

Chapter 4: Autoignition

Objectives

The objectives of this Chapter are:

- To discuss the nature and applications of autoignition phenomena.
- To introduce a one-step chemical model and the concept of conserved scalar.
- To predict the autoignition time of a uniform mixture without heat losses.
- To qualitatively discuss autoignition with heat losses.
- To explore the theory to explain certain combustion practices.

Introduction

Assume we have a vessel with very thick metal walls kept at a temperature of T_0 under vacuum (Fig 4-1a). From a small passage through the wall, reactants are admitted in the vessel. The mixture quickly reaches a constant pressure P and a temperature T_0 . If we monitor the evolution of the system, the resulting temperature in the vessel will be of the shape shown in Fig 4-1b. After a period of time, called the *ignition delay time*, the temperature will rise abruptly, the fuel will be burnt, and then the temperature will drop again due to heat losses to the walls. This is an example of an *autoignition* (or *self-ignition* or *spontaneous ignition*) phenomenon.

Autoignition is very important for safety issues and may occur when large amounts of combustibles, e.g. coal and oily rags are stored. It is also the controlling phenomenon in diesel engines: fuel is injected in high-temperature, high-pressure air close to TDC and combustion begins spontaneously after the ignition delay time. In spark-ignition engines, as the flame propagates across the cylinder, the accompanying pressure rise heats-up the unburnt mixture, which may then spontaneously ignite. This is the so-called “knock” and is unwelcome. In many other combustion applications (e.g. in gas turbines), autoignition may happen upstream of the place designed for the flame to sit, which almost certainly causes structural damage. Hence, it is important to be able to predict the ignition time of a mixture, given a description of the chemistry, the initial temperature and pressure, and other flow-specific parameters, e.g. heat losses. This is the topic of this Chapter.

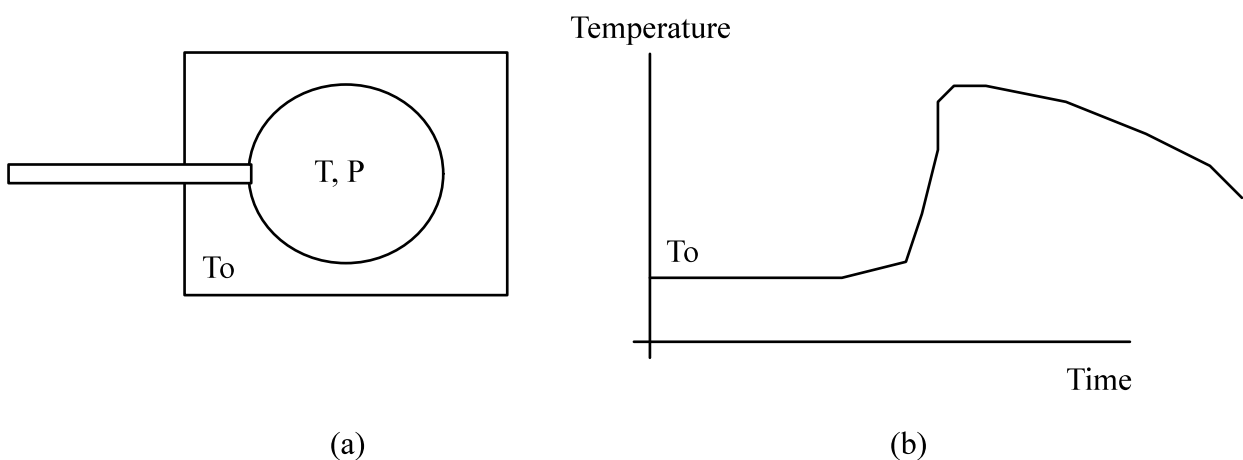


Figure 4-1. Schematic for an autoignition process. Such “bombs” are actually used in combustion experiments to measure the “autoignition temperature”.

A simple thermochemical model

Conserved scalars

Consider a mixture of fuel and air at a pressure P and temperature T . Assume that the chemistry is described by the one-step global reaction, $\text{Fuel} + \nu \text{Air} \Rightarrow \text{Products}$, and that the overall stoichiometry is such that 1 kmol of fuel needs ν kmol of air. In terms of mass, 1 kg of fuel needs S kg of air, where $S = \nu MW_{\text{air}}/MW_{\text{fuel}}$. Assume that the reaction rate can be described by the one-step global mechanism

$$\frac{d[F]}{dt} = -A \exp\left(-E/R^0T\right) [F][Ox] \Leftrightarrow$$

$$\dot{w}_{fu} = -A \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho^2 Y_{fu} Y_{ox} \exp(-E/R^0T) \quad (\text{in kg/m}^3/\text{s}) \quad (4.1)$$

Consider now the fuel conservation equation (1.30) and the temperature equation (1.31) at constant pressure and c_p :

$$\rho \frac{\partial Y_{fu}}{\partial t} + \rho U \frac{\partial Y_{fu}}{\partial x} = \frac{\partial}{\partial x} \left(\rho D \frac{\partial Y_{fu}}{\partial x} \right) + \dot{w}_{fu} \quad (4.2)$$

$$\rho c_p \frac{\partial T}{\partial t} + \rho c_p U \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) - Q \dot{w}_{fu} \quad (4.3)$$

If we multiply Eq. (4.2) by Q and add to Eq. (4.3), we obtain

$$\rho \frac{\partial (QY_{fu} + c_p T)}{\partial t} + \rho U \frac{\partial (QY_{fu} + c_p T)}{\partial x} = \frac{\partial}{\partial x} \left(\rho D \frac{\partial (QY_{fu} + c_p T)}{\partial x} \right) \quad (4.4)$$

We have also assumed that $Le=1$, i.e. $\lambda/c_p = \rho D$. The compound scalar $Z = QY_{fu} + c_p T$ is a *conserved scalar*, i.e. it does not have a source term in its governing equation. The solution to Eq. (4.4) is a unique function of the initial and boundary conditions, and not of the degree of reaction. For a homogeneous system, Eq. (4.4) says that the quantity Z is a constant and hence the same in the reactants and the products. In other words, that the fuel consumption and the temperature rise are not independent (as expected!). Then, by denoting with the subscript 0 the state corresponding to unreacted mixture,

$$QY_{fu} + c_p T = QY_{fu,0} + c_p T_0 \Leftrightarrow Y_{fu} = Y_{fu,0} - c_p (T - T_0)/Q \quad (4.5)$$

Similarly,

$$Y_{ox} = Y_{ox,0} - S c_p (T - T_0)/Q \quad (4.6)$$

Quantities like $QY_{fu} + c_p T$ are very useful in reducing our analytical burden to have to carry all species and temperature equations. If the system is adiabatic, the temperature rise is always related to how much fuel has reacted. The result in Eq. (4.5) is valid also for constant-volume combustion, but c_v replaces c_p . We will use Eqs. (4.5) and (4.6) very often in the future.

The maximum temperature

In the context of our model, Eq. (4.5) shows that the maximum temperature (i.e. the adiabatic flame temperature) is given by

$$T_f = Y_{fu,0} Q / c_p + T_0 . \quad (4.7)$$

which of course is the same as Eq. (1.20).

The reaction rate

If we use Eqs. (4.5) and (4.6) in (4.1), we obtain that $-\dot{w}_{fu} = C f(T)$, where $f(T)$ is a function of **temperature only**, qualitatively shown in Fig. 4-2. At low T , the reaction rate is very low (but not zero!), and rises exponentially. At the maximum possible achievable temperature (i.e. the adiabatic flame temperature), the reaction rate must drop to zero, as there are no reactants left. Hence there must be a peak at some intermediate temperature. Due to the exponential dependence on T , the peak occurs very close to the maximum temperature. **The shape of this curve should be memorized because it explains many combustion phenomena.**

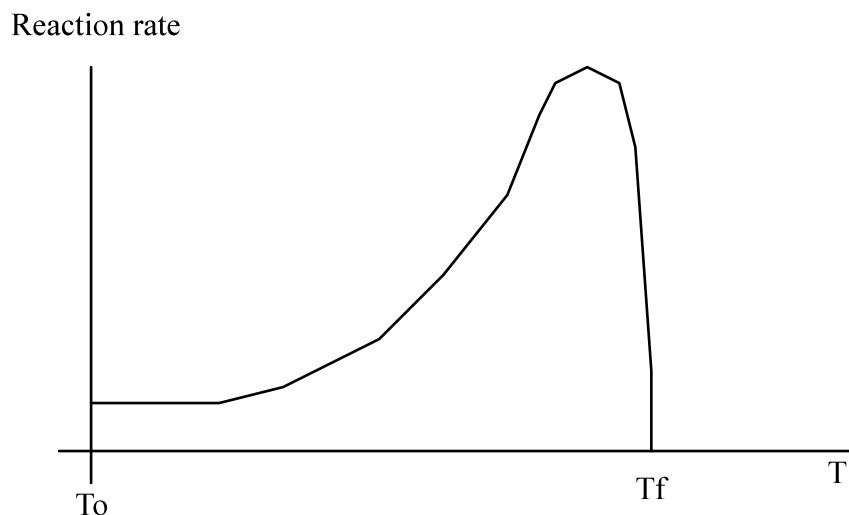


Figure 4-2. Dependence of the reaction rate on the temperature for an adiabatic system obeying Eqs. (4.1), (4.5) and (4.6). T_0 is the initial temperature and T_f the adiabatic flame temperature.

Autoignition without heat losses

Physical description

Consider a constant-pressure adiabatic closed vessel filled with a homogeneous stagnant mixture. Initially, the mixture has $Y_{fu,0}$, $Y_{ox,0}$, and T_0 . The temperature is low and hence the reaction rate is slow. As time evolves, the reaction releases heat, the temperature rises, the reaction rate increases, the rate of temperature increase is even higher, and eventually fully-fledged combustion breaks out. This self-acceleration is the characteristic feature of autoignition. The term “*thermal runaway*” is also used to describe it. The temperature cannot rise forever, though, as the reactants

will eventually be consumed and the rate will drop to zero. The theory below applies until the first occurrence of combustion and is used to quantify the ignition delay time.

Formulation

For our constant-pressure adiabatic homogeneous stagnant mixture, there is no convection and diffusion. Hence our governing equation for energy becomes:

$$\rho c_p \frac{\partial T}{\partial t} = Q \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho^2 A Y_{fu} Y_{ox} \exp(-E/R^0 T)$$

$$\Leftrightarrow \frac{\partial T}{\partial t} = \frac{Q}{c_p} \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho A Y_{fu} Y_{ox} \exp(-E/R^0 T) \quad (4.8)$$

The mass fraction of fuel and oxygen can be related to the temperature from Eq. (4.5) and (4.6). Hence the r.h.s. is a function of temperature only. Equation (4.8) describes the temperature evolution with time and can be solved by numerical methods because it is not easy to solve it analytically.

A very good analytical approximation until ignition can be obtained if we assume that throughout the ignition process, the consumption of reactants is small, and hence (4.8) becomes

$$\frac{\partial T}{\partial t} = \frac{Q}{c_p} \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho_0 A Y_{fu,0} Y_{ox,0} \exp(-E/R^0 T) \quad (4.9)$$

i.e. the reaction rate is evaluated at the local temperature, but at the initial reactant concentrations and density. We will check the validity of this assumption later. Equation (4.9) can be written as

$$\frac{\partial T}{\partial t} = B \exp(-E/R^0 T) \quad (4.10)$$

with

$$B = \frac{Q}{c_p} \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho_0 A Y_{fu,0} Y_{ox,0} \quad (4.11)$$

To make (4.10) even simpler, we perform a “trick”, typical of ignition problems: we linearise the reaction rate term assuming a small temperature increment over the initial temperature T_0 . Writing $T = T_0 + \Delta T$,

$$\exp\left(-\frac{E}{R^0 T}\right) = \exp\left[-\frac{E}{R^0 T_0 (1 + \Delta T / T_0)}\right] = \exp\left[-\frac{E}{R^0 T_0} (1 - \Delta T / T_0 + \dots)\right]$$

$$\Leftrightarrow \exp\left(-\frac{E}{R^0 T}\right) \approx \exp\left(-\frac{E}{R^0 T_0}\right) \exp\left[\frac{E(T - T_0)}{R^0 T_0^2}\right] \quad (4.12)$$

Equation (4.10) then becomes:

$$\frac{\partial T}{\partial t} = B \exp\left(-\frac{E}{R^0 T_0}\right) \exp\left[\frac{E(T - T_0)}{R^0 T_0^2}\right] \quad (4.13)$$

which can be integrated subject to $T=T_0$ at $t=0$. The solution is

$$t = \frac{1}{B} \frac{R^0 T_0^2}{E} \exp\left(\frac{E}{R^0 T_0}\right) \left(1 - \exp\left[-\frac{E(T - T_0)}{R^0 T_0^2}\right]\right) \quad (4.14)$$

The **ignition delay time** can be defined in a number of ways, e.g. as the time when the temperature crosses a given threshold. Equation (4.14) also allows a more objective definition: **τ_{ign} is the time when the temperature becomes infinite.** Then, using Eq. (4.11) we obtain as our autoignition time:

$$\tau_{ign} = \left(\frac{Q}{c_p} \frac{MW_{fu}}{MW_{fu} MW_{ox}} \rho_0 A Y_{fu,0} Y_{ox,0} \right)^{-1} \frac{R^0 T_0^2}{E} \exp\left(\frac{E}{R^0 T_0}\right) \quad (4.15)$$

This is the final and most important result of the present analysis. It contains all the trends we are interested in.

The ignition delay time

1. Initial temperature

As temperature increases, the ignition time decreases very fast. Differentiating Eq. (4.15) with respect to T_0 , we obtain that

$$d\tau_{ign}/dT_0 = \tau_{ign} / T_0 (2 - E/R^0 T_0)$$

For a typical hydrocarbon with activation temperature $T_{act}=E/R^0=20000$ K and around a typical diesel engine temperature of 800 K, the ignition delay time decreases to about 35% of its value for a temperature rise of 47K. This shows the great sensitivity of the ignition delay time to the initial temperature. The exponential term in Eq. (4.15) dominates the other terms.

2. Pressure

The pressure appears through the density ρ_0 in Eq. (4.15). Hence, the ignition delay time is inversely proportional to pressure. This dependence is substantiated by experiment.

3. Fuel and oxygen mass fractions

As Eq. (4.15) shows, the higher the mass fractions of reactants, the shorter the ignition delay time.

Limitations of the analysis

The major assumptions are that we have neglected reactant consumption and that the temperature does not rise much before ignition occurs. Let us check the validity of these assumptions. From Eq. (4.14), we can say that, for example, at $t=0.95\tau_{ign}$, $-E(T-T_0)/R^0 T_0^2 = \ln(0.05)$. Therefore $T-T_0=2.99 T_0^2/T_{act}$. For typical values of $T_{act}=20000$ K and $T_0=800$ K, at 95% of the ignition time the temperature rise is about 100K. If the overall temperature rise possible by combustion is of the order of 2000K, then we see that indeed ignition occurs with very small fuel consumption.

We have assumed one-step global chemistry, but this reproduces adequately the trends found in experiments with temperature and pressure. Indeed, experiments such as that shown in Fig. 4-1a and the present theory are used to find the global chemistry parameters (Ex. 4-1). However, real autoignition chemistry is more complex (see “Internet-based learning”).

Autoignition with heat losses

The problem

Now we consider a situation that introduces a very important feature of combustion: *the balance between heat generation and heat loss*. Consider the vessel shown in Fig. 4-1a. **There is no bulk fluid motion**, but there are heat losses to the walls. This implies that Eqs. (4.5) and (4.6), which relate the temperature to the fuel mass fraction, are not valid any longer, but Eqs. (4.1) and (4.3) are valid. If we integrate over the volume V of the vessel we obtain our energy equation:

$$\frac{\partial T}{\partial t} = \frac{1}{\rho c_v} Q \dot{w}_{fu} - \frac{A_V}{V \rho c_v} h(T - T_0) = G - L \quad (4.16)$$

where the second term on the r.h.s. (L) represents the heat losses to the wall (kept at T_0) through the area A_V . **h is the heat transfer coefficient (not to be confused with enthalpy)**. The first term in the r.h.s. (G) is the rate of heat release due to chemical reaction. It varies with temperature in a non-linear way as shown in Fig. 4-2. The second term (L) increases linearly with T . The balance of these two terms (heat generation and heat loss) will determine the behaviour of the system, as discussed below.

A graphical solution

Figure 4-3 shows various possibilities for Eq. (4.16). For high heat losses (Curve L1), point A is a stable solution: heat generation and heat loss balance and hence $dT/dt=0$, $T=T_A$, and thermal runaway does not occur. Hence the vessel keeps reacting at a very low rate and heat is lost as soon as it is generated. Point B is not realizable (unstable): any small deviation away from this point will move the system away, either back towards A or towards ignition (for $T>T_B$, generation is higher than heat loss, and hence ignition becomes possible). For very low heat losses (Curve L3), generation is always larger than the loss, and hence ignition will always occur. Curve L2 shows the critical condition where the heat loss curve is tangent to the heat generation curve. This marks a “point of no return”: if the heat loss is less than L2, ignition will always occur. For a given fuel, pressure, and vessel (i.e. A_V/V and h), if T_0 increases, Curve G1 shifts upwards to Curve G2 and hence ignition will again become possible. We see that **the nature of the behaviour of the system changes: with high heat losses, autoignition is precluded, while low heat losses allow autoignition to happen.**



Important physics

The switch between behaviours of the system (e.g. ignition vs. no ignition) is typical also of other combustion problems, for example extinction of flames and spark-ignition in engines (Chapters 5 and 6). In general, successful combustion is possible only if the heat loss is not excessive. This concept is extremely important in qualitative understanding of combustion. All combustion technologies, one way or another, are built around an exploitation of the balance between heat generation and heat loss.

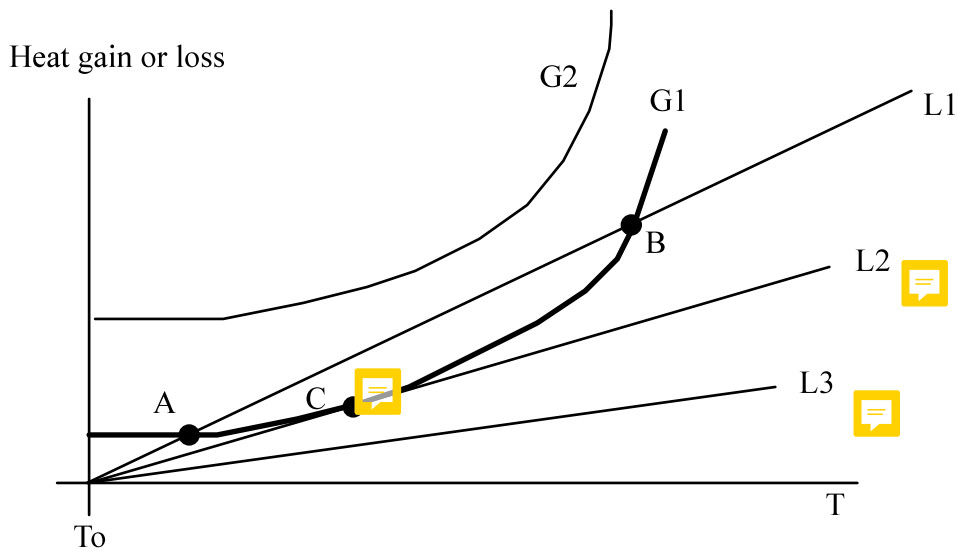


Figure 4-3. The heat generation and heat loss in a uniform mixture as a function of temperature.

The autoignition temperature

Analysing point C in Fig 4-3 allows a definition of the *autoignition temperature* $T_{ign}=T_C$. The autoignition temperature characterizes the propensity of substances to ignite spontaneously. If the autoignition temperature is high, ignition is difficult. The analysis below due to Semenov relates T_{ign} to T_0 , and hence allows T_{ign} to be quantified for a given fuel.

At point C, $G=L$, and hence

$$\frac{\partial T}{\partial t} = 0 \Leftrightarrow 0 = \frac{1}{\rho c_v} Q \dot{w}_{fu} - \frac{A_V}{V \rho c_v} h(T - T_0) \Leftrightarrow \gamma B \exp(-E/R^0 T) = \frac{A_V}{V \rho c_v} h(T - T_0) \quad (4.17)$$

The slopes of the curves are also equal:

$$\frac{\partial G}{\partial T} = \frac{\partial L}{\partial T} \Leftrightarrow \gamma B \frac{E}{R^0 T^2} \exp(-E/R^0 T) = \frac{A_V}{V \rho c_v} h \quad (4.18)$$

Therefore

$$(R^0 T^2)/E = T - T_0 \Leftrightarrow T^2 - (E/R^0)T + (E/R^0)T_0 = 0 \quad (4.19)$$

Hence at point C, the temperature is a function of E/R^0 and T_0 only. This implies that by performing an experiment like in Fig. 4-1a and measuring the T_0 below which no ignition occurs, we get a measure of the autoignition temperature. This then can be used to characterize the fuel (Example 4-2). In general, long-chain hydrocarbons have low autoignition temperatures, while methane (a very strong molecule) has the highest T_{ign} of all alkanes.

Relevance to practical situations

Safety

Following the previous analysis, it is easy to see that it is safer to store a given amount of combustible in many small piles, rather than a single large one. It is also clear that we should not

allow heat to build up. Autoignition has been named as the culprit for some coal mine, landfill, and forest fires.

Internal combustion engines



In diesel engines, the autoignition time is controlled not only by the choice of fuel, but by the pressure and temperature of the air at the time of fuel injection. Diesel engines have a high compression ratio so that the air temperature is high and hence the ignition delay time is short. In gasoline engines, on the other hand, autoignition must be avoided and hence the compression ratio is lower.

Ramjets

In ramjets, combustion is caused by spontaneous ignition of fuel injected into high-pressure and high-temperature air. The autoignition time should be short enough that combustion occurs inside the limited length of the combustor. Autoignition is the phenomenon that will determine the success of future high Mach number supersonic aviation.

Gas turbines

In some new gas turbines designs, the fuel and air are well-mixed before reaching the combustor and hence the danger of autoignition rises. This implies that designers must be in a position to quantify ignition time. Other industrial gas turbine engines rely on autoignition of extra fuel into the exhaust from the first turbine stage to boost the power output from a second turbine stage (Ex. Paper 1, Q 8).

Summary of main points

- Autoignition is a phenomenon of interest to internal combustion engines, to gas turbines, to safety. It describes the spontaneous beginning of vigorous combustion following a period of weak, but “self-feeding”, reaction.
- For an adiabatic system, fuel consumption and temperature rise are related and this gives rise to the concept of conserved scalar (Eqs. 4.5, 4.6).
- The reaction rate peaks at a temperature close to the adiabatic flame temperature (Fig. 4-2).
- The temperature rise before ignition is small due to the high activation energy of most fuels.
- For a homogeneous adiabatic mixture, the ignition delay time can be calculated analytically (Eq. 4.14) after linearising the exponential in the reaction rate (Eq. 4.11), a standard trick in ignition problems.
- The ignition delay time decreases very fast with increasing temperature.
- For a homogeneous non-adiabatic mixture, autoignition will not occur if the heat losses are excessive (Fig. 4-3). A change in behaviour (combustion possible vs. combustion impossible) occurs often in combustion and depends on the balance between heat generation and heat loss.

Suggested reading

Glassman: Ch. 7 (pp. 330-335)

Kuo: Ch. 10 (pp. 734-742)

Spalding: Ch. 15.

Worked examples

Example 4-1. An experiment gives the following values of ignition delay times vs. initial temperature:

T_0 (K)	1200	1250	1300	1350	1400
τ_{ign} (ms)	5.7	3.3	1.9	1.15	0.682

Calculate the activation energy for a one-step chemical model for this fuel.

Taking logarithms in Eq. (4.15), we obtain $\ln(\tau_{ign}) = C_1 + C_2 \ln T_0 + \frac{E}{R^0 T_0}$. Hence a curve of $\ln(\tau_{ign})$ vs. $1/T_0$ is approximately a straight line, with slope equal to E/R^0 . Plotting the data, we get that E/R^0 is about 18000 K. Hence $E=150$ MJ/kmol.

Notes:

- There is a small deviation from linearity due to the $\ln(T_0)$ term, but this is small. With enough data, the activation temperature can be found accurately.
- This procedure is done very often in combustion, in order to measure chemical parameters for various fuels.
- Get a feeling for the ignition time delay sensitivity to temperature: between 1200 and 1400 K, the ignition delay time is reduced by almost a factor of 10.

Example 4-2. By employing Eq. (4.12) in Semenov's analysis, estimate $T_{ign} - T_0$.

We re-visit Eqs. (4.17) and (4.18), but we now use (4.12):

$$\frac{\partial T}{\partial t} = 0 \Leftrightarrow \gamma B \exp\left(-\frac{E}{R^0 T_0}\right) \exp\left[\frac{E(T_{ign} - T_0)}{R^0 T_0^2}\right] = \frac{A_V}{V} h(T_{ign} - T_0)$$

$$\frac{\partial G}{\partial T} = \frac{\partial L}{\partial T} \Leftrightarrow E / R^0 T_0^2 \gamma B \exp\left(-\frac{E}{R^0 T_0}\right) \exp\left[\frac{E(T_{ign} - T_0)}{R^0 T_0^2}\right] = \frac{A_V}{V} h$$

Hence, $R^0 T_0^2 / E = T_{ign} - T_0 \Leftrightarrow T_{ign} = T_0 + R^0 T_0^2 / E$.

Therefore the autoignition temperature is higher than the initial temperature by an amount $R^0 T_0^2 / E$. For example, a typical hydrocarbon fuel has $E/R^0=20000$ K. For $T_0=500$ K, we obtain $T_{ign}= 512.5$ K.

Notes:

- The region of stable, weak combustion at low temperatures with heat losses (e.g. to the left of point C in Fig. 4-3) can only happen over a very limited temperature “window” from T_0 to $T_{ign} = T_0 (1+R^0 T_0/E)$. Such combustion is sometimes called “cool flame” and is indeed observed in diesel engines before the main heat release.

Internet-based learning

Go to http://diesel.me.berkeley.edu/~gri_mech/cal22/

In this site, a famous research group from the University of Berkeley has posted a Java applet that solves the species and temperature equation for a closed vessel filled with natural gas and air (i.e. Eqs. 4.2 and 4.3 for uniform mixtures). The user controls the composition of the reactants to a very large degree of detail and supplies the initial pressure or volume and temperature. The output is the temperature (e.g. Fig. 4-1b) and species mole fractions time traces. The applet does not use simple one-step chemistry, but a full detailed mechanism for hydrocarbon combustion, as discussed in Chapter 2. The exercises below should take 20-30 mins. As with our other Internet-based activities, this material is not examinable.

In the left of the page, click on “Reactor”. Then select “Batch reactor”, constant P , adiabatic, and click “Set”. Enter 1200 K in “Initial Temperature”, 10 bar in “Pressure”, and 5000 μs in “Time” (i.e 5 ms). Click “Set”. Now, set how much natural gas you want in the fuel-air mixture: click on “Natural gas” and enter the percentage, e.g. 10%. Now, specify the composition of the natural gas. UK natural gas can be taken as 88% CH_4 , 7% C_2H_6 , and the rest as N_2 . For each of these species, select the corresponding species from the drop-down menu, enter the %, and click “Assign”. When you’ve finished, click “Set”. Now, assign 79% N_2 and 21% O_2 for the “Air”. Your mixture and problem specification should now be complete.

Click “Start Calculation”. Examine the output and look for autoignition (i.e. the sharp temperature rise). You should locate ignition around 2.2ms for the above input values. Visualize the nature of combustion (e.g. fuel disappearance, products appearance, temperature rise etc) by using the “Graphical Output” feature of the applet. Were we right to assume little temperature increment before ignition in our theory in this Chapter?

Experiment with different initial temperatures, pressures, compositions. Convince yourselves that the trends predicted with our simple one-step theory are reproduced by the detailed chemistry calculation in this applet.

Relation to equilibrium (another 15 mins):

Examine the final species list (i.e. at the bottom of the page of the output data): these are not the products of complete combustion, but of full equilibrium (the system started at low T , autoignited, and then reached equilibrium – a steady state). Experiment with 100% methane and set the initial percentage in air at 9.5%, which corresponds to $\phi=1$. Set 10bar. The final temperature should be 2750K, for an initial temperature of 1200K. Compare with a separate equilibrium calculation from the Wiley applet, described in Chapter 3, by choosing methane, the same pressure, $\phi=1$, and supplying the 2750K. There are small differences because the real system has more species than the system based on a limited number of equilibrium constants (from Wiley), but we see that the equilibrium constant approach is very accurate.