Pyrotechnics

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Strobes: Pyrotechnic Compositions That Show a Curious Oscillatory Combustion

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Strobes are pyrotechnic compositions which show an oscillatory combustion; a dark phase and a flash phase alternate periodically. The strobe effect has applications in various fields, most notably in the fireworks industry and in the military area. All strobe compositions mentioned in the literature were discovered by trial and error methods and the mechanisms involved remain unclear. Many oscillatory systems such as Belousov–Zhabotinsky reactions, cool flames, self-propagating high-temperature synthesis have been observed and theories developed to elucidate their unstable behavior based on chemical interactions or based on physical processes. These systems are compared to experimental observations made on strobe mixtures.

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1. Introduction

In physics, oscillating behavior is obtained by moving a system away from its equilibrium position. For instance, the pendulum moved from one side of its equilibrium position to the other until it stabilizes. In chemistry, however a system cannot deviate from its equilibrium spontaneously, as this would contradict the second law of thermodynamics. Hence, chemical oscillators must evolve far from their equilibria and never pass through them. Therefore, they are governed by the law of non-equilibrium thermodynamics.[1]

Various chemical oscillators have been discovered.[2] They are either homogeneous or heterogeneous, isothermal or non-isothermal, closed or open systems, and induce oscillations in various variables: concentrations of species (gaseous, liquid, or solid), reaction rate, temperature and/or pressure. Some oscillators have been widely studied such as the Belousov–Zhabotinsky reaction which is a liquid-phase system.[3] It exhibits regular variations in the concentration of intermediate species of the reaction. This induces a periodic change of the color of the solution. The mechanisms of this type of reaction have been widely studied in contrast with most other chemical oscillators. In particular, oscillations in non-isothermal systems remain unexplained in terms of detailed chemical mechanisms because of their complexity. Oscillating non-isothermal combustion phenomena are observed in, for instance, cool flames,[4] solid-propellant burning,[5–9] and pyrotechnics.[10–12] Contrary to the Belousov–Zhabotinsky reaction, most of these systems are heterogeneous and several variables oscillate at the same time. It adds complexity to the system and makes it harder to model because of the increased number of variables and parameters.

Strobe reactions belong to the group of heterogeneous systems. They are pyrotechnic mixtures that produce flashes of white or colored light by intermittence. Their applications are mainly in the fireworks industry (twinklers pots). They were also developed in the military field as flares.[13–17] A few theories have been proposed to explain this phenomenon[18–21] but the current knowledge of these mechanisms is only based on empirical methods and the physical and chemical processes that trigger the occurrence of flashes is still unclear.

In this Review, various chemical oscillators are summarized and their mechanisms and theories concerning them are compared to what is currently known about strobe reactions yielding hypotheses to explain their oscillatory behavior.

2. Non-Pyrotechnic Intermittent Phenomena: Isothermal Oscillators

2.1. Isothermal Oscillators

The first chemical oscillator was discovered in 1828 by Fechner. He observed repetitive bursts of effervescence (escape of gas bubbles) from iron immersed in nitric acid.[22] This is an electrochemical oscillator; the chemical reaction is accompanied by chemical charge-transfer steps at the electrode. It is the interplay of chemical and electrical variables that drive the system away from the stable stationary state. Many other electrochemical oscillators are mentioned in the literature.[23,24] A famous one is the so-called "beating mercury heart".[25] A drop of mercury is placed in a watch glass and covered with a dilute aqueous solution of a strong acid (e.g. HNO_3, H_2SO_4, HCl) containing a few crystals of $K_2Cr_2O_7$, $Na_2S_2O_8$, or $KMnO_4$. If an iron wire is brought up to touch the mercury drop from the side, the drop rhythmically changes its shape with frequencies of two or three seconds. The description of electrochemical oscillators is often complex but the mechanisms involved in those systems frequently include at least one autocatalytic variable, that is either a chemical species or an electrical quantity.[26]

Electrical oscillators are heterogeneous isothermal oscillating systems and it was initially believed that a homogeneous system cannot oscillate until Bray and later his student Liebhafsky discovered, in 1921, the first liquid-phase (homo-

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geneous) isothermal chemical oscillator, known as the Bray–Liebhafsky reaction (BL reaction).[27,28] It is an iodate-catalyzed decomposition of hydrogen peroxide into water and oxygen.[29,30] The concentration of iodine molecule oscillates and oxygen builds up in pulses. This phenomenon is due to an alternation between a free-radical process and a non-radical process that respectively consumes and creates iodine.

The Belousov–Zhabotinsky reaction (BZ reaction)[3,31,32] developed by Belousov in the 1950s and rediscovered by Zhabotinsky in 1961 is another isothermal, homogeneous, oscillating reaction. It is a solution of malonic acid, a catalyst, bromate ions, and water. The color of the solution oscillates from a light yellow to a dark blue in presence of ferroin as a result of variations in the concentration of intermediate species. Cerium was originally used as a catalyst later on ferroin was added later to the composition to intensify the color change (ferroin is blue in oxidized form). Zhabotinsky discovered that the oscillations also occurred without cerium and concluded that the ferroin could act as a catalyst instead of cerium. The mechanisms involved in that reaction are complicated and have been studied thoroughly. Field, Koros, and Noyes[33–35] formulated a model for the most important parts of the kinetic mechanism. It is known as the FKN mechanism. It consists of two processes (A and B) which compete to reduce the bromate ions; the alternation of the two processes depends on the concentration of bromate ions.

The last famous isothermal homogeneous chemical oscillator is the Briggs–Rausher reaction (BR reaction) discovered in 1972.[36,37] It is a hybrid of the BL and the BZ reaction. It combines the iodate and the hydrogen peroxide from the BL reaction and the malonic acid from the BZ reaction with manganeous salt as a catalyst and a starch indicator. The system undergoes 15 or more cycles of colorless↔yellow↔blue before ending as a purplish solution with a strong odor of iodine. Oscillations are observed in the concentration of oxygen, carbon dioxide gas, and iodine ions.

Many other similar chemical oscillators have been studied.[33,38,39] They all undergo two competing pathways. One of these pathways produces a specific intermediate, while the other pathway consumes it. The concentration of this intermediate triggers the switching of pathways. However, the detailed chemical mechanisms remain unknown.

2.2. Chemical Models

Chemical models were developed to describe these oscillation phenomena and most of them were inspired by the Lotka–Volterra model. It was developed for the analysis

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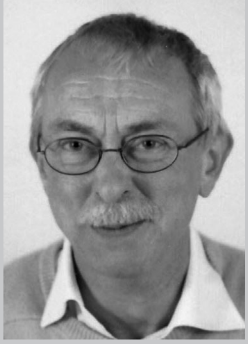

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of a predator–prey problem and is described by a non-linear system.[40,41] It is a simple scheme of an autocatalytic chemical reaction that undergoes sustained oscillations in the concentration of the autocatalytic species. However, the mechanisms present do not apply to any real chemical system. On the contrary, the Brusselator model, created 1968 by Prigogine and Lefever,[42] presented in Table 1, proposes simple mechanisms for the BZ reaction.[43] The reactants A and B are converted into products D and E by a four-step mechanism, including an autocatalytic reaction. If the concentrations of A and B are maintained constant, the concentrations of the intermediates X and Y oscillate with time. The Brusselator is the simplest model that describes the BZ reaction. Other models describe the BZ reaction with more complexities in the sub-reactions.[44] For instance, Field, Koros, and Noyes presented a five-step model based on the mechanisms observed in the BZ reaction: the Oregonator model.[45,46] This model also uses an autocatalytic step as in the Brusselator and the Lotka–Volterra models, but the BZ reaction is achieved through more than four sub-reactions.

Table 1: Brusselator model.

Reactions	Rate constant
$A \rightarrow X$	k_1
$B + X \rightarrow Y + D$	k_2
$2X + Y \rightarrow 3X$	k_3
$X \rightarrow E$	k_4

The chemical models presented above were developed for isothermal homogeneous oscillators (BL, BZ, and BR reactions). However, they are often used as basis for models that describe non-isothermal or heterogeneous chemical oscillators.

3. Intermittent Combustion: Non-Isothermal Oscillators

Non-isothermal oscillators are intermittent combustion processes. They occur either in a homogeneous medium, such as cool flames, or in a heterogeneous medium, such as solid flame combustion. The chemical oscillators mentioned in this Section present variations in the concentration of an intermediate species, as with the BZ oscillator, but also in temperature and sometimes in pressure.

3.1. Combustion in Homogeneous Media: Cool Flames

3.1.1. Description of the Phenomena

Cool flames are homogeneous chemical oscillators but unlike the BZ reaction, the temperature of the system varies and when the system is closed the pressure can also vary. It is a phenomenon that occurs during the combustion of hydrocarbons such as carbon monoxide,[47,48] acetaldehyde,[49–52] ethane,[53] propane,[54] *n*-butane,[55] di-*tert*-butyl peroxide,[56] diethyl ether,[57] polypropylene,[58] hexadecane,[59] and many others.[60] They emit a faint bluish luminescence by intermittence, caused by the excitation of formaldehyde, and occur at relatively low temperature, between 500 and 800 K. Their oxidation leads to the formation of H_2O and CO_2 through several intermediate reactions known as free-radical branching chain mechanisms which involve autocatalysis. Temperature and pressure pulses in the reacting gases are the result of a fast acceleration of the reaction rate. However, the pulses are not intense and only a small quantity of reactants is consumed. As a consequence, the acceleration stops and the reaction rate decreases spontaneously, while the concentration of the reactant is still high. Therefore, the cool flame process is able to self-accelerate and self-decelerate. This ability is considered as the main distinguishing property of cool flames as well as the occurrence of a negative temperature coefficient of the reaction rate, that is, a region where the rate of reaction decreases while the temperature still increases. The acceleration of the reaction rate of a self-ignition process (a hot flame) is limited exclusively by depletion of reactants, whereas the acceleration of the reaction rate of cool flames is limited by kinetic mechanisms with increasing temperature. Consequently, cool flames are thermokinetic phenomena. A careful balance between heat release and heat loss is necessary for their occurrence.

Cool flames are studied in both open and closed systems. In the former case (open system), the hypothesis of the continuous stirred tank reactor (CSTR) is often used. It can be defined as an ideal reactor in which reactants are continuously admitted and products withdrawn. It assumes a perfect mixing, constant density, and isothermal conditions. Because of the continuous flow, steady states are attained contrary to the situation in closed-vessel systems.[4]

3.1.2. Chemical Models

The chemistry of cool flames is complex and involves many intermediate reactions. Attempts have been made to model this homogeneous oscillatory reaction.[41] Frank-Kamenetskii proposed a kinetic Scheme based on the Lotka–Volterra scheme.[4,61,62] This three-step model involves one reactant, one product, and two intermediates species that react through autocatalytic steps. The system is capable of sustaining oscillations between the concentrations of intermediates (peroxides and aldehydes). However, this scheme applies only to an isothermal system which is unacceptable for cool flames. In addition, autocatalytic steps are often involved and they have the form $A + B \rightarrow 2B$ or $A + 2B \rightarrow 3B$ which are respectively cubic and quadratic autocatalytic reactions.[63–66] The terms "quadratic" and "cubic" are used because the reaction rate has the form $a[A][B]^n$ (where a is the reaction rate constant); for $n = 1$ the reaction is quadratic and for $n = 2$ the reaction rate is cubic. For instance, the autocatalator[67–69] model, developed in the 1980s, combines a cubic autocatalytic step, $A + B \rightarrow 2B$ where A is the reactant and B the autocatalyst, with a simple linear decay of B to the product C, $B \rightarrow C$. Those theories were first analyzed in the continuous stirred-tank reactor (CSTR). However this model can also be adapted to closed systems by adding a step (precursor decay) to the scheme.[67,70] Those theories are all independent of temperature and cannot be applied to cool flames since they are thermokinetic phenomena.

Later on, Sal'nikov described a thermokinetic model[4,71–79] in which oscillations in temperature of the reacting medium and in concentration of a critical intermediate (aldehydes) occur. The mechanisms are described in Table 2. A precursor P is converted to a product A via an active intermediate X. The model is capable of sustained oscillations in the concentration of X and temperature, with the usual following assumptions: $E_1 = 0$ (so the reaction rate is constant), $E_2 > 0$, $\Delta H_2 > \Delta H_1$. Under those conditions, the intermediate species X produced by the first step is immediately consumed by the second step and because of the exothermicity of the two reactions, the temperature increases. This accelerates the consumption of intermediate X while its production remains constant. Consequently, the second reaction decelerates, the temperature decreases and the concentration of intermediate X increases again. The analysis of this model shows that the system undertakes a bifurcation and exhibits self-sustained oscillations.[65] Oscillating solutions are obtained by the variation of some parameters (the bifurcation parameters). This model is consistent with the thermokinetic nature of cool flames but does not fit the other essential features of cool flame processes, such as autocatalysis or the negative temperature coefficient of reaction rate.

Table 2: Sal'nikov model.

Reactions	Heats of reaction	Activation energies
$P \rightarrow X$	ΔH_1	E_1
$X \rightarrow A$	ΔH_2	E_2

Later in 1969, Gray and Yang combined a chain-branching system with the thermokinetic approach of Sal'nikov and proposed a dynamic system with two variables: the autocatalytic chain carrier and the temperature.[4,47,79] The model considers the energy and the kinetic equations of a chain reaction. The scheme for initiation, branching, and termination of the chain is postulated in Table 3. The termination reaction is assumed to go through two parallel paths concurrently. Even if the complexity of the cool flame is not fully included in this theory, the Gray–Yang model remains the best approximation of the cool flame mechanism because it is based on a chain-thermal autocatalytic process.[80]

In cool flames, the oscillating behavior is based on the production and depletion of an intermediate species as in isothermal oscillators (BL, BZ, and BR oscillators). Consequently, the models used to describe those phenomena are often alike. For instance, cubic autocatalysis used to model a cool flame is also found in the Brusselator mode created for the BZ reaction (see Table 1). The difference is that the reactions involved in cool flames are exothermic leading to thermal oscillation. Autocatalysis is the main feature to explain the periodic variations in the concentration of species or the temperature in homogeneous oscillators. In heterogeneous combustion, when the heterogeneities in the compositions are small compared to the thickness of the combustion wave, a homogeneous approach can be applied to describe combustion processes. However, spatial fluctuations of the temperature and the concentration cannot be neglected for most of the systems. Physical parameters are involved in the combustion process and oscillations are either the result of chemical processes, as for homogeneous oscillators, or/and physical processes.

Table 3: The Yang and Gray model.

Reactions	Rate constants	
$A \rightarrow Y$	k_i	Initiation
$Y \rightarrow 2Y$	k_b	Branching
$Y \rightarrow$ stable products	k_{t1}	Termination
$Y \rightarrow$ stable products	k_{t2}	Termination

3.2. Combustion in Heterogeneous Media

3.2.1. Various Heterogeneous Unstable Combustion

The burning of solid propellant often results in pressure oscillations in the combustion chamber, such as in a rocket motor[6] or whistles.[81–83] They are mostly closed systems and the oscillating behavior is often the result of the confinement of the compositions,[84] the geometry of the propellant and/or the design of the combustion chamber.[85–88] In whistle devices, the confinement of the composition is responsible for the acoustic waves that induce pressure and temperature variations. These oscillations control the reaction rates resulting in a two-stage burning. Since strobe compositions are open systems, the case of oscillatory closed systems is not detailed in this Review.

Thermites and self-propagating high-temperature synthesis (SHS) are other kinds of solid combustion in open systems that present more similarities with strobe compositions. The SHS mixtures were discovered in 1967 by Merzhanov et al.[89] They are mostly binary compositions in which, when ignited, the combustion front propagates through the powdered ingredients leaving behind a metallic alloy or a high quality ceramic material. Sometimes, spatial oscillations or "banded structures" are observed in the product material as a result of periodic variations in the front flame velocity.[8,90,91] This is not a desired effect. It may affect the homogeneity and the mechanical properties of the product material. Many oscillating systems have been reported: $Ti + C$ (producing TiC), $Ti + 2B$ (TiB_2), $Ti + Al$ ($TiAl$), $Ni + Al$ ($NiAl$), $Ta + C$ (TaC), etc.[7,92–99] Thermal, kinetic (in the combustion propagation front), and spatial oscillations were observed.

Depending on variables, such as the porosity of the sample (or density), the reactant particle size, the diameter and shape of the sample, the dilution of the reactants, the initial temperature (pre-heating of the sample), the initial composition (stoichiometry),[100,101] the combustion mode can evolve from stable to unstable.[102–105] For all the binary systems, three modes of combustion are observed:

- Stable, no variation of the combustion front velocity.
- Oscillatory (1D instabilities), oscillations in combustion velocity that result in a periodic structure perpendicular to the combustion front.

- Spinning or spiral wave propagation (2D instabilities) is observed under special conditions of burning of cylindrical samples and results in the formation of one or more luminous points that move in an helical fashion through the unburned part of the sample.

Most parameters that influence the occurrence of combustion instabilities are correlated with the thermal conductivity. The first theories on SHS combustion used only physical processes to explain the self-oscillating behavior and the spinning combustion.[7,106,107] A second less-common approach was also envisaged; it uses both physical and chemical processes to explain the instabilities.[108,109] The chemical processes present many similarities with the homogeneous oscillators (BZ type reaction and cool flames), involving two competing chemical pathways or autocatalysis to explain the occurrence of oscillations.

3.2.2. *Physical Approaches*

The instabilities of the SHS combustion were first explained using a physical approach. For the oscillatory mode where the "banded" or laminated structures were observed, the hypothesis was that the combustion front moved from one layer to the next. Not only the occurrence of this spatial structure but also the thickness depended on parameters correlated to the heat transfer coefficient.[90] The assumption was made that the top layer when ignited with an external source (burner) underwent an exothermic chemical reaction. Part of the heat released is transferred to the next cold layer. Thermal, kinetic, and eventually spatial oscillations occur when the reaction time is much smaller than that of the characteristic time of heat transfer to the next layer.[7,106] The heat released by the reaction in the first layer increases the temperature in the next layer. The reaction rate, which obeys an Arrhenius law, also increases. The thermal conductivity is low, so most of the heat is dissipated and the second layer is only slowly ignited while the reaction proceeds rapidly in the first layer. When the reactants in the first layer are entirely consumed, the front propagation velocity decreases and the cycle starts again in the next layer.

Similar mechanisms are thought to be responsible for the spinning combustion but at a different scale. The appearance of small (10 to 100 μm) bright hot spots, called "scintillations", was observed. They correspond to the high temperature region on the combustion surface.[9,101,110,111] Some of these hot spots appear and dissipate; others initiate the reaction in the neighboring areas. It was also noticed that the propagation front moves forward as a consequence of their appearance. Their size is strongly dependent on the particle size and shape of the reactants. In these local scintillation zones, the reaction rate is high. The characteristic reaction time is much smaller than the time required to transfer the heat to the neighboring areas. In the case of an oscillating mode, kinetic and thermal parameters allow the complete layer to be ignited at the same time while in the case of spinning combustion, only a part of the layer is ignited and the reaction must propagate in the direction of the front combustion and also perpendicularly to it. It was suggested that the hot spots are located on the microstructural heterogeneities of the surface and linked to parameters such as the melting point of one of the reactants.[104,112] The assumption was made that hot spots form in the location of the most refractory reactant at the melting point of the other reactant. For instance, in the Ti–Si system, hot spots occur in titanium particles when the melting point of silicon has been reached. As the reactant Si melts it spreads around the solid particles of Ti enhancing the inner contact between the particles and as such affecting the heat transfer between the particles. Hence, the reactant's melting points are an indicative factor of the ignition temperature of the scintillations.

Numerical studies were developed to determine the boundary between stable and unstable combustion (bifurcation point). In all cases, nonlinear systems are used to describe the combustion modes. Most of the models developed use a quasi-homogeneous approach.[106,113–115] This approach is based on the assumption that both heat transfer and heat evolution can be described in terms of a continuous function of space coordinates and only a particular form of reaction kinetics denotes the specifics of the heterogeneous reaction. Oscillating and spinning systems were obtained by varying the heat-transfer parameter. 1D, 2D, and 3D models were studied.[104,116–119] The bifurcation parameters obtained from those models depend only on the physical properties of the system, such as heat capacity, heat of formation, activation energy and combustion temperature.[113,114,120] A melting parameter was also added to incorporate the melting effect.[115] These bifurcation parameters provide a good estimation of the propagation mode when the activation energy is relatively low.

Recent studies highlight the discrete mode of the propagation of the combustion front in SHS compositions[107,116] that gave rise to different numerical models where two assumptions were made. First, the reaction media consist of clearly distinguishable elementary cells or reaction cells and, second, the reaction time in the cell is smaller than the time of heat transfer to the neighboring reaction cells. Contrary to the quasi-homogeneous approach, the nature of the heat transfer is not a continuous function of space coordinates. As a result, the process called the "relay-race" mechanism was used: the combustion front first undertakes a rapid burning of the specific local area (resulting in scintillations) and then a relatively long ignition delay occurs during which the neighboring areas were preheated.[9] Consequently, the propagation of the combustion front is limited by heat transfer between the reaction cells while heat is released relatively quickly inside the cell. The parameter p is introduced. It depends on the ratio between the characteristic time for heat transfer and the time of reaction. When $p \approx 1$ a quasi-homogeneous approach is sufficient to describe the mechanisms. However, when $p \gg 1$, a discrete approach is necessary. A bifurcation parameter was obtained from the Equation (1)[107]

$$Ar_c = \frac{R \times (T_C - T_0)}{E} = \frac{R \times T_C}{E} - Ar_0 \qquad (1)$$

where E is the activation energy, T_0 is the initial temperature.

Ar_0 is the Arrhenius number and can be controlled by preheating the composition. Ar_c depends on the Arrhenius number and can be changed by diluting the mixture with an inert material, which should change the temperature composition T_c. For a quasi-homogeneous combustion wave a boundary factor of $Ar_c = 0.15$ was found while for discrete a combustion wave, a value of $Ar_c = 0.03$ was obtained. Contrary to the bifurcation parameters mentioned previously, this parameter applies for systems with higher activation energy.

3.2.3. *Importance of the Chemical Parameters*

Other studies emphasize the importance of the chemical factors in the occurrence of oscillating combustion.[108,109] They considered not only thermal oscillations but also variations in concentrations of intermediate species (e.g. suboxides) formed during the combustion, such as in isothermal oscillators and cool flames. As a result, the bifurcation condition depends on the concentration of these intermediate species. For instance, Mo + B and Ta + C systems have been studied.[108] After ignition by any external source, a pore structure, called the "heat-affected" zone forms. At relatively low temperature there is the formation and evaporation of B_2O_3 (for the Mo + B system) and CO_2 (oxide formed during the combustion of the Ta + C composition). As the system is heated, the next endothermic reaction occurs producing suboxides [Eq. (2)]

$$a\mathrm{X}_{(s)} + b\mathrm{XY}_{n(g)} \xrightarrow{k_p} c\mathrm{XY}_{n-1(g)} \tag{2}$$

where X is identified as B in the Mo + B system and C in the Ta + C system, XY_n corresponds to the oxide (B_2O_3 or CO_2), XY_{n-1} is the suboxide (B_2O_2 or CO) and k_p is reaction rate coefficient. *a*, *b*, and *c* are the stoichiometric coefficients that must be adapted to the system studied. For the Mo + B system, $a = 2$, $b = 2$, and $c = 3$. For the Ta + C system, $a = 1$, $b = 2$,and $c = 2$. Simultaneously, the exothermic reaction described below takes place [Eq. (3)]

$$d\mathrm{M} + e\mathrm{XY}_{n-1(s)} \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} f\mathrm{MX}_{(s)} + g\mathrm{XY}_{n(g)} \tag{3}$$

where M is the metal (Mo or Ta), MX is the product (MoB or TaC) and k_s and k_{-s} are the reaction rate coefficients. *d*, *e*, *f*, and *g* are the stoichiometric coefficients. For the Mo + B system, $d = 2$, $e = 3$, $f = 2$, and $g = 2$. For the Ta + C system, $d = 1$, $e = 2$, $f = 1$, and $g = 1$. As the temperature is increased by this reaction, the combustion wave forms and the second reaction [Eq. (3)] becomes dominant. The decay of suboxides is 5 to 7 orders of magnitude higher than their formation. As a consequence, the reaction rate of the second reaction decreases. As the temperature goes down, the combustion wave stops and a new "heat-affected" zone is created. Then, the first reaction is dominant again followed by the subsequent acceleration of the second reaction. The diffusion of the gaseous oxides extends the reaction to the unburned part of the sample. In this theory, the variation of concentrations of suboxide is responsible for the oscillation. A simple linear system is derived from the mass balance equation. Solving these equations leads to a condition of bifurcation for the occurrence of oscillations [Eq. (4)]:

$$4D \times \frac{k_{-s} - k_p}{u^2} > 0 \tag{4}$$

where D is the diffusion coefficient for gas and u is the average burning velocity. However, the auto-oscillating combustion is rather described by a non-linear coupling of kinetics and thermal factors.

The hypothesis was also made that some of the SHS system showing a "banded" structure may undergo a BZ type reaction.[109] The Brusselator scheme (see Table 1) was used to model the Ti + B and the Ni + Al combustion processes with a bifurcation condition stated as Equation (5)

$$[\mathrm{B}] > \frac{k_4}{k_2} + \frac{k_3 \times k_1^2}{k_2 \times k_4^2}[\mathrm{A}] \tag{5}$$

where [A] and [B] are respectively $Ti_{(s)}/Al_{(s)}$ and $B_{(s)}/Ni_{(s)}$. The coupling of this model with a quasi-homogeneous model of combustion[121] allows for more accurate modeling of the thermal and spatial oscillations observed experimentally. This model also involves oscillations in the concentration of intermediate species by the use of the Brusselator model. This confirms that not only physical processes, but also kinetic mechanisms must be taken into account in heterogeneous oscillating reactions. Chemical models used for homogeneous oscillators provide a good start to model the chemical steps involved in heterogeneous combustion.

Based on the data in previous Sections, several oscillating systems were identified. They were either isothermal or non-isothermal, homogeneous or heterogeneous, and they showed oscillations in intermediate species, temperature, and/or reaction rate. Several hypotheses have been emphasized. For homogeneous oscillators (BL, BZ, BR reactions and cool flames), the oscillations in intermediate species and temperature (only for cool flames) were explained by a chemical approach: two pathways compete to create and consume intermediate species. Autocatalysis was often involved to model these types of reaction. On the other hand, the oscillating behavior observed in SHS compositions (mostly on the front propagation rate and temperature) was explained using a physical approach. Indeed, the assumption that the reaction time is much larger than the characteristic time of heat transfer was sufficient to model the observed oscillating behavior. However, the possibility of creation and depletion of intermediate species that compete was also envisaged for this kind of reaction. With this knowledge in hand, strobes will now be analyzed. They are pyrotechnic compositions that produce flashes of light by intermittence. They belong to the class of solid, heterogeneous combustion processes, such as SHS mixtures. However, the chemical and physical processes responsible for the oscillations are not well understood. After a review of the current knowledge of strobe reactions, they are compared to the oscillating systems described previously (BZ reaction, cool flames, and SHS combustion).

4. Strobe Reactions

4.1. Historical Review

The discovery of flickering compositions was probably a coincidence related to the increased use of magnalium (magnesium–aluminum alloy) instead of aluminum in pyrotechnic mixes and propellants. The first reference to strobe compositions appears in 1898 in an old mixing book of the firm Brock's Fireworks Ltd[122] under the heading "Orion Flashing Guns" (see Table 4). The composition burned periodically producing white flashes of light. In 1969, Russian patents[123–125] were published describing pyrotechnic compositions which produced a colored-light emission at regular intervals (at a frequency around 2–3 Hz). The compositions mainly consisted of magnalium, used as the fuel, and barium nitrate or strontium nitrate, used as the oxidizer, as in the Orion formulae. Other examples of strobe compositions are mentioned in the literature[10,11,126–128] or in patents.[13–17] Their compositions are mostly the result of trial and error and not based on understanding the strobing mechanisms.

Table 4: Orion formula.

"Orion flashing guns" (1898)	1 [% by weight]	2
Sulfur	51	55
Fine magnesium powder	17	18
Fine aluminum pyroflake	6	
Barium nitrate	26	27

The first studies aimed at understanding strobe reactions were carried out by Krone[13,18] and Wasmann[19,129] during the 1970s. Krone experimented with compositions that consisted of:

- A fuel: magnalium (50:50) was used in all compositions in an amount of 20 % (by weight) and with several mesh sizes.
- An oxidizer: nitrates of the alkali-earth metals and some perchlorates are used in an amount of 65–75 % (by weight).
- Other compounds were added to the composition to improve or control the strobing behavior. Krone noted that the variation of 0.5 % of the composition resulted in a change of the burning behavior: the strobing effect may even disappear.

The main observation of Krone was the occurrence of a zone he called "semi-slag" before a flash. This foam, partly solid and partly molten, contained only a trace of magnesium. Moreover, he noticed that the addition of a compound that releases a large amount of gas, such as oxamide, guanidine nitrate, or ammonium sulfate, provided a better flash separation and an improved sharpness. Thus, Krone hypothesized that most of the magnesium was oxidized during the dark phase while the oxidation of aluminum was slow. After the magnesium was entirely consumed, the oxidation of the aluminum located in the "semi-slag" zone suddenly increased as a result of the higher surface area available and the action of gases, such as NO_2 and NO. This reaction was fast and accompanied by a light emission. He also noticed the poor strobe effect of compositions containing potassium nitrate and sodium nitrate, whereas barium nitrate and strontium nitrate provided a better strobing behavior. According to Krone, the lower melting point of potassium and sodium nitrates causes the composition to melt down more easily. This generates extra flashes on the molten slag covering the surface of the composition causing uncontrolled burning and explosions with many flying sparks. Finally, Krone studied factors that help stabilizing the frequency of a strobe and he had the idea to use a catalyst to control the frequency of the flashes. He added a small amount of copper chrome oxide (0.03 % to 0.1 %) to the composition. Later, Cardwell[127] listed products that are used as catalysts in strobe reactions (oxides of iron, cupric oxide, antimony trisulfide, some transition-metal salts). Shimizu[20] also noticed the advantages of using potassium dichromate to enhance the regularity and sharpness of flashes. The conclusion of Krone's study is that strobe mechanisms are based on competing chemical reactions with opposite reaction pathways (slow oxidation of magnesium and fast oxidation of aluminum) as observed in the BZ oscillator and cool flames.

Wasmann experimented with strobe compositions containing organic materials. He studied a system of copolymers of unsaturated monomers containing nitrate groups with conventional unsaturated monomers (such as pentaerythritoldinitrate diacrylate with methacrylic acid methylester) to which metal perchlorates soluble in the monomers used are added as oxidizer (such as strontium perchlorate tetrahydrate).[19,129] He observed the formation of a microporous residual mixture that Krone identified as the "semi-slag". The heat accumulates in this mixture until the ignition point is reached followed by a fast burning responsible for the flash. Because of the low conductivity of the composition only a small part of the heat is transferred to the rest of the composition so the reaction decelerates and a new microporous residual mixture is formed on the surface. Contrary to Krone, Wasmann explained the pulsating burning based on physical parameters that are like mechanisms occurring in SHS combustion. His hypothesis was that the oscillations are controlled by the heat flow from the burning surface into the interior of the system. However, he also mentioned the possibility of competing reactions responsible for the oscillating behavior: "*a smolder reaction of the nitrate group containing monomers and a fast reaction which is initiated by the physical process of heat accumulation in the microporous zone*".

Both Krone and Wasmann[13,18,19,129] studied binary strobe compositions with an oxidizer, a fuel, and compounds added in small amounts to improve the strobe behavior (sharpness and regularity of flashes). Contrary to Krone theories, Wasmann described mechanisms that are based on both competing reactions and physical processes. The innovation brought by Shimizu was to consider strobe compositions as two couples of oxidizers and fuels: one for a dark reaction and another for a flash reaction. This is the current hypothesis to explain strobes mechanisms. After testing many strobe compositions,[20] Shimizu argued that two reactions occur: a dark (or smolder) reaction and a flash (or light) reaction that alternate periodically. The trigger factor for the occurrence of a flash is the temperature.

The mechanisms are schematically depicted in Figure 1. First the composition is ignited on the surface and the dark reaction starts. The temperature in the dark zone is not uniform and hot spots appear on the surface and they magnify as the temperature increases (as the heat accumulates).[130] Those hot spots are located in the molten part of the surface.[131] After a while, the maximum temperature of the dark zone reaches the ignition temperature of the flash composition and the flash reaction starts. A small layer of dark zone remains on the burning surface because its temperature was too low to be raised to the ignition temperature. This zone starts the next dark reaction leading up to the next flash reaction. In this manner the dark and the flash reactions alternate. Through those observations, Shimizu claimed a few necessary conditions for the production of the strobe light effect:[20]

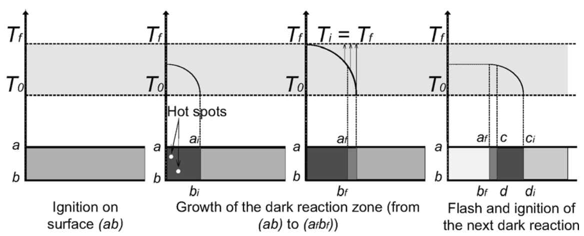

Figure 1. Scheme illustrating the Shimizu hypothesis on strobe mechanisms, adapted from Ref. [20] The evolution of the temperature is shown as a function of time, T_0 is the temperature at the beginning of the dark reaction. The composition is ignited on the surface (ab). When T_i the temperature in the layer (aba_ib_i) reaches the ignition temperature of the flash reaction T_f, the layer (aba_fb_f) is consumed by the flash. Then the temperature drops and a thin layer (a_fb_fcd) remains the surface (cd) initiating the next dark reaction.

- The dark composition must produce a smoldering temperature which is lower than the ignition temperature of the flash composition.
- The dark reaction produces a minimal amount of visible light.
- The dark composition must give rise to heat accumulation during the reaction to ignite the flash composition. The faster the heat accumulates, the higher the frequency of the light flashes.
- A catalyst may help the accumulation of heat.
- The dark zone must be uniform, because heterogeneities disturb the heat accumulation and prevent ignition of the flash composition.

This theory implies that strobe compositions contain two mixtures: one that gives rise to the dark reaction (the dark composition) and the other that gives rise to the flash reaction (the flash composition). Moreover, Shimizu studied mainly compositions containing a metal as fuel (magnesium or magnalium mostly). Nowadays various strobe compositions mentioned in the literature do not satisfy this criterion and the discovery of new strobe mixtures is still the result of a trial and error method.[132–134] For instance, a few binary compositions containing a perchlorate and hexamine are known to burn in an oscillatory manner.[132,134] Hexamine is an organic material and reminiscent of the experiments performed by Wasmann.[19,129] In these mixtures, hexamine is supposed to act as fuel.

Early studies on strobe compositions (Wasmann and Krone) already revealed similarities with SHS combustion such as the layer-by-layer burning, that are further confirmed by experiments (see Section 4.2). A critical balance between heat generated and heat transferred has even been envisaged to explain the strobe behavior. On the other hand, Shimizu highlighted the possibility of competing chemical pathways, such as in BZ reactions or cool flames, being responsible for the oscillations. Thermokinetic models of the strobe behavior that are described in Section 4.3 use the cubic and quadratic autocatalysis model as the Brusselator scheme and the Sal'nikov scheme, originally created for cool flames, to model the periodic variations in temperature and also in concentration of species.

4.2. Physical Mechanisms

Based on the strobe compositions mentioned in the literature, eleven mixtures were tested (see Table 5) and their combustions were recorded with a high-speed camera (Redlake digital imaging system; 5000 frames per second; 160 × 160 pixels; details on the experimental conditions for assembling the strobes and recording the strobe behavior can be found in reference [135]).

A general observation from the experiments is that some compositions give rise to a good strobe effect (regular and intense flashes, separated by clear time intervals) while others do not give a typical strobe behavior (irregular flashes). The analysis of the high-speed camera movies helps to observe and analyze the differences and it reveals important parameters for the strobe effect. Figure 2 shows a selection of images of the combustion of Composition C (Table 5) recorded with the high speed camera. The pictures reveal the formation of a porous layer on top of the pellet. This confirms the observations made by Wasmann, Krone, and Shimizu who called this the "microporous residual mixture", the "semi-slag", and the "semi-reacted zone" respectively.[18–20] The layers of the compositions that produce a good strobe effect (Compositions C, I, and J in Table 5) propagate on the surface of the pellet, become thicker and red while the other compositions (A, G, H ,and K) produced foams on their surface from where gaseous species may escape (see Figure 3 a). The layers formed are not uniform in color and in shape. As Krone already observed, those compositions contain an oxidizer that has a lower melting point than the other compounds (nitrates or sodium sulfate, calcium sulfate, potassium perchlorate).[18] The top layer is heated up by an exothermic reaction that Shimizu called the dark reaction.[20] This layer is consumed during the flash by what Shimizu identified as the flash reaction and the next layer is ignited on the top of the pellet. The pellet is consumed

Table 5: Selection of classical strobe mixtures mentioned in the literature and tested.[18,20,127,134,136]

Composition	A	B	C	D	E	F	G	H	I	J	K
Ammonium perchlorate	×	×	×	×	×	×	×	×		×	×
Sulfur									×		
Magnalium		×	×	×					×	×	×
Magnesium	×				×	×	×	×			
Barium sulfate			×								
Potassium perchlorate		×							×		×
Strontium sulfate					×					×	
Calcium sulfate						×					
Sodium sulfate								×			
Sodium nitrate							×				
Guanidine nitrate				×							
Strontium carbonate										×	
Sodium oxalate											×
Potassium dichromate		×	×		×	×	×	×		×	
Parlon										×	
Boric acid									×		
Dextrin									×		
Strobe effect[a]	+-	++	++	++	++	+-	–	–	–	++	–

[a] The signs ++, +- and – mean that the strobe effect is respectively good, intermediate and bad. The strobe effect was evaluated regarding the regularity, sharpness of flashes.

linearly, layer-by-layer which is the first similarity established with SHS combustion.

The second similarity is the presence of hot spots on the surface combustion, also called scintillations for SHS compositions.[9] With most strobe compositions tested, points of light were observed on the surface layer (see Figure 2 at $t = 3.94$ ms). They occur and grow during the dark phase. According to Shimizu,[130] the hot spots are a result of the accumulation of the heat released by a reaction. Some of them are called "flash sites" because they evolve into flashes (see Figure 2: $t = 6.88$ and 6.93 ms). Grose et al.[131] suggested that hot spots occur in the molten part of the dark layer blowing off those zones by a small flash. Consequently, the flashes are ignited from the melting part of the layer. Haarmann also reported on strobe mixtures containing metal sulfates, such as Compositions C, E, F, H, and J and claimed that flashes occur each time the sulfate reaches its melting point or decomposition temperature.[137] Recently, a study on strobes with metal sulfate based compositions emphasized the importance of the melting point of the sulfates.[135] The use of high melting point sulfates, such as in Compositions C, E, and J, improves the strobe effects (sharpness and regularity of flashes) and also decrease the frequency of flashes. This was ascribed to the formation of more solid layers on top of the compositions. The number of similarities with SHS combustion is increased. In SHS reactions, hot spots are supposed to occur in the melting

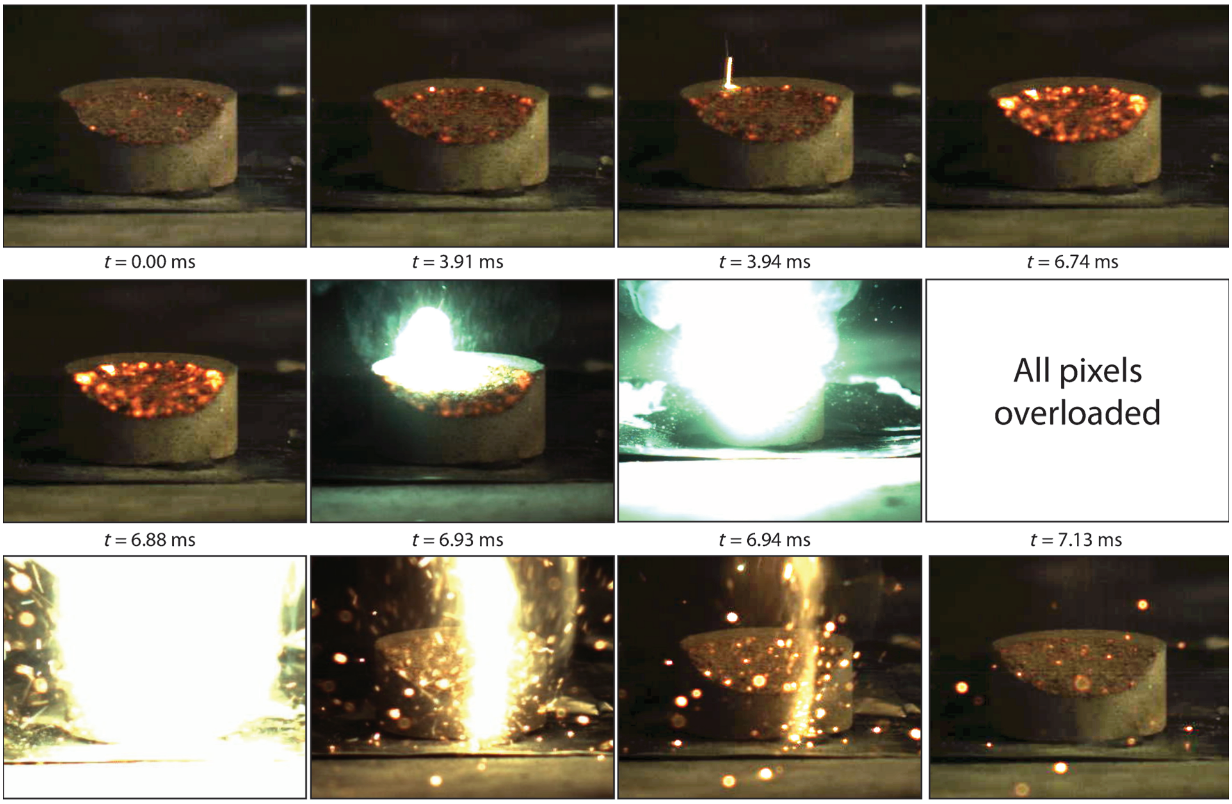

Figure 2. Time resolved images of the burning of a strobe pellet (Composition C in Table 5) before, during and after a flash.

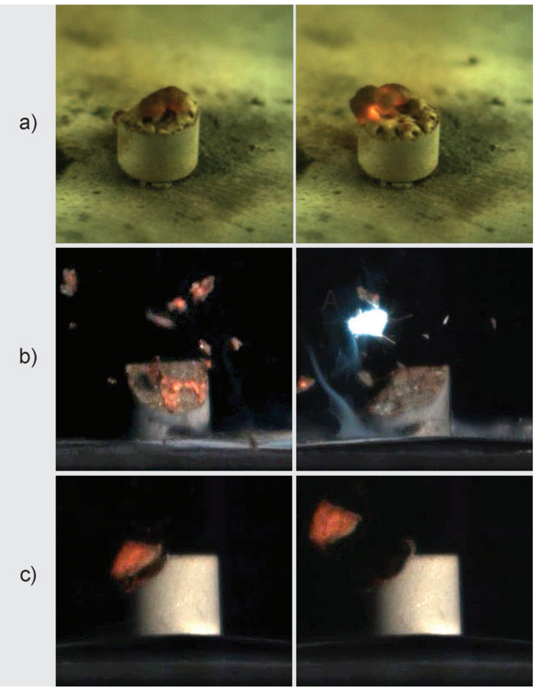

Figure 3. a) Images of the combustion of Composition H recorded with the high-speed camera. Formation of a foam on the surface combustion. b),c) Examples of flying particles and flash sites observed during the strobe reaction of Composition C (b) and Composition E (c).

area of the surface combustion at the melting point of the most refractory material.[104,112] This confirms the hypothesis that mechanisms in strobe compositions and SHS are similar and theories such as the "relay-race" mechanism may be applied to strobes. The reaction cell is then identified as an entire layer.

Another phenomenon was observed for strobe compositions: the occurrence of flying particles on partly solid layers as show in Figures 3 b and c (Compositions C, E, F, I, and J) and the formation of bubbles on molten layers (Compositions A, G, H, and K). This observation reveals the presence of gaseous species that form under the surface during the dark phase. When the layer melts the gas escapes through the foam forming bubbles and when the surface remains partly solid pressure builds under the layer. Sometimes the gas escapes breaking the layer and ejecting parts of it or the entire layer. When too much gas escapes though, flashes are irregular and less sharp. It suggests that those gaseous species are necessary for the occurrence of oscillations. They may be identified as the intermediate species present in the BZ reactions[3] or in cool flames.[4] In both cases, two pathways compete to create and consume the intermediate species resulting in oscillations in their concentrations.

4.3. Theoretical Approaches

Based on their experimental observations, two thermokinetic models were developed by Davies[21] and by Feng et al.[138] Both models adapt a scheme that was created to model homogeneous oscillators (BZ type reactions and cool flames). They are based on a binary composition of magnesium and ammonium perchlorate. They both hypothesize that competing oxidation reactions occur between the three phases of magnesium (solid, liquid, and gaseous) with gas formed from the decomposition of ammonium perchlorate. The first one is a three-step model based on standard autocatalytic models. The model, described in Table 6, is studied with $n=2$ and $m=3$ which corresponds to cubic autocatalysis initially used to model cool flames.[64] The two first steps of the model reflect the evaporation of magnesium and its partial oxidation; this corresponds to the dark phase. The last step of the model is the rapid oxidation of gaseous magnesium which is the flash phase. The mass conservation equation applied to this system gives rise to a non-linear system of two equations. Steady-state solutions and oscillatory behavior were achieved using non-linear analysis methods. The control parameter used was related to diffusion between $Mg_{(g)}$ and O_2. No temperature dependence is included in the model through the Arrhenius law and a pool chemical approximation has been used for $Mg_{(s,l)}$ (The concentration of this compound is supposed to be constant). Both observations are not consistent with the strobe reaction, but this model emphasizes the possible autocatalytic nature of the strobe reaction.

Table 6: Chemical model developed by Feng et al.[138]

Chemical model	Simplified model[a]
$Mg_{(s,l)} + O_2 \rightarrow 2\,MgO + Mg_{(g)}$	$A + B \rightarrow C$
$m\,Mg_{(g)} + Mg_{(s,l)} + O_2 \rightarrow n\,Mg_{(g)} + 2\,MgO$	$A + m\,B \rightarrow n\,B$
$Mg_{(g)} + (^1/_2)O_2 \rightarrow MgO$	$B \rightarrow C$

[a] $A=O_2$, $B=Mg_{(g)}$, $C=Mg_{(s;l)}$, $D=MgO$.

The second model proposed by Davies[21] takes into account the temperature dependence of the strobe reaction by using the Sal'nikov model originally created for cool flames.[72] This thermokinetic model is described as Equation (6)

$$P \xrightarrow{k_1} X \xrightarrow{k_2} B + Q_2 \qquad (6)$$

where P corresponds to $Mg_{(s,L)}$, X is $Mg_{(g)}$ and B is MgO and Q_2 is the heat released by the second reaction.

A set of compounds (solid and liquid magnesium) react first in a slow reaction, identified as the dark reaction. It produces intermediate species (gaseous magnesium) and then those species react in a fast and exothermic reaction, identified as the flash reaction. The mass conservation equation is applied to this model and a non-linear system of two equations is obtained with the two variables mentioned: the temperature of the mixture and the concentration of the intermediate species. Four parameters are used: the ambient temperature, the initial concentration of reactants, the ratio of activation energies, and the heat transfer coefficient.

The last parameter (the heat transfer coefficient) is a control parameter; steady-state or oscillatory behavior are obtained by varying this parameter. Figure 4 left, shows the

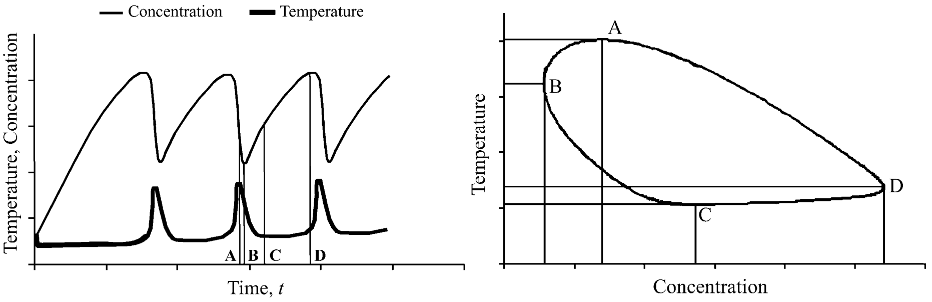

Figure 4. Left: Evolution of the temperature and the concentration of intermediate species with time during a strobe reaction. Right: Correlation between the temperature and the concentration of intermediate species (reproduced from Ref. [21]).

evolution of the temperature and the concentration of intermediate species with time while Figure 4 right, shows the correlation between the two variables. Points A, B, C, and D are characteristic states of the system during one cycle. The flash occurs only if the heat generated is sufficient and if the concentration of flash species has reached a critical level to start the flash reaction. This situation implies that the dark and the flash reactions cannot be studied separately since the first one gives rise to the second one. This last model, developed by Davies, uses a combination of both physical and chemical parameters which is more likely to explain the strobe mechanisms. Consequently, not only thermal oscillations are involved in strobe reactions but also periodic variations in the concentration of gaseous intermediate species. The coupling of both physical and chemical processes enabled the prediction of thermal, spatial, and kinetic oscillations observed in SHS combustion[108,109] that reinforces this theory to describe the strobe behavior.

5. Summary and Outlook

Various oscillating systems were reviewed and some of their features and similarities are emphasized and used to build a hypothesis for strobe mechanisms. The first important mechanism is the autocatalysis associated with competing pathways that have been observed in the Belousov–Zhabotinsky type reaction and cool flames. This phenomenon has been applied to model strobe reactions but no experiments have been undertaken to confirm this hypothesis. In our experiments, the formation of gaseous species under the surface layer has been noticed. When they escaped too quickly because of an irregular and molten layer, the strobe effect is less efficient. Chemical reactions occur underneath the surface layer and may be necessary for the production of sharp flashes. It may be that intermediate species are produced in a first pathway (dark phase) and consumed with a second pathway (flash phase). The identification and the measurement of the concentration of those species is required to validate this hypothesis and to know if autocatalysis is involved in this process.

The second important feature is the phenomenon of heat transfer from the reacting zone to the unburned composition. Many similarities have been noticed between the SHS combustion and strobe mechanisms and confirmed by the experiments: the layer-by-layer burning, the occurrence of hot spots on the molten areas of the surface layer. In SHS combustion, a change of behavior was observed when a parameter related to the thermal conductivity was modified. The mechanism proposed to explain this phenomenon is called the "relay-race" mechanism and is based on the hypothesis that the characteristic reaction time is much smaller that the characteristic time of heat transfer to neighboring areas. This results in successive accelerations and decelerations of the propagation front.

The experiments and analysis presented above give more insight into strobe reactions. The thermal conductivity of the composition and the nature of the exothermic reaction (fast/slow) are clearly involved in the oscillatory behavior, but may not be the only parameter responsible for the alternation between dark and flash phases. The gaseous species detected underneath the surface layer imply possible chemical mechanisms, such as autocatalysis, that are also necessary to produce the oscillatory behavior. Moreover, the strobe compositions currently in existence use compounds such as metal sulfates, nitrates, perchlorates, and additives such as dichromates, that are not environmentally safe. The development of environmentally friendly strobe compositions, in particular the replacement of potassium dichromate, is a potential area to explore.

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