Shock wave heating* (nonisentropic) is the most localized in space and time (e.g., <1 ms), whereas *adiabatic compression heating* (isentropic) is more spatially distributed and, therefore, should effect ignitions of combustible mixtures at lower temperatures. Table 5 compares the air temperatures possible in shock wave and adiabatic compression heating at various pressure ratios; it is apparent that shock compression temperatures are noticeably greater than adiabatic compression temperatures at a given pressure ratio. According to this table, it would appear that a combustible-air mixture with an AIT of 200° C could be ignited at a shock pressure ratio of at least 5 or an adiabatic compression ratio of 10. However, in both cases, much higher pressure ratios would be required because of the short duration of heating involved (milliseconds) as opposed to those associated with minimum AIT's (minutes). Essentially, ignition will not

occur unless the elevated heating conditions are maintained for a duration that exceeds the ignition delay at the given temperature.

Other hot gas ignitions can involve *heated jets* of air, inert gas, or gaseous combustion products, including luminous and nonluminous flames. They are intermediate on the temporal and spatial scale of heating by hot gases. Although these ignitions involve more complex heat and mass transport processes than in hot surface ignitions, they are also a thermal type and depend upon the enthalpy or heat flux of the heat source. The heat flux of the hot gas jet will depend upon its temperature, diameter, velocity, and composition. Reported ignition temperatures by hot gas jets tend to be higher than those by hot surfaces, but the differences are not likely to be great when compared at the same heat source diameter and fuel contact time with the heat source.

4. *Thermal Radiation*.—Ignitions under this category include those in which a combustible is raised to its AIT by exposure to the thermal radiation of a hot gas, hot surface, or other infrared heat sources, including a fire. Solid or condensed combustibles have the greatest capacity to absorb radiative heating and, therefore, are most likely to be ignited by this heating mode. The radiative ignition requirements for any combustible are usually defined in terms of a critical heat flux. For ordinary combustible solids, the critical *radiant heat flux* for ignition can be a relatively small value (1 to 2 cal/(cm²·s)), depending upon the ignition temperature of the solid. Such critical radiation intensities can be easily encountered when the combustible is exposed to a nearby flame source since the maximum radiation intensity can be 10 to 30 cal/(cm²·s) near the flame surface. Generally, approximately 15 to 40 pct of the theoretical thermal output of a large flame source will be radiated to the surroundings (7). Assuming spherical geometry and a flame point source, the radiant heat flux (h_x) at various distances (x) from a flame source, such as a burning pool of radius r , can be estimated by

$$h_x = \frac{h_r \pi r^2}{4 \pi x^2}, \quad (33)$$

where h_r is the maximum radiative heat flux at the flame surface. The assumption of a hemispherical pool fire model will yield twice the irradiances predicted by equation 33. Factors that can determine the level of thermal flame radiation include fuel-oxidant stoichiometry, soot formation (fuel-rich hydrocarbon flames), and radiative properties of the gaseous combustion products. Hydrogen flames are typical of a low-radiative emitter, and benzene flames, which tend to produce considerable soot, are representative of a high-radiative emitter.

Chemical Ignition

This category represents a special case of autoignition in which the heat of chemical reaction alone can produce ignition at or below ambient temperature. One type is a *pyrophoric reaction* where the combustible ignites spontaneously upon mere exposure to air, as in the self-reaction of alkali metals, metal alkyls, or metal hydrides. Such reactions are usually promoted by the presence of moisture and can involve the formation and ignition of a flammable gas; the combustibles in this case are also referred to as water-reactive substances.

Another type is a *hypergolic reaction* where spontaneous ignition occurs when a combustible is intimately mixed

Table 5. — Shock wave and adiabatic compression temperatures of air (66, p. 516)

($P_1 = 14.7$ psia; $T_1 = 0^\circ$ C)

Compression ratio (P_2/P_1)	Gas compression temperature (T_2)	
	Shock wave °C	Adiabatic compression °C
2	62	57
5	208	152
10	432	242
50	1,988	521
100	3,588	677
1,000	18,840	1,435

with a highly reactive oxidizer. These ignitions can occur with ordinary and high-energy fuels and particularly with such high-strength oxidizers as fluorine, hydrogen peroxide, nitrogen tetroxide, and concentrated acids. Their heats of reaction can be calculated from available heats of formation. In the case of acid-base systems, heats of neutralization are typically about 13 to 14 kcal/mol for a strong acid and strong base in aqueous solution. If one also considers the heats of solution, the total heat release can be about 25 to 35 kcal/mol and sufficient to initiate a combustion reaction.

Chemical ignitions also result from *catalytic reactions*. The most common catalysts in organic reactions are finely divided metals, but many different substances can serve as catalysts, depending upon the chemical reactants. Contaminants that accumulate on the walls of a reaction vessel may serve as either ignition catalysts or inhibitors.

FLAME PROPAGATION PROCESSES

Flammable Mixtures

A flammable gaseous mixture of combustible and oxidant is one that, when ignited, will propagate flame beyond the influence of the ignition source. All combustible gases and combustible vapors of liquids or solids form flammable mixtures over a limited range of combustible concentrations, depending upon temperature, pressure, and nature of the oxidant. The critical combustible concentrations are known as the *limits of flammability* or explosion limits of the system and are defined as the fuel-lean or *lower limit* (L) and the fuel-rich or *upper limit* (U). These limits are usually in volume percent and refer to homogeneous combustible vapor-oxidant mixtures. Since the flammability limits vary with temperature and since the vapor formation of a combustible in its liquid or solid state is strongly dependent on temperature, it is useful to construct a flammability concentration-temperature diagram of the type shown in figure 6. A three-dimensional plot to include the pressure effect would be required to completely define the flammability domains.

As shown in figure 6, the flammable mixtures of a combustible liquid-air system may consist of mists (droplets + saturated vapor + air), saturated vapor-air mixtures (vapor pressure curve), or neat vapor-air mixtures (region beyond saturated vapor temperatures). The temperature range over which the liquid can form flammable vapor concentrations is defined by its *temperature limits of flammability* (T_L and T_U); intersections of these temperature limits with the vapor pressure curve define the *concentration limits of flammability* (L and U) at liquid-vapor equilibrium conditions. At higher temperatures, flammability domains for the neat vapor-air mixtures become widened, particularly on the fuel-rich side. Eventually, the temperature can be sufficient to produce autoignition of the mixtures, as illustrated in figure 6.

The lower temperature limit (T_L) is of great practical interest because it defines the minimum temperature to which a combustible liquid or solid must be heated to form a flammable vapor-air mixture, i.e., the lower limit of flammability (L). In practice, this temperature corresponds approximately to the *flashpoint* of the combustible, which is determined under less ideal conditions (downward flame propagation and nonuniform mixtures) than those used in flammability limit determinations (upward propagation

and uniform mixtures). *Closed cup flashpoints* are the most reliable values. It is evident from figure 6 that flammable mists, sprays, or foams can form below the flashpoint or T_L of the combustible. However, their ignition energy requirements are much more severe than for neat vapor-air mixtures. The flammability characteristics of mists can be expected to approximate their vapor behavior when the droplet size of the mist is less than about 10 μm .

Various flammability diagrams are used to present complete limit of flammability data for combustible vapor-oxidant-inert systems (II0). Most data are presented in the form of a rectangular plot, as in figure 7 for the aviation gasoline vapor-air-nitrogen system (42). In this plot, the flammability limits in the oxidant alone (air) are found on the ordinate (1.3 and 7.1 pct combustible); also, the variations of these limits with added inert (N_2) are indicated

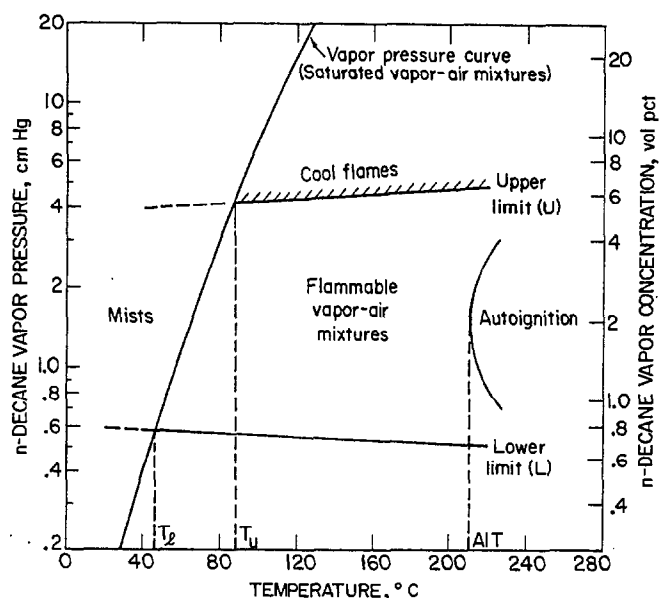


Figure 6.—Flammability and vapor pressure diagram for n-decane vapor-air system at various temperatures and atmospheric pressure.

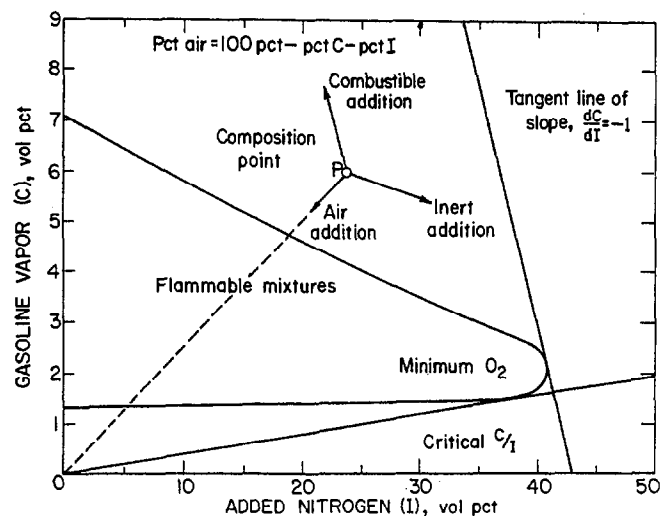


Figure 7.—Flammability diagram for the aviation gasoline vapor (100/130 grade)-air-nitrogen system at 25°C and 1 atm.