

# CHAPTER 2

## COMBUSTION AND EXPLOSION FUNDAMENTALS

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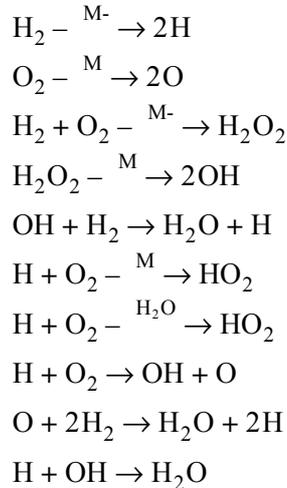
### Some Underlying Theory

This chapter presents a simplified view of the development of a combustion wave. It provides the basis for a qualitative understanding of the effects of changing the properties of the combustible material or the characteristics of the ignition source. The inclusion of the term “explosion” in the title is deliberate to emphasize that “combustion” and “explosion” are simply two faces of the same phenomenon. The term “explosion” is used in this book to denote any uncontrolled and undesired combustion. Our definition of the term includes unconfined phenomena, which others prefer to call flash fires or deflagrations and high-speed detonations. Although some authors associate some degree of confinement of combustion to make an explosion, this distinction is not, in the context of this book, essential.

An explosion is not a unique phenomenon. It is only a self-propagating combustion wave that is not kept under control. There is no fundamental difference between an industrial fire or explosion that destroys property and combustion in a domestic gas stove, except that the former is not kept under control. This basic similarity is well understood by anyone who has first turned on the gas in the oven and then had difficulty lighting the match.

A theoretical treatment of ignition phenomena and combustion theory is beyond both the scope of this book and the author's ability. However, a detailed treatment of chemical kinetics and thermodynamics is unnecessary for profitable consideration of the relationship of electrical apparatus to ignition of flammable gases, vapors, and dusts. (This chapter will focus on gases and vapors. Dusts will be discussed in Chapter 13.) It is possible to view the ignition process in an approximate phenomenological manner and gain useful understanding of it. The material that follows treats the ignition process in a highly oversimplified manner, using simple concepts and models that the author and engineers of his acquaintance have found useful. The material is presented as an aid to visualization of the ignition process. For a consistent, theoretically grounded treatment of ignition and combustion phenomena the reader is referred to the writings of specialists such as Lewis and von Elbe and Khitrin.

Combustion is not at all simple. The reaction that we simplistically summarize as:  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ , with a release of 115.6 kilocalories of energy, is in reality a collection of simultaneous and consecutive reactions, each with characteristic thermochemical, thermodynamic, and kinetic properties. M indicates the presence of a solid body, such as the wall of the vessel.  $\text{H}_2\text{O}$  indicates the presence of water.

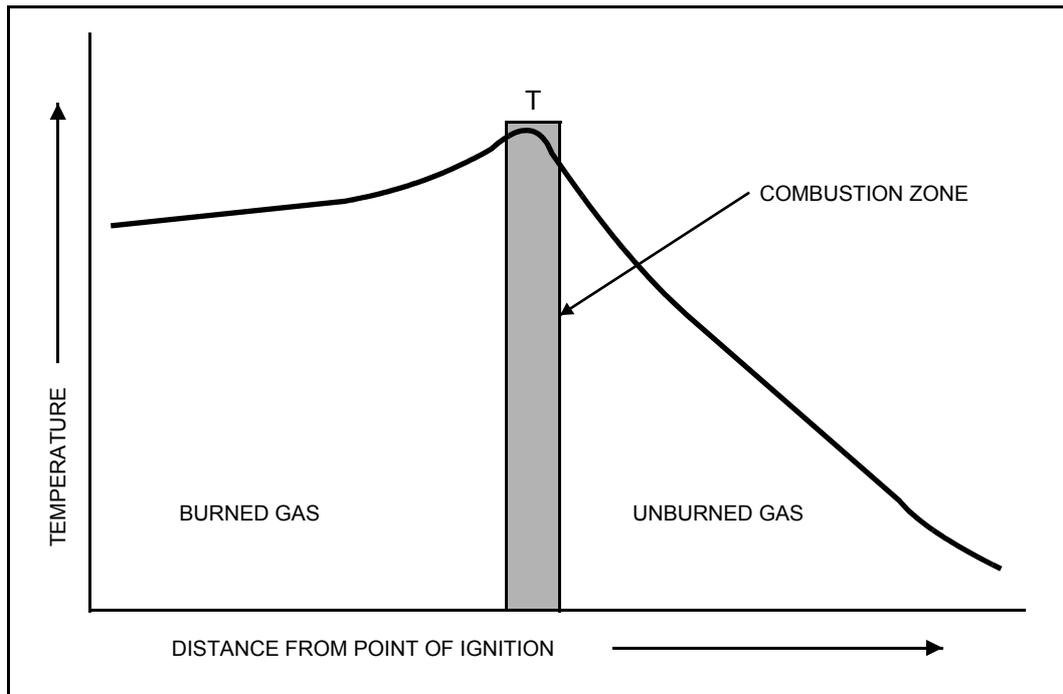


Some of the reactions are exothermic. Some are endothermic. The several species are present in vastly differing concentrations. Some can be involved in catalytic effects at the walls of the containing vessel.

The combustion of hydrocarbons is even more complex. In addition to the species noted above there are C/C, C/H, C/O and even C/N fragments in all conceivable configurations and combinations. Most of the species are in very low, transient concentrations.

A summary overall reaction can give a first approximation of flame temperature and the explosion's potential, particularly when combustion takes place in air. The heat capacity of the nitrogen in air opposes the attainment of extremely high flame temperatures. Were the nitrogen not present the calculation of flame temperature, taking into account the many reactions which occur, is extremely tedious and error prone.

In most cases energy must be provided to produce significant quantities of species formed by endothermic reactions. These species then initiate exothermic reactions, releasing energy for the formation of more endothermic species. The integration of all these reactions results in a high temperature within the flame zone and for some distance behind it. This is illustrated in Figure 2-1.



**Figure 2-1** Temperature Profile in Flame

The time during which the initiating energy is supplied is critical. If the energy is not supplied fast enough, or if there isn't enough energy supplied, concentration of endothermically generated species may be too low, and these will react exothermally too slowly to provide the required energy feedback to cause a self-sustaining reaction. All this verbiage can be summarized by referring to the classical Arrhenius equation:

$$\frac{dx}{dt} = Ae^{-E/RT}(b-x)(c-x)\dots$$

where

$x$  = concentration of product species

$t$  = time

$A$  = a constant dependent on the frequency of occurrence of the species

$E$  = activation energy

$R$  = the gas constant

$T$  = absolute temperature

$b, c, \dots$  = initial concentration of reacting species

With known values of  $A$  and  $E$ , this equation can be used to calculate the rate of the component reactions, or, if desired, the rate of the overall reaction. In this latter case the constants are close to those of the slowest reaction, the rate-controlling reaction.

Even though we will not use the Arrhenius function for quantitative purposes, it is useful to look at the function from a qualitative standpoint. Increasing temperature increases the speed of a reaction. Except for concentration of reactants, we have no control over the other factors in the equation. Concentration is expressed in absolute terms, moles/liter, not in percent. The effects of diluents and pressure, as well as initial temperature, on the rate equation can be assessed.

The autoignition temperature (AIT), also called the spontaneous ignition temperature (SIT) is a value determined by a standard method such as that in ASTM E659-79 or IEC Publication 79-4. In the IEC method, liquid or gas is injected into a 200 ml Erlenmeyer flask that has been heated to a predetermined temperature. Great pains are taken in the design of the apparatus to ensure that the entire flask is at the same temperature. When a sample is injected, a timer is started. The timer is allowed to run until a flame is observed or until 5 minutes has passed. The test is repeated with different sample volumes and different flask temperatures until no ignition occurs. Finally, the test is repeated five times at the lowest temperature at which ignition was observed, rounded down to the nearest lower Celsius degree. If no ignition is observed that value of temperature is reported as the ignition temperature. The time lag before ignition is recorded, along with the barometric pressure. The entire process takes place in a darkened room. The IEC standard states that duplicate tests by the same operator are suspect if they differ by more than 2%; differences between laboratories should not exceed 5%. The ASTM method is similar and is stated to have similar reproducibility. The method differs from the IEC method in that (1) the flask is a 500-ml spherical-body laboratory flask, (2) the maximum waiting time for ignition delay is 10 minutes, and (3) a new flask is to be used when testing a new material. The IEC standard specifies a chemically clean flask.

Because wall effects on the combustion process are reduced in larger volume apparatus and because the allowable ignition delay is 10 minutes instead of 5 minutes, the ASTM method should lead to somewhat lower values of AIT than the IEC method. However, for the purposes of safety standards and practices, the differences are not important. The ASTM method referenced here replaces an older standard method which, except for a 250-ml flask volume, parallels the IEC method. Much of the AIT data in the U.S. literature is based on the earlier method of measurement.

To electrical engineers and instrument engineers a reproducibility of 5% among laboratories may seem to be a rough measurement indeed, but few

measurements of combustion parameters are as reproducible—another reason that neat, clean correlation functions between parameters continue to elude the hopeful.

Consideration of the Arrhenius equation helps us understand that the ignition lag is observed to be longer at lower temperatures. The exothermic reaction rate is temperature-dependent. We can also see why some materials will ignite spontaneously at temperatures below the accepted AIT. All it takes is the proper combination of accelerative endothermic reactions and poor heat transfer to the outside, as in the case of the oily rag, which doesn't know that it has only 5 minutes to burst into flame.

Much more importantly, understanding the significance of the rate equation helps us realize that the autoignition temperature has no direct quantitative correlation with the sensitivity of a compound to ignition by electrical arcs, friction, static electricity, optical sources, or even by hot surfaces. The value of the autoignition temperature is also known to be susceptible to significant variation if the flask is made of a different material or if coupons of some metals are inserted into the flask, presumably because some of the reactions are subject to catalytic wall effects.

Steady-state flame propagation, then, involves the generation of heat, and its effective use to promote further reaction. In the combustion zone, on the order of 0.1 mm thick, heat is generated by the chemical reactions. Both the temperatures in this zone and the concentration of reactive species are higher than would be predicted by steady-state theory, probably because the equilibria are temporarily unstable. Ahead of the combustion zone, heat is conducted and radiated into the unburned gases, raising its temperature to a value that depends on the flame temperature, the duration of exposure, the distance from the flame front, and its heat capacity. Exposure duration and distance regulate the propagation rate. The steady state is not necessarily constant velocity unless the front is planar and of unchanging geometry. Neither does the flame front always adjust its velocity to maintain a continuous steady state from ignition by a source to completion of the combustion process. In the initial stages, the flame may expand too rapidly and outrun its ability to pass sufficient energy to the unburned gases to ignite them.

## Ignition By a Point Source

Assume that a point source of energy imparts an amount,  $W_e$ , Joules of energy to a combustible mixture, raising the local temperature at the site of energy injection until a small kernel of the combustible mixture ignites. After ignition, the burning material adds energy to the kernel of gas. At the same time thermal conduction and radiation transfer heat to the surrounding unburned gas. The gas layer immediately surrounding the

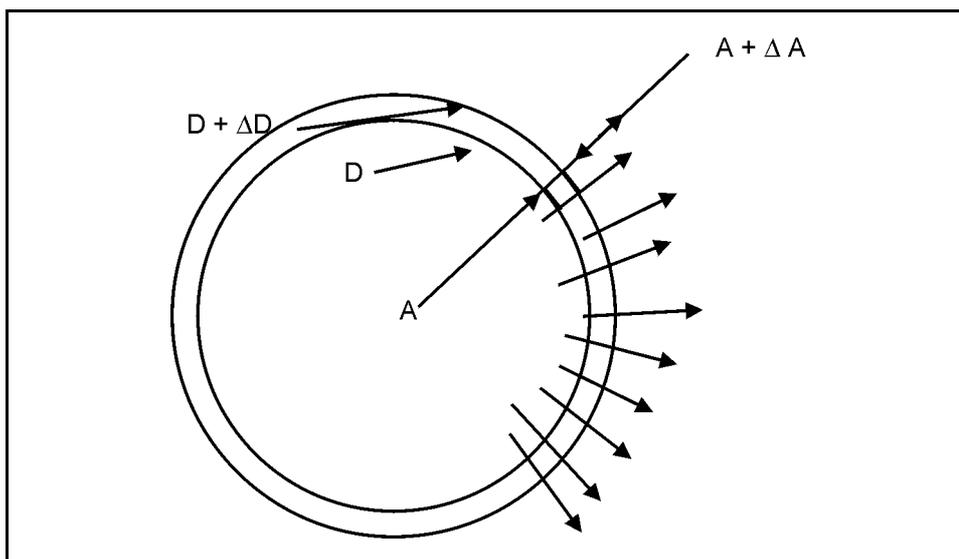
initially ignited kernel in turn reaches ignition temperature; the ignition of this new layer of gas and thermal expansion of the previously burned gas cause the kernel to grow in size. In the ideal case, it will grow spherically. The combustion wave can be considered to act very much like the skin of a bubble. In this case, the bubble starts with almost zero initial volume and grows spherically. The combustion wave progresses into the unburned gas, leaving behind burned gas at a higher temperature.

Experimental evidence shows that there is a critical ignition energy,  $W_c$ , that must be injected into any particular flammable mixture to cause the incipient flame sphere to grow indefinitely. Experimental evidence also shows that this amount of energy is related to a critical flame sphere diameter,  $D_q$ . If the energy  $W_e$  supplied initially is less than the critical ignition energy  $W_c$  the combustion wave will die out before it reaches the critical flame diameter,  $D_q$ . If the energy  $W_e$  imparted to the mixture is equal to or greater than the critical energy  $W_c$ , the combustion wave will continue to grow. It will reach the critical flame sphere diameter,  $D_q$ , and the flame will continue to propagate—in conventional terms, there is an explosion.

The interrelationship between the critical ignition energy and the critical flame sphere diameter can be viewed in the following manner. This is an oversimplification of the conclusions drawn by Lewis and von Elbe in their detailed theoretical treatment of the ignition process.

In a steady-state plane combustion wave (or in a spherical wave whose diameter is large compared to the width of the reaction zone) the amount of energy per unit volume of wavefront,  $W_A$ , added in the reaction zone by combustion is just sufficient to raise the adjacent unburned gas to ignition temperature and supply losses to the burned gases behind the combustion zone. In a small-diameter spherical wave, however, the energy in the reaction zone must be greater than it is in a plane wave or the spherical wave will not propagate. This can be seen as follows (refer also to Figure 2-2).

Assume that the energy density in the reaction zone of a kernel of diameter  $D$  is  $W_A$ , the critical energy density required for propagation of a plane wave. When energy is transferred to an adjacent zone of diameter,  $D + \Delta D$ , the energy density will be less because the volume of the reaction zone is larger. This energy density is less than the critical density,  $W_A$ , so that the flame dies out. If the incipient wave is to live through the highly divergent early stages of growth, the energy density must be greater than that required for plane-wave propagation from inception until the critical diameter is reached. The excess energy must be supplied by the ignition source.



**Figure 2-2** Divergence in Expanding Flame

Another view of this same phenomenon, which the author finds aids understanding when coupled with the previous one, has been stated by Litchfield. His view is that, if the expanding flame sphere is considered to be an expanding bubble, the ignition energy must be of the same order as the mechanical energy,  $pV$ , required to cause the expanding sphere to reach the critical diameter,  $D_g$ .  $p$  is the pressure within the bubble, nearly atmospheric, and  $V$  is the volume of the bubble. In support of this thesis he presents the data which have been summarized in Table 2-1.

Components of Flammable Mixture	Quenching Distance (mm)	$pV$ (mJ)	Measured Ignition Energy (mJ)
Acetylene-oxygen	0.18	0.0003	0.0002–0.0004
Acetylene-air	0.64	0.014	0.017–0.018
Hydrogen-oxygen	0.25	0.0008	0.0012–0.0014
Hydrogen-air	0.64	0.014	0.017–0.018
Ethylene-oxygen	0.23	0.0006	0.0009–0.001
Ethylene-air	1.22	0.095	0.07–0.08
Methane-oxygen	0.30	0.0014	0.0027
Methane-air	2.03	0.44	0.3
Nitric oxide-hydrogen	6.35	13.47	8.7
Methane-nitric oxide	6.35	13.47	8.7

**Table 2-1** Comparison of Mechanical and Ignition Energies

Lewis, in his contribution to ISA Monograph 111, noted that Litchfield's data include several cases in which the measured ignition energy is less than the mechanical energy calculated at the critical diameter. He stated that this is consistent with an equation he presented that predicts that mixtures with a high flame temperature reaction could have ignition energies lower than predicted from consideration of mechanical energy alone. The equation he presented is as follows:

$$W_e = \frac{(pV - n_b R T_f) C_p}{R}$$

where

- $C_p$  = mean molar heat capacity of burned and unburned reactants (an assumption that they are the same)
- $R$  = gas constant
- $pV$  = mechanical energy to reach critical bubble diameter
- $n_b$  = moles of burned gas in the critical bubble
- $T_f$  = flame temperature

Lewis did not present the derivation of this equation. The author believes that the equation can be justified by the following argument:

$$\frac{pV}{R} = nT$$

where

- $n$  = the number of moles of burned and unburned gas in the critical sphere volume
- $T$  = the average temperature in the sphere

Because combustion has taken place during the time it takes the sphere to grow to the critical diameter, a quantity of heat,  $n_b C_p (T_f - T)$ , should be subtracted from the mechanical energy  $pV$ . This amount of heat is the heat contributed by the  $n_b$  moles of burned gas cooling from the flame temperature,  $T_f$ , to the average temperature of the gas in the critical sphere,  $T$ . Because  $T_f$  is much higher than  $T$ , the term  $n_b C_p T$  can be neglected.

This equation's significance is more apparent if the parentheses are removed:

$$\begin{aligned} W_e &= \frac{C_p pV}{R} - n_b C_p T_f \\ &= n C_p T - n_b C_p T \end{aligned}$$

The first term is the total heat used to raise a volume,  $V$ , of burned and unburned gas to the average temperature within the critical sphere. The second term is the heat contributed by the combustion process. Lewis states that generally the ratio  $C_p/R$  is about 3 to 4 so that the ignition energy would be greater than the mechanical energy,  $pV$ . However, if the flame temperature is high, as it is in reactions involving nitric oxide or undiluted oxygen, the second term may be of significant size, and the ignition energy may be lower than the mechanical energy,  $pV$ . Lewis noted that the equation he presented is not of value for computation; it is useful only for helping understanding of the ignition phenomenon, because the value to be assigned to  $n_b$  is difficult to assess.

If one examines Litchfield's data with Lewis' comments in mind the pattern of calculated ignition energies and measured ignition energies is anything but clear. If there is a lesson, it is that the process is incredibly complex and simple answers to combustion questions seem ever to be elusive.

The critical diameter,  $D_q$ , can be inferred from several kinds of measurements. The diameter of the smallest tube through which flame will propagate (or the largest through which it will not propagate) provides an estimate of  $D_q$ . The tube length is many times the diameter. Similar estimates of  $D_q$  can be determined by measuring the distance between flanges or plates that form a narrow channel through which flame tries to propagate. A third method, described in Chapter 9, measures the distance between the flanges on electrodes between which a spark passes. The distance at which there is a large increase in the amount of spark energy required to cause ignition is taken to be the critical diameter.

The critical diameter is frequently called by the name of the experimental measurement. It is sometimes called quenching diameter and, more frequently, quenching distance. In all three measurements a surface—either the tube, the plates, or the flanges—extracts heat from the combustion wave. This quenches it before it can reach self-sustaining dimension.

Figure 2-3 is a plot of data taken from Lewis and von Elbe, and similar data from Calcote. It demonstrates the definite correlation in a particular experimental arrangement between ignition energy and quenching diameter.