

Pyrotechnic Ignition and Propagation: A Review

K. L. and B. J. Kosanke

PyroLabs, Inc., 1775 Blair Road, Whitewater, CO 81527, USA

ABSTRACT

The ideal pyrotechnic is completely stable in storage and handling, yet performs its mission completely with absolute reliability upon demand. Many accidents in pyrotechnics are the result of unintentional ignitions during handling and storage. There can also be serious safety ramifications of ignition and propagation failures of pyrotechnic devices. This review article presents a fairly rigorous, but mostly non-mathematical discussion of the ignition and propagation processes.

Keywords: ignition, propagation, heat of reaction, activation energy, spontaneous ignition, thermal run-away, cook-off

Introduction

An understanding of the mechanism of pyrotechnic ignition and propagation will improve one's ability to identify and solve problems with ignition failures (duds) and unintended ignitions (accidents). In addition, many of these same principles play an important role in understanding the control of pyrotechnic burn rates. This article will examine these important topics thoroughly, however, not at a mathematically rigorous level. For more detailed and rigorous discussions, readers are referred to the writings of Merzhanov and Abramov.^[1,2]

Pyrotechnic Reaction Energy Considerations

Pyrotechnic compositions are mixtures of fuel(s) and oxidizer(s) and possibly other materials. They are used to produce energy on demand in the form of heat, light, sound, etc. Pyrotechnic compositions are said to be in a "meta-

stable" state. That is to say under typical conditions they are stable and do not react to release their internal chemical energy unless externally stimulated in some way. Probably the most common stimulus is the addition of heat, such as provided by a burning match or fuse. Ignition is the process of stimulating a pyrotechnic composition to release its internal energy and can be defined as "the initiation of self-sustained burning or explosion of a pyrotechnic material".^[3]

Figure 1 illustrates the process of ignition by graphing the internal energy of a tiny portion of pyrotechnic composition during the progress of its chemical reactions and is typical of non-spontaneous exothermic chemical reactions.^[4] At the left of the graph, where the process begins, the pyrotechnic composition has a certain amount of internal energy. To accomplish ignition, external energy is supplied, such as from a burning match. This addition of energy increases the internal energy of the composition and is seen as a rise in the curve of Figure 1. This is indicated as the "Energy In" part of the reaction. As the process continues, eventually the pyrotechnic composition ignites to release its stored chemical energy to the surroundings.

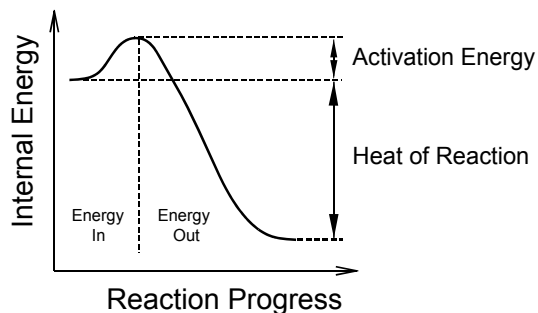


Figure 1. A graph illustrating the flow of energy into and out of a tiny portion of pyrotechnic composition.

Table 1. Heats of Reaction of Binary Pyrotechnic Compositions.^[5a]

Fuel (%)	Oxidizer (%)	ΔH_r (kcal/g)
Magnesium (37)	Potassium chlorate (63)	2.29
Magnesium (40)	Potassium perchlorate (60)	2.24
Magnesium (32)	Barium nitrate (68)	1.65
Aluminum (34)	Potassium perchlorate (66)	2.45
Aluminum (40)	Sodium nitrate (60)	2.00
Aluminum (25)	Iron(II) oxide (75)	0.96

This loss of internal energy is seen as a drop in the curve of Figure 1 and is indicated as the “Energy Out” part of the reaction. The energy that was required to stimulate this release is commonly referred to as the “Activation Energy” (E_a). The net amount of energy produced by the pyrotechnic reaction is referred to as the “Heat of Reaction” (ΔH_r).^[a]

Even the smallest particles of fuel and oxidizer in the pyrotechnic composition, are clusters of many billions of atoms bound together to form the particle. It is possible to think of the two-step process, energy in and energy out, as first when old chemical bonds are being broken in the fuel and oxidizer, and second, when new chemical bonds are being formed to make the reaction products. This also helps to make it clear why the activation energy^[b] requirement acts as a barrier that must be surmounted to initiate the chemical reaction. Until the necessary energy is supplied to break the original chemical bonds, thus freeing individual fuel and oxidizer atoms, they are not available to react with each other to form new chemical bonds.

In a pyrotechnic chemical reaction, a net amount of energy will be produced, providing the new chemical bonds being formed in the reaction products are stronger than the old bonds that must first be broken in the fuel and oxidizer. Table 1 is a listing of the heats of reaction for some two-component pyrotechnic reactions. The reason that varying amounts of energy are produced is that in each case different numbers and strengths of chemical bonds are broken and formed.

A collection of atoms, such as those bound together in a particle of fuel or oxidizer, are not held in absolutely rigid positions. The individual atoms jostle about (vibrate), back and forth,

and up and down. Because of these internal motions, the individual atoms possess energy, often referred to as thermal energy. In the process of jostling with one another, the atoms transfer some of their thermal energy from one to another. The net result of this jostling and energy sharing is that some atoms have much energy while others have little, and an atom that has much energy now may have little energy later.

Figure 2 is a graph illustrating the distribution of thermal energies^[4] of individual atoms in fuel and oxidizer particles in a pyrotechnic composition at some temperature T_1 . The curve goes through the origin of the graph, meaning that zero atoms have zero energy. Thereafter an increasing number of atoms have increasing energy, until a peak is reached, followed by continuously decreasing numbers of atoms possessing higher and higher energies. Also shown in Figure 2 is the activation energy E_a , which is

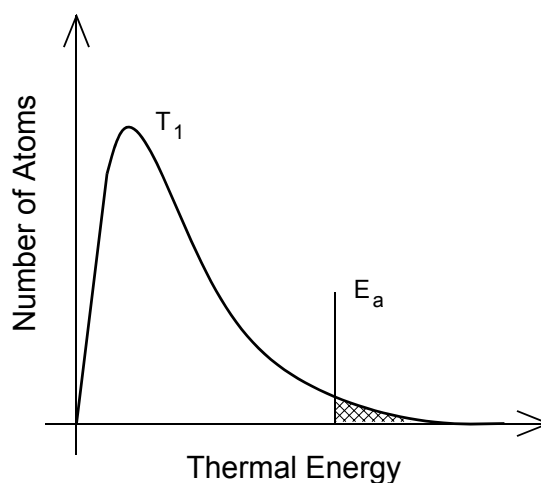


Figure 2. A graph illustrating the distribution of thermal energies of atoms in a pyrotechnic composition.

required to initiate the pyrotechnic reaction. Note that the composition contains some atoms with energies exceeding the activation energy barrier. (In Figure 2 the number of atoms with energies greater than E_a has been exaggerated for clarity.)

Since some atoms in the pyrotechnic composition have sufficient energy to react, the question should be, “Why isn’t the pyrotechnic composition reacting?” The answer is, “It is reacting, but very, very slowly.” To see why this is the case, consider the following: At room temperature, only 1 atom in roughly every million billion (10^{15}) has the needed activation energy.^[6] Additionally, it is only the fuel atoms that are in direct contact with oxidizer atoms that can react. When considering the fraction of atoms in a tiny particle that are on its surface, and the fraction of surface atoms that are likely to be in direct contact with the right atoms on the surface of other particles, only 1 atom in roughly every thousand billion billion (10^{21}) is capable of reacting at any given time.

Thermal Run-Away and Spontaneous Ignition

If the temperature of the pyrotechnic composition is raised, from T_1 to a higher temperature T_2 , as illustrated in Figure 3, on average the atoms jostle around with more energy. More significantly, however, the number of atoms with energies exceeding the activation energy barrier increases greatly.^[4] As a consequence, there are now many more atoms capable of reacting, and there is a corresponding increase in the rate at which the reactions occur. Recall, however, that these chemical reactions produce thermal energy; thus an increase in the reaction rate causes an increase in the rate of production of heat; which would seem to produce a further increase in temperature; which causes still more atoms to have energies exceeding the activation energy barrier; which causes a still greater increase in reaction rate and the rate of heat production; which causes a further increase in temperature; etc. This accelerating cyclic process is outlined in Figure 4 and leads to what can be called “thermal run-away” and ignition.

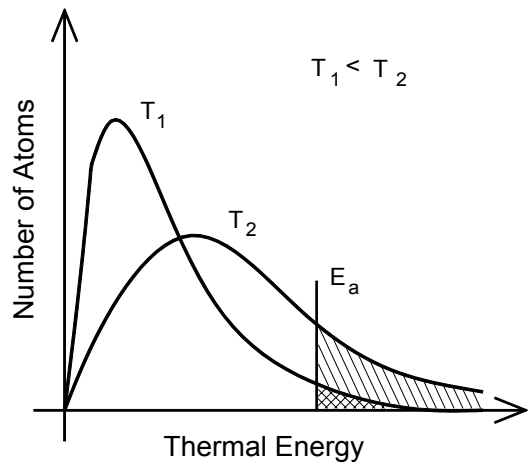


Figure 3. An illustration of the effect of increasing temperature on the distribution of the thermal energy of atoms.

Taken literally, the process outlined in Figure 4, suggests that the slightest temperature rise of a pyrotechnic composition will eventually lead to thermal run-away and ignition. Obviously, this is not correct. The reason is that, thus far, only the rate of thermal energy production has been considered, which is only half of the total picture. The rate of thermal energy

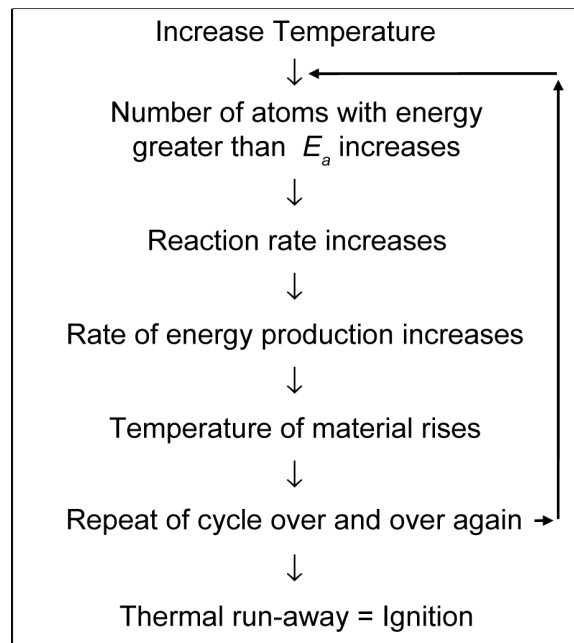


Figure 4. Outline of the accelerating cyclic process leading to thermal run-away and ignition.

loss from the pyrotechnic composition to the surroundings must also be considered. This more complete energy picture is presented in Figure 5, with both heat-gain and heat-loss rates plotted as a function of temperature.

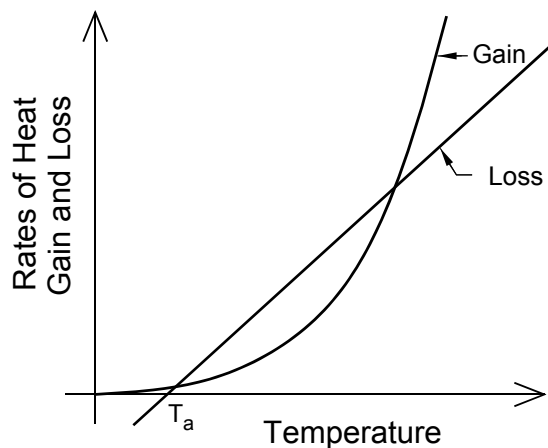


Figure 5. Graph illustrating the rates of heat gain and loss for a pyrotechnic composition as a function of temperature.

The rate of the pyrotechnic chemical reaction k follows an exponential relationship,^[4] sometimes referred to as the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (1)$$

where A and R are constants, and T is absolute temperature. The rate of heat gain Q_g is just the reaction rate multiplied by the heat of reaction:

$$Q_g = k \cdot \Delta H_r \quad (2)$$

Thus, in Figure 5, the rate of heat gain curve passes through the origin and rises ever more steeply with increasing temperature.

For a mass of pyrotechnic composition, heat loss from the surface will primarily be from convection through contact with the air. However, any heat generated internally, will first need to be conducted to the surface. Accordingly, for spontaneous heat generation, temperatures at the center of the mass would normally be highest.^[c] The rate of heat loss Q_l from the center of the pyrotechnic composition depends on the thermal conductivity of the composition and any packaging, the convective heat loss coefficient, the geometry of the sample (or

item), and the difference in temperature between the center of the composition T and ambient temperature T_a . This may be expressed as:^[6]

$$Q_l = C(T - T_a) \quad (3)$$

where C is a constant derived from the geometry and thermal properties of the pyrotechnic sample (or item). Accordingly, in Figure 5, the rate of heat loss curve is a straight line crossing the temperature axis at ambient temperature and with a slope equal to C .

To illustrate why, under typical storage conditions, pyrotechnic compositions are meta-stable and do not spontaneously ignite, as suggested by the process outlined in Figure 4, consider Figures 6 and 7. Figure 6 is an enlarged view of the low temperature region from Figure 5. If a pyrotechnic composition is formulated from materials at ambient temperature, the composition will be at the same temperature, at least initially. In Figure 6, note that at ambient temperature, the rate of heat loss is zero, while the rate of heat gain is greater than zero. Accordingly, the temperature of the sample will begin to increase. The temperature of the sample will continue to rise until the rates of gain and loss are equal. This occurs at the crossing point of the “gain” and “loss” curves, where the temperature of the sample T_s has risen to slightly above ambient temperature. (Note that in Figure 6, the temperature difference between T_a and T_s has been exaggerated for clarity.)^[d]

Now imagine that for some reason the pyrotechnic composition were momentarily raised from temperature T_s to T_1 , somewhat further

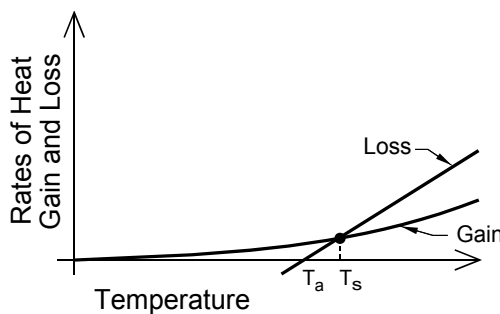


Figure 6. Enlarged view of the low temperature region of Figure 5.

above ambient, see Figure 7. In this case, both the rate of heat gain of the pyrotechnic composition and the rate of heat loss from the composition, increase. However, the rate of loss is greater than the rate of gain. Accordingly, the net effect will be a loss of thermal energy with time. Thus, the temperature of the composition will decrease and must continue to fall to the temperature where the rates of loss and gain are equal (at temperature T_s). From the above discussion, it can be seen that pyrotechnic compositions are at least meta-stable, in that any small addition of energy will not ultimately cause thermal run-away and ignition.

Figure 7 shows that if the temperature of the pyrotechnic composition were to be raised momentarily to a still higher temperature T_2 , that the results would be quite different. In this case, again both the rate of heat gain and the rate of heat loss increase. However, this time the rate of gain has overtaken the rate of loss. At this temperature, there is a net accumulation of heat, producing a further increase in temperature. In fact, this is an ever accelerating process, because as the temperature increases, the rate of gain increases much faster than the rate of loss. In this case, the process outlined in Figure 4 does apply and leads to thermal run-away and spontaneous ignition.

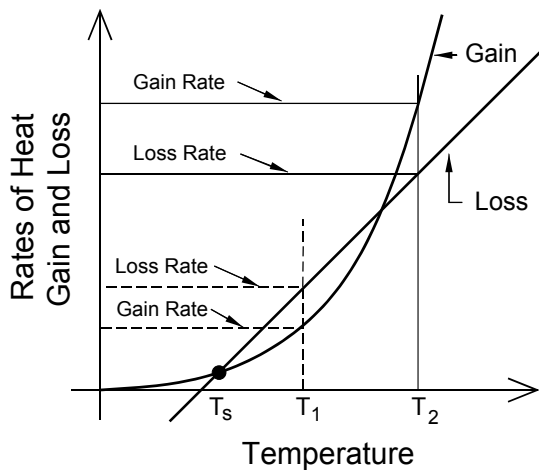


Figure 7. Illustration of the effect of raising the temperature of a pyrotechnic composition.

Thermal Run-Away Temperature^[e]

Obviously the temperature at which thermal run-away can occur for each pyrotechnic composition is of great importance from a safety standpoint. Whenever a pyrotechnic composition is raised above this temperature, it will begin to undergo thermal run-away and will eventually ignite spontaneously. In Figure 8, the run-away temperature is designated as T_r and is the temperature corresponding to where the gain and loss curves cross for the second time. For any composition, this temperature could be established experimentally (with some effort and much time) or mathematically (providing the gain and loss relationships are known).

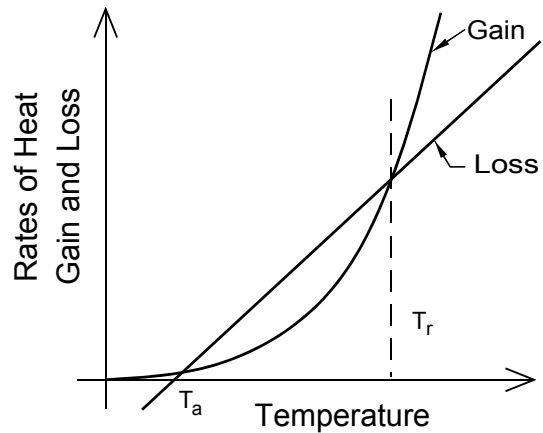


Figure 8. Illustration of the thermal run-away temperature of a pyrotechnic composition, under one set of conditions.

From equations 1 and 2 it can be seen that the rate of heat gain depends on the activation energy and the heat of reaction, which are determined by the formulation of the pyrotechnic composition. The heat of reaction is easy to calculate, providing one knows the equation for the chemical reaction,^[5b] or it can be determined experimentally.^[5c] Determination of activation energy must be established through experimentation.^[9,10] From equation 3, as expressed by the constant C , it can be seen that the rate of heat loss depends on the thermal conductivity, the convection coefficient and geometry of the composition, and on ambient temperature. All of these parameters can be determined with only modest effort. However, the

rate of heat loss depends on many things other than the pyrotechnic formulation. For example, the degree of compaction of the composition, the size (mass) of the item or sample, and the packaging of the composition all affect the thermal conductivity of the composition or item. Also, the rate of heat loss is a function of ambient temperature. Thus, for each pyrotechnic formulation there is not just one thermal run-away temperature, rather there is one for each of an infinite number of different conditions. This illustrates the problem in trying to use thermal run-away temperatures to characterize a pyrotechnic formulation (and why many pyrotechnists have never heard of it).

Spontaneous Ignition Due to Thermal Run-Away

Even though the use of thermal run-away temperature as a way of characterizing pyrotechnic compositions is of limited value, the concept is important because it helps to identify some potentially dangerous conditions where there will be delayed spontaneous ignitions. For example, Figure 9 illustrates the effect of varying sample size. Note that the rate of heat gain (per gram of composition) is unaffected by sample size, but the rate of heat loss is sample-size dependent. Small samples generally lose heat easily and have a rate of heat-loss curve that is steep, with two crossing points, the higher of which is the thermal run-away temperature. As the sample size increases (medium sample size in Figure 9), the slope of the curve decreases, lowering the run-away temperature more and more with increasing sample size. At some point, for a large sample, there will only be a single point of contact between the curves. This represents the largest sample, under a specific set of conditions, that theoretically will not spontaneously run-away and ignite. For samples larger than this, the rate of heat gain is always more than the rate of loss, and the sample will always run-away thermally. It may take a very long time, but for large enough samples, eventually, there will always be a spontaneous ignition.

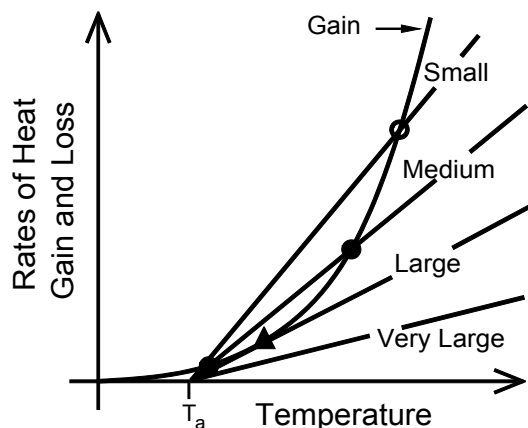


Figure 9. An illustration of the effect of increasing sample size on the rate of heat loss and therefore on thermal run-away temperature.

The rate of heat loss is sample-size dependent because sample size is one factor that affects the constant C in equation 3. Another factor is the thermal conductivity of the pyrotechnic composition and its packaging. In Figure 9, poorly conducting compositions and insulating packaging, produce effects equivalent to a large sample size.

A somewhat similar situation arises for increasing ambient temperature, see Figure 10. When the ambient temperature is low, samples lose heat to the surroundings fairly easily. This places the heat-loss rate curve fairly high on the heat-gain curve, producing two crossing points, the higher of which is the thermal run-away temperature. As the ambient temperature increases, it becomes more difficult for the sample to lose heat. The slope of the heat-loss curve is unchanged, but its position relative to the heat-gain curve is lower. This lowers the run-away temperature more and more with increasing ambient temperature. At some point, for high enough ambient temperature, there will only be a single point of contact between the curves. This represents the highest ambient temperature, for this type and size of sample, that will not spontaneously run-away thermally (ignite). For ambient temperatures greater than this, the rate of heat gain is always more than the rate of heat loss, and the sample will always run-away thermally. It may take a long time,

but for such hot ambient conditions there will eventually be a spontaneous ignition.

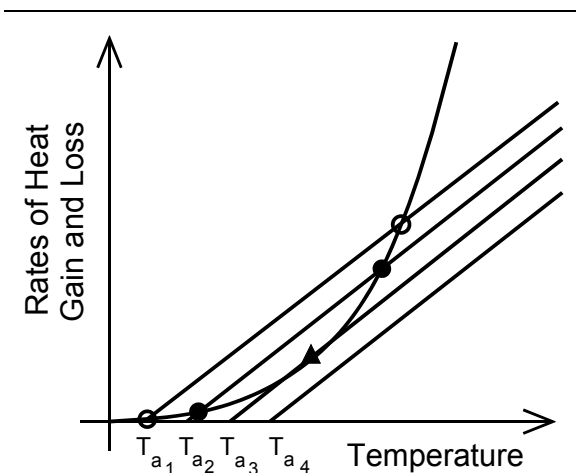


Figure 10. An illustration of the effect of increasing ambient temperature on the rate of heat loss and therefore on thermal run-away temperature.

Just how large a sample and just how high an ambient temperature are required for thermal run-away and spontaneous ignition depends on the chemical formulation and the conditions of its packaging and storage. For some compositions under favorable conditions, it may require millions of tons of material and take years to run-away and spontaneously ignite. However, under more extreme conditions, or for other compositions, tiny samples of composition may ignite very quickly.

Time to Ignition, Cook-Off Tests

The time for any given pyrotechnic composition to ignite is a function of the temperature to which it is exposed, as illustrated in Figure 11. If a sample is placed in an oven, its temperature will begin to rise from ambient temperature T_a , eventually reaching the temperature of the oven. If the temperature of the oven T_1 is less than the run-away temperature T_r for the pyrotechnic composition, the sample will never ignite (i.e., the time to ignition is infinite).

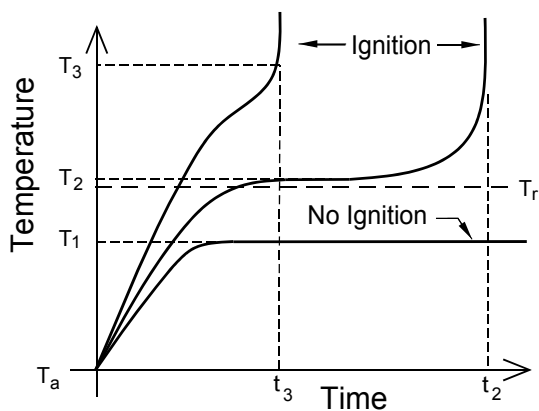


Figure 11. An illustration of the dependence of time to ignition on the temperature to which a pyrotechnic composition is heated.

If the temperature of the oven T_2 is slightly higher than the run-away temperature, upon placement in the oven, the sample will start to heat up and will eventually rise to the temperature of the oven. For a while, it may appear that nothing is happening with the sample. However, inside the sample, heat is slowly accumulating, raising the temperature, at first perhaps imperceptibly. As the internal temperature rises, the rate of reaction increases, increasing the rate of heat gain, and further increasing the temperature (i.e., thermal run-away has begun). As a result of this ever accelerating process, the internal temperature rises ever more rapidly, until eventually there is an ignition, at time t_2 in Figure 11.

If the temperature of the oven (T_3) is significantly higher than the run-away temperature, upon placement in the oven, the sample again will heat up, approaching the oven temperature. However, under these conditions, the sample's temperature rise may not slow significantly as it reaches the oven temperature, before thermal run-away is at an advanced state with ignition occurring more quickly at time t_3 .

Determining the time to ignition as a function of temperature, has important ramifications for the storage of pyrotechnics (and explosives). If one were to guess wrong, the consequences of an accidental spontaneous ignition could be disastrous. Tests performed to discover the time-to-ignition and temperature relationship are sometimes called "cook-off" tests.^[11] In these

tests, samples or items are typically placed in a heated bath, after having thermocouples installed internally. Bath and sample temperatures are monitored as a function of time from the start of the test, and the time to ignition or explosion (if either occurs) is recorded.

Ignition and Ignition Temperature

Ignition is one of the more difficult terms to define in pyrotechnics. Obviously it cannot be defined as when chemical reactions start. As was discussed earlier, some pyrotechnic reactions are occurring all the time, although at a very, very low rate. Even after the thermal runaway temperature has been reached, there may be no obvious sign anything is happening. For most observers, the appearance of a flame (high temperature radiant gases) or at least obvious incandescence of the solid phase is taken as the indication that ignition has occurred. As suggested in Figure 11, at the time of ignition very rapidly accelerating reaction rates produce a near instantaneous rise in temperature, typically from several hundred to two thousand degrees Celsius or higher. Thus the physical manifestations of ignition develop very rapidly as ignition is occurring.

Ignition temperature can be defined as “the minimum temperature required for the initiation of a self-propagating reaction”.^[12a] However, from the above discussion, that temperature can vary widely depending on sample conditions and on how long one is willing to wait for the ignition to occur. These problems are mostly eliminated for ignition temperature measurements, because the conditions and delay time are usually specified in the procedure to be used. Unfortunately, there are many different procedures that are used; the *Encyclopedia of Explosives*^[13] alone lists 14 different methods. This means there can be more than one ignition temperature reported for the same pyrotechnic composition, depending on which method was used. Fortunately, the various ignition temperatures of the most commonly used methods all tend to be in the same general range, primarily because the measurement conditions of the various methods tend to be somewhat similar.

Obviously, however, the most consistent results will be achieved if all measurements are made using the same method. Also, when evaluating reported ignition temperature data, it is useful to know which method has been used. Three hot bath methods and one differential thermal analysis method are described in the following paragraphs.

Hot Bath Method One: Ignition temperature is the lowest temperature of a bath of Wood’s metal,^[1] to within 5 °C, that results in ignition within 5 minutes for a 0.1 g sample in a pre-heated small glass test tube inserted 1/3 its length into the bath.^[5a]

Hot Bath Method Two: Ignition temperature is the temperature of a bath of Wood’s metal that results in ignition in 5 seconds (determined graphically using time to ignition data) for a 1.0 g sample in a thin-walled brass or copper tube (typically a No. 6 detonator shell).^[10]

Hot Bath Method Three: Ignition temperature is the temperature of a bath of Wood’s metal, heated at a rate of 5 °C per minute, at which ignition occurs for a 0.5 g sample in a tightly corked glass test tube (125 mm long by 15 mm inside diameter with a 0.5 mm wall thickness).^[13]

Differential Thermal Analysis Method: Ignition temperature is the temperature of onset of the ignition exotherm for a 10 to 100 mg sample heated at a rate of 50 °C per minute.^[14]

A collection of ignition temperatures for a series of two-component, stoichiometric pyrotechnic compositions is presented in Table 2. Shidlovskiy reports the method as one using an electric furnace instead of a bath of Wood’s metal. Unfortunately, he provides no information on the method, other than an estimate of the accuracy of the results to be within 10 °C. (This data was chosen for inclusion because it is the most systematically complete set of data known to the authors.)

It might be of interest to note that a typical pyrotechnic composition raised to its ignition temperature will have about 30 million times more atoms with energies exceeding E_a than at room temperature.^[6]

Table 2. Ignition Temperatures for Binary Pyrotechnic Compositions.^[5c]

Oxidizer	Ignition Temperature (°C)				
	Sulfur	Lactose	Charcoal	Mg powder	Al dust
Potassium chlorate	220	195	335	540	785
Potassium perchlorate	560	315	460	460	765
Potassium nitrate	440	390	415	565	890

The Effect of Melting and Tammann Temperature

For a pyrotechnic reaction to occur, the atoms (or molecules) must have the required activation energy, and they must be in direct contact with another atom of the correct type. Even for well-mixed solid particles, there are relatively few points of contact between individual particles; see the top illustration of Figure 12. Thus the number of fuel and oxidizer atoms that are in contact with one another is normally quite small. However, if one of the components melts to flow around the surfaces of the other particles, there is a great increase in the number of atoms in contact; see the bottom illustration of Figure 12.

Accordingly, melting can have a significant effect on the likelihood of ignition. The potential effect on ignition is outlined in Figure 13. If the percentage of atoms in physical contact increases upon the melting of one component, then more atoms with energies exceeding the activation-energy barrier will be in contact with one another. That means the reaction rate will then be greater, and with it the rate of production of thermal energy, which means that thermal run-away and ignition can occur at a lower temperature. Thus it is suggested that if a composition is nearing its ignition temperature, and one component of the composition melts, that could result in ignition occurring at that lower temperature. For example, the melting point of potassium nitrate and the ignition temperature of Black Powder are effectively the same.^[12b]

Melting can be thought of as occurring when the thermal vibrations of a solid are so strong that some of the bonds, which had been holding the solid together, are broken. While for most pure chemicals melting has a sudden onset at a

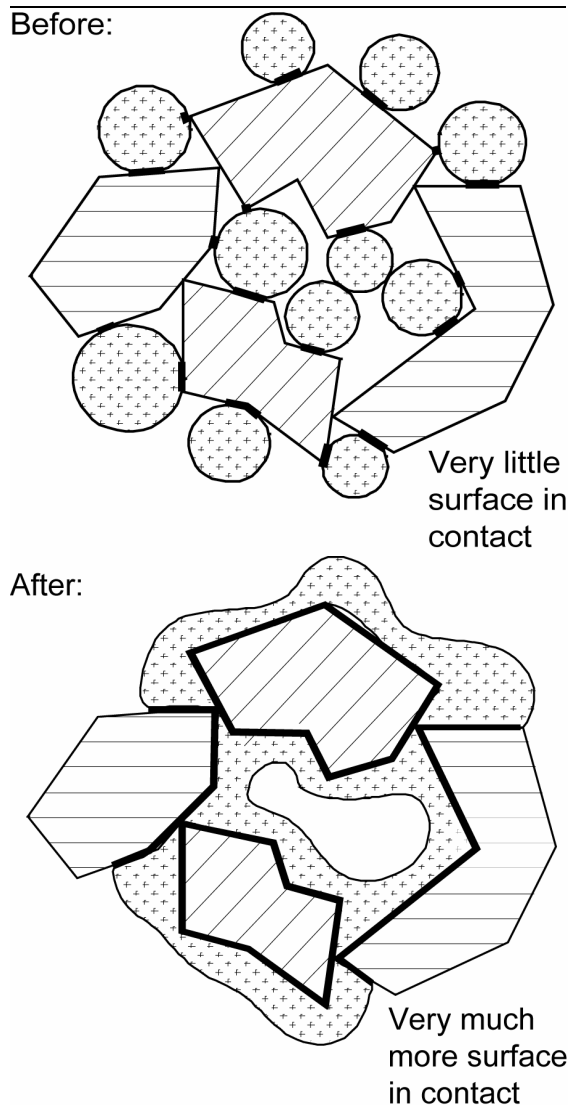


Figure 12. An illustration of the great increase in contact between fuel and oxidizer after one component melts.

specific temperature, the vibrations of the atoms in the solid become increasingly strong as the temperature is increased toward the melting point. This can be thought of as the loosening

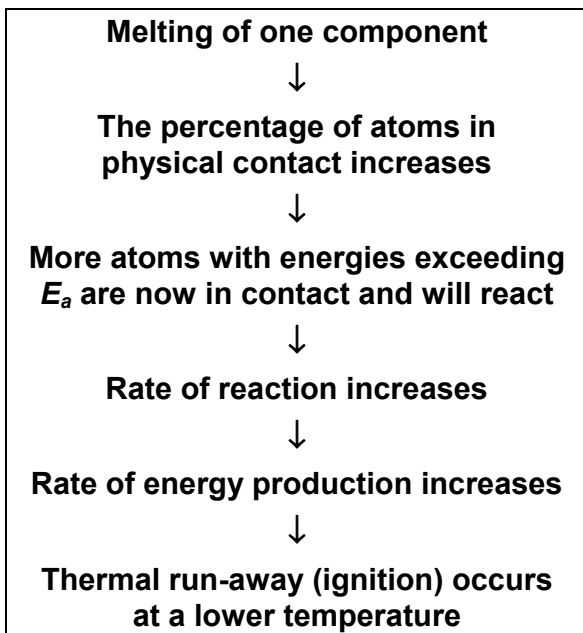


Figure 13. An outline of the effect of melting on thermal run-away and ignition temperature.

of the bonds holding the solid together. It has been suggested that at an absolute temperature halfway to the melting point, the bonds become so loose that there can be a significant commingling of the atoms of particles that are in direct contact.^[8b] This temperature is called the Tamman temperature after the researcher making this observation.

Tamman temperatures are of interest because samples at or above these temperatures demonstrate significantly increased sensitivity to accidental ignition. Table 3 lists the Tamman temperatures for some common pyrotechnic oxidizers.

Table 3. Tamman Temperatures for Common Pyrotechnic Oxidizers.^[12c]

Oxidizer	Tamman Temp. (°C)
Sodium nitrate	17
Potassium nitrate	31
Potassium chlorate	42
Strontium nitrate	149
Barium nitrate	160
Potassium perchlorate	168
Lead chromate	286
Iron(III) oxide	646

Propagation and the Propagation Inequality

Having successfully ignited a pyrotechnic composition is no guarantee that the reaction will propagate throughout. This is because the application of an external stimulus, such as a flame, typically provides thermal energy to only a small portion of the composition, and the ignition stimulus is usually of relatively short duration. After its application, the pyrotechnic combustion reaction will continue to propagate through the composition only so long as the pyrotechnic reaction provides sufficient energy to the unreacted composition. What is needed is sufficient energy to raise the unreacted composition above its ignition temperature. This process is illustrated in Figure 14. The portion of the rod of pyrotechnic composition to the extreme right has already been consumed by burning. Just to the left of that is shown a thin disk of composition that has ignited and is still reacting (burning). Just left of that is another thin disk of composition, labeled “pre-reacting material”, which has not yet ignited. This disk of pre-reacting material will only ignite if it is raised above its ignition temperature, which means that a significant number of its atoms and molecules will have received at least the required activation energy E_a .

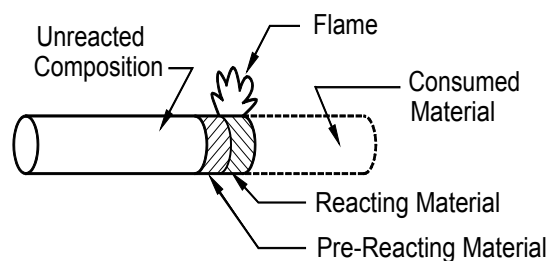


Figure 14. Illustration of a propagating rod of pyrotechnic composition.

Most of the energy being produced by the reacting material (the heat of reaction ΔH_r) is lost to the surroundings. However, some fraction F_{fb} of the energy will be fed back from the reacting layer to the pre-reacting layer. The actual amount of energy fed back is just the product of the heat of reaction and this fraction (i.e., $\Delta H_r \cdot F_{fb}$). Propagation will occur providing more

energy is fed back than is required for ignition of the pre-reacting disk of composition. This statement, then, gives rise to something that could be called the “propagation inequality”

$$\Delta H_r \cdot F_{fb} > E_a \quad (4)$$

Obviously, the probability of successful pyrotechnic propagation is increased by anything that results in more energy being produced by the burning composition, a greater percentage of that energy being fed back, or a reduction of the activation energy requirement. The heat of reaction and the activation energy are determined by the chemical nature of the composition; however, a thorough discussion is beyond the scope of this article.^[g] Energy is fed back to the pre-reacting layer through any combination of conduction, convection, or radiation. These are more fully described in Figure 15, where some of the factors influencing the efficiency of these mechanisms are also presented.

Figure 16 is similar to Figure 14 but provides a more complete description of the propagation process, including information on the relative temperatures expected. Zone (a) is unreacted pyrotechnic composition, which has thus far been unaffected and remains at ambient temperature. Zone (b) is described as the warm-up zone, where the temperature has started to rise above ambient, as a result of thermal conduction and possibly convection. It is in this zone where reaction rates are first beginning to increase. These reactions are sometimes referred to as “pre-ignition reactions”^{[8c][h]} and contribute relatively little thermal energy. In Zone (c), the temperature has risen significantly, at least one component of the composition has melted, and some gaseous materials may be bubbling to the surface. Because of the rise in temperature and the greatly increased contact between fuel and oxidizer, the reaction rate in Zone (c) and the production of heat is greatly increased. In Zone (d), much of the reaction is occurring in the gas phase; however, some droplets of reacting composition ejected from the surface may be present. Again the reaction rate and the thermal energy being produced has increased substantially from the previous zone, and the temperature has peaked. In the final region, Zone (e), the energy producing reactions have ceased, and as a result of heat loss to the sur-

Conduction:

- **Thermal energy (molecular vibration) is conducted along solids, from hotter to cooler.**
- **Factors maximizing conductive feedback:**
 - **Compacted composition**
 - **Metal fuels**
 - **Metal casing or core wire**

Convection:

- **Hot gases penetrate the solid composition along spaces between grains (fire paths).**
- **Factors maximizing convective feedback:**
 - **Uncompacted composition**
 - **Granulated composition**

Radiation:

- **Thermal (infrared) radiation, emitted from flame and glowing particles, is absorbed by incompletely reacted composition.**
- **Factors favoring radiative feedback:**
 - **Solid or liquid particles in flame**
 - **Dark or black composition**

Figure 15. Outline describing the mechanisms of pyrotechnic energy feed back and the factors that affect them.

roundings, the temperature begins to fall significantly.

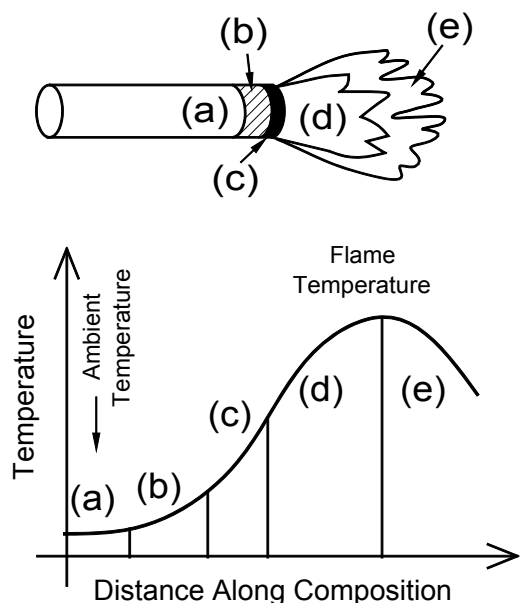


Figure 16. A more complete description of the processes of pyrotechnic propagation: *a*, unreacted composition; *b*, warm-up zone; *c*, condensed phase reactions; *d*, gas phase reactions; and *e*, reactions complete. (Reference based on 5d.)

Conclusion

The subjects of ignition and propagation could have been dealt with much more expeditiously. Specifically, it could simply have been stated that ignition requires raising at least a portion of a pyrotechnic composition to its ignition temperature, and that propagation requires the feed back of sufficient energy for continuing self-ignition of the composition. However, while this would have saved much time, it would have provided little understanding of the important principles involved. Accidents caused by unintentional ignitions continue to plague the pyrotechnics industry. In addition, ignition failures with fireworks, whether leaving an unfired-aerial shell in a mortar that needs to be cleared or resulting in a dud shell left after a fireworks display, have serious potential for accidents as well. Ignition failures with signaling smokes or flares may cause someone to not be rescued. It is through a more thorough understanding of the basis for ignition and propagation, that pyrotechnists will be better able to solve potential problems before accidents occur.

Acknowledgments

The authors gratefully acknowledge the technical and editorial assistance of J. Domanico and L. Weinman in the preparation of this article.

Notes

- [a] More recent usage of this term is “Enthalpy of Reaction”.
- [b] The use of the term “activation energy” in the context of solid-phase pyrotechnic compositions has a slightly different meaning than in aqueous or gas-phase chemistry. In aqueous and gas-phase chemistry, molecules can be thought of as reacting individually, or at least in small groups. In that case, activation energy can be thought of as the amount of energy needed for a collision between two individual molecules to cause them to react. However, a typical pyrotechnic composition is composed of solid particles of fuel and oxidizer, with each particle comprised of many billions of atoms or molecules. In this case, activation energy takes on much more of a macroscopic and less precise meaning. For the purpose of this article, activation energy of solid-phase pyrotechnic compositions is generally taken to mean that amount of thermal energy needed to induce a sustained exothermic reaction within a tiny portion of the composition.
- [c] Pyrotechnic compositions, especially those of dark color, exposed to bright sunlight may be an exception to the generalization about the highest temperature expected to be in the middle of the composition.
- [d] Note that it is assumed the composition is physically at rest (i.e., it is not being mixed, which adds energy to the system).
- [e] In some texts thermal run-away temperature is called the critical temperature^[1] or the reaction temperature.^[8a]
- [f] Wood’s metal is a eutectic alloy of bismuth, lead, tin and cadmium. It melts at 70 °C.
- [g] Some oxidizers are known for producing compositions with low activation energies (e.g., chlorates), while other oxidizers tend to produce compositions with high activa-

tion energies (e.g., oxides and sulfates). Fuels with low melting points or low decomposition temperatures (e.g., sulfur, lactose and acaroid resin) tend to form compositions with low activation energies. Metal fuels tend to produce compositions with high heats of reaction.

- [h] Pre-ignition reactions are typically reactions taking place in the solid state. While such reactions can be a source of energy, they generally only contribute in a minor way to promoting ignition. This is because solid-state reaction rates are constrained by the difficulty of fuel and oxidizer commingling while both remain solid.

References

- 1) A. G. Merzhanov and V. G. Abramov, "Thermal Explosion of Explosives and Propellants, A Review", *Propellants and Explosives*, Vol. 6, 1981, pp 130–148.
- 2) A. G. Merzhanov and V. G. Abramov, "The Present State of Thermal Ignition Theory: An Invited Review", *Combustion and Flame*, Vol. 16, 1971, pp 89–124.
- 3) *The Illustrated Dictionary of Pyrotechnics*, Journal of Pyrotechnics, 1995, p 64.
- 4) Any General Chemistry Text, e.g., B. H. Mahan, *University Chemistry*, Addison-Wesley, 1965, pp 329–334.
- 5) A. A. Shidlovskiy, *Principles of Pyrotechnics*, reprinted by American Fireworks News, 1997; [a] pp 64–65; [b] pp 61–63; [c] p 84; [d] p 96–98.
- 6) W. D. Smith, "Estimating the Distribution of Molecular Energies", *Journal of Pyrotechnics*, No. 6, 1997.
- 7) Any General Physics Text, e.g., F. W. Weston and M. W. Zemansky, *University Physics*, Addison-Wesley, 1970, p 239.
- 8) J. H. McLain, *Pyrotechnics, From the Viewpoint of Solid State Chemistry*, Franklin Institute Press; 1980; [a] p 186; [b] p 30 and 40; [c] pp 3–6.
- 9) R. N. Rogers and E. D. Morris, "On Estimating Activation Energies with a Differential Scanning Calorimeter", *Analytical Chemistry*, Vol. 38, 1966, pp 412–414.
- 10) H. Henkin and R. McGill, "Rates of Explosive Decomposition", *Industrial and Engineering Chemistry*, Vol. 44, 1952, pp 1391–1395.
- 11) D. B. Olsen, "Gas Evolution, Henkin and 1-Liter Cook-Off Tests", *Explosives Firing Site and Laboratory Safety Course Notes*, Center for Explosives Technology Research, New Mexico Tech, 1990.
- 12) J. A. Conkling, *Chemistry of Pyrotechnics*, Marcel Dekker, 1985; [a] p 97; [b] p 43 & 103; [c] p 102.
- 13) B. T. Fedorff, O. E. Sheffield, and S. M. Kaye, *Encyclopedia of Explosives and Related Terms*, Picatinny Arsenal, 1975, Vol. 7, pp 12 – 129.
- 14) T. J. Barton, N. Williams, E. L. Charsley, J. Ramsey and M.R. Ottaway, "Factors Affecting the Ignition Temperature of Pyrotechnics", *Proceedings of the 8th International Pyrotechnics Seminar*, 1982, p 100.