APPM 4650: Spontaneous Explosions

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Abstract

In this project we explore some of the properties of non-adiabatic chemical reactions. We specifically examine the reaction between a fuel and an oxidizer in system that is not perfectly insulated. In such a system there is heat lost to the surroundings. Further, due to the high activation energy of the reaction, heat builds up within the system over a very long period of time. Eventually, if the heat loss is sufficiently low, there is a net energy gain leading to an explosion. On the other hand, if the heat loss is high, the result is a fizzle.

We study the interaction between the reaction rate and the heat loss. We first develop a model that non-dimensionalizes the problem to make it amenable to numerical methods. Then, using numerical integration algorithms, we explore two different scenarios - explosion and fizzle - by varying the amount of heat loss. We also discover what the dividing line between an explosion and a fizzle is.

1 Introduction

The first principle is that you must not fool yourself. And you are the easiest person to fool.

– Richard Feynman

An adiabatic reaction is a type of reaction that occurs without any transfer of heat between the system and the surroundings. In other words, it is a reaction that occurs in a perfectly insulated environment. And in a non-adiabatic reaction, there is exchange of heat between the system and the surroundings. This reaction takes place in a poorly insulated environment.

In this project, we will explore some of the properties of non-adiabatic explosions. In particular, we will study the process for both a good and a poor insulator. The insulator determines the amount of heat transfer between the system and the surroundings i.e., it is a measure of the heat loss factor. If the heat loss in large enough, a fizzle, or continuous burn, will occur. And if the heat loss is kept small enough, as in the case of an adiabatic reaction, an explosion will still occur. The goal of this project is to study explosions and fizzles as a property of the insulation.

The rest of the report is organized as follows: In Section 2, we will present the problem scenario in detail. In Section 3, we will develop a simple mathematical model that describes the problem while accounting for a few nuances. In Section 4, we will derive some numerical approximations that will help us verify our final solutions. Section 5 will present and discuss the solutions of our model, while delving more into the physics. Finally, Section 6 will conclude our discussion on non-adiabatic explosions.

2 Problem Statement

Nothing is too wonderful to be true, if it be consistent with the laws of nature.

– Michael Faraday

In this problem, we have a fuel and an oxidizer in a semi-insulated container. The fuel and oxidizer constitute the system, and the box the boundary between the system and the surroundings. The fuel and oxidizer are allowed to react, but the molecules can react only if they possess enough energy. The minimum energy required for the molecules to react is called the activation energy. As the molecules continue to react, thermal energy is generated. This thermal energy causes an increase in temperature. If our container was a perfect insulator, the thermal energy would continue to increase and result in an adiabatic explosion. However, since the container is not a perfect insulator, there will be some heat transfer between the system and surroundings. In fact, as the Second Law of Thermodynamics dictates, the system will only lose heat as more thermal energy is generated.

The amount of heat lost varies depending on the thermal insulation property of our container. This property is characterized by the convective heat transfer coefficient of the container. If the heat transfer coefficient is low, over time there will still be a net energy gain in the system, which results in temperature reaching a threshold value that sets off an exponential reaction i.e., explosion. However, if the heat transfer coefficient is large enough, a fizzle, or continuous burn, will occur instead of an explosion.

The reaction occurs because temperature is not a static property of the molecules. The molecules of fuel and oxidizer possess different amounts of kinetic energy due to collisions with other molecules and the walls of the container. Overall, the temperature of the molecules follow a normal distribution. Therefore, at any given time, there is a small probability that two molecules of the reactants have the enough energy to react, even if the average thermal energy of the system is much lower than the activation energy.

This is an exothermic process and creates a positive feedback loop. Individual reactions build up over a long period of time gradually increasing the average temperature. This continues until the system attains sufficient thermal energy that allows a larger number of molecules to easily reach the activation energy. This rapidly accelerates the reaction, and leads to an explosion.

In the case of a fizzle, the heat loss does not allow the system to have a net energy gain. Thus, there is no rapid acceleration of the reaction that leads to a sudden increase in thermal energy. The molecules continue to react at a constant rate over time.

In the following section, we will come up with a mathematical model that will allow us to simulate such explosions and fizzles. We will also find the dividing line between explosions and fizzles.

3 Model

The greatest shortcoming of the human race is our inability
to understand the exponential function.

– Alan Bartlett

We are interested in knowing if and when the explosion will take place i.e., we want to know the temperature of the reactants, T, as it varies over time, t. In our problem, there are two different phenomena that cause a change in temperature. The first is the reaction itself which tends to increase the temperature. The second is the heat loss to the surroundings which tends to decrease the temperature. We can think of these two factors as opposing forces trying to cause (and prevent) the explosion.

We know that the rate of reaction (rate of transformation of fuel) can be expressed as $\dfrac{dA}{dt} = -\bar{c}Ae^{-E/RT}$ where A is the concentration of the fuel, R is the universal gas constant,

E is the activation energy, and $\bar{c}$ is the constant of proportionality. We can also model the heat loss using Newton's Law of Cooling i.e., $\frac{dQ}{dt} = h(T - T_0)$, where Q is the heat lost, h is the convective heat transfer coefficient of the insulating material, and T_0 is the temperature of the surroundings.

Now, we can put these different pieces together using the law of conservation of energy as

$$\underbrace{c_v \frac{dT}{dt}}_{\substack{\text{Rate of change}\\ \text{of internal energy}}} = \underbrace{-\bar{c}\frac{dA}{dt}}_{\substack{\text{Rate of thermal energy}\\ \text{generation by reaction}}} - \underbrace{\frac{dQ}{dt}}_{\substack{\text{Rate of heat lost}\\ \text{to surroundings}}}$$

$$\implies c_v \frac{dT}{dt} = -\bar{c}_2 e^{-E/RT} - h(T - T_0) \tag{1}$$

where c_v is the specific heat at constant volume. We know that initially the temperature of the reactants is the same as the temperature of the surroundings. This gives the initial condition $T(0) = T_0$.

Notice that there are a couple of computational problems with Equation (1) before we can use any numerical integration scheme. Firstly, we have no prior knowledge about when to expect the explosion. This means we might stop our integration scheme concluding that there is no explosion, while the explosion happens at a later time. On the other hand, we might integrate indefinitely hoping to witness an explosion, while there is no explosion at all! Secondly, even if we do reach the explosion, depending on our integration step size, we might step over the explosion.

To solve these issues, we non-dimensionalize the problem. We can start by scaling temperature as $\overline{T} = \frac{T}{T_0} = 1 + \epsilon\theta$ where $\epsilon = \frac{RT_0}{E}$. Since we are dealing with a high activation energy problem, $\epsilon \ll 1$. Notice that $\overline{T}$ is 1 plus a small correction i.e., our new temperature θ is an order-one size variable. Now, we can scale time as $\tau = \frac{t}{t_{ref}}$ where t_{ref} is a reference time (usually the adiabatic explosion time). Finally, we introduce δ which is proportional to $\frac{1}{h}$ and redefine time as $\sigma = \frac{\tau}{\delta}$. This leads to the following transformed differential equation where each term's physical significance is similar to that in Equation (1):

$$\underbrace{\frac{d\theta}{d\sigma}}_{\substack{\text{Rate of change} \\ \text{of internal energy}}} = \underbrace{\delta e^{\theta}}_{\substack{\text{Rate of thermal energy} \\ \text{generation by reaction}}} - \underbrace{\theta}_{\substack{\text{Rate of heat loss} \\ \text{to surroundings}}} \tag{2}$$

The temperature transformation gives us the new initial conditions, $\theta(0) = 0$.

We saw earlier that the term dominating the right hand side of Equations (1) and (2) determine whether we witness an explosion or a fizzle. So, it can be reasoned that the margin between explosions and fizzles can be determined by setting the right hand side to 0.

$$\begin{aligned} \frac{d\theta}{d\sigma} &= \delta e^{\theta} - \theta = 0 \\ &\implies \delta e^{\theta} = \theta \end{aligned} \tag{3}$$

It turns out that the solution to Equation (3) is an osculation point i.e., their slopes are the same. Now, we can solve this equation.

$$\begin{aligned} \delta e^{\theta} &= 1 && \text{(taking derivative of Eq. (3))} \\ \implies \theta &= 1 \\ \implies \delta &= \frac{1}{e} \end{aligned}$$

Thus, $\delta = 1/e$ is the dividing line between explosions and fizzles. There are three cases:

(i) $\delta > 1/e$ - The thermal energy generated by the reaction dominates the heat loss. Therefore, we can expect an explosion. This also corresponds to a smaller h i.e., a very good insulator, which intuitively confirms our expectation of an explosion.

(ii) $\delta = 1/e$ - The thermal energy generated by the reaction is the same as the heat loss. Therefore, we can expect an explosion as $t \to \infty$.

(iii) $\delta < 1/e$ - The heat loss dominates the thermal energy generated by the reaction. Therefore, we can expect a fizzle. This also corresponds to a larger h i.e., a poor insulator, which intuitively confirms our expectation of a fizzle.

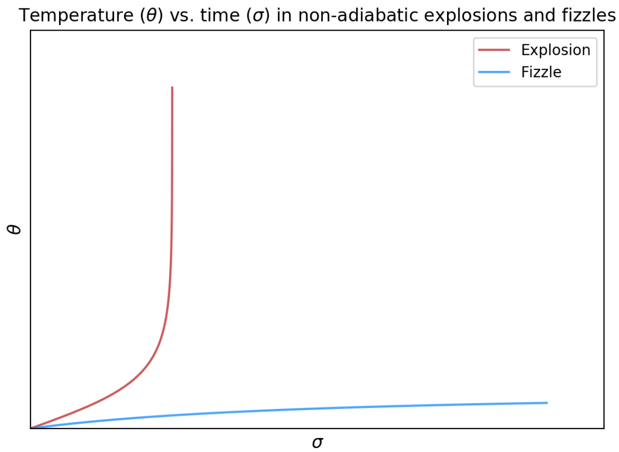

Figure 1: *Example curves for explosions and fizzles*

Now, since we have a good understanding of the problem, we are ready to come up with approximations and numerically integrate the initial value problem in Equation (3).

4 Numerical Approximations

Truth is much too complicated to allow anything but approximations.

– John Von Neumann

We saw earlier that depending on our value of δ, we get either an explosion or a fizzle. Figure 1 graphically shows both of these events. Notice how the explosion curve has a vertical asymptote. When we perform numerical integration schemes corresponding to an explosion, there is a good chance that, depending on our step size, we might jump over the interesting explosion. So, we can convert this vertical asymptote into a more amenable horizontal asymptote by swapping our coordinate axes i.e., instead of solving for $\theta(\sigma)$, we can instead solve for $\sigma(\theta)$. This produces a curve that looks very similar to the fizzle plot. Figure 2 shows an example of an explosion where the axes are swapped.

This means that we need to solve two different systems of differential equations – one for a fizzle and the other for an explosion. These initial value problems are described in Equations (4) and (5) respectively. We can use any numerical integration scheme to solve these problems. For this particular situation, we will use a fourth-order Runge-Kutta technique to solve numerically. Further, for the fizzle, we will use $\delta = 1/3$, and for the explosion, we will use

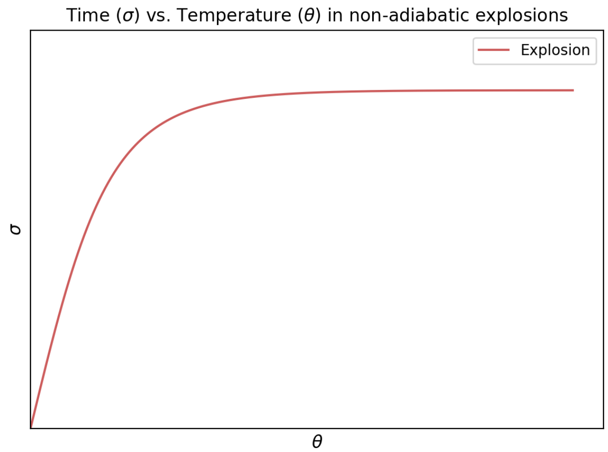

Figure 2: *By flipping the coordinate axes in an explosion, we have a horizontal asymptote that is amenable to numerical integration schemes.*

$\delta = 1$.

$$\frac{d\theta}{d\sigma} = \delta e^{\theta} - \theta \quad , \quad \theta(0) = 0 \qquad \ldots \text{Fizzle} \tag{4}$$

$$\frac{d\sigma}{d\theta} = \frac{1}{\delta e^{\theta} - \theta} \quad , \quad \sigma(0) = 0 \qquad \ldots \text{Explosion} \tag{5}$$

To verify that our numerical solvers produce correct results, we will now approximate the early and late solutions to both phenomena, and later compare them with the numerical solutions.

4.1 Early Solutions

In both cases, explosions and fizzles, during the beginning, the temperature is small for a long time because of the high activation energy. This means that θ should also be small during early periods. Therefore, we can use the Taylor series expansion of e^x as follows:

$$
\begin{aligned}
&\frac{d\theta}{d\sigma} = \delta e^{\theta} - \theta \\
\implies &\frac{d\theta}{d\sigma} = \delta\Big(1 + \theta + \frac{\theta^2}{2!} + \frac{\theta^3}{3!} + \dots\Big) - \theta \qquad \text{(Taylor series expansion of } e^{\theta}\text{)} \\
\implies &\frac{d\theta}{d\sigma} \approx \delta + \theta(\delta - 1)
\end{aligned}
$$

By analytically solving this, we can approximate the early solutions for fizzles and explosions with Equations (6) and (7) respectively.

$$
\theta(\sigma) = \frac{\delta}{\delta - 1}\left[e^{(\delta-1)\sigma} - 1\right] \tag{6}
$$

$$
\sigma(\theta) = \frac{1}{\delta - 1}\ln\left[\frac{\theta + \frac{\delta}{\delta-1}}{\frac{\delta}{\delta-1}}\right] \tag{7}
$$

However, if we set $\delta = 1$, which corresponds to an explosion, the approximations become undefined. So, if we use L'Hospital's Rule to find $\sigma(\theta)$ as $\delta \to 1$, we get the approximation described in Equation (8)

$$
\begin{aligned}
\lim_{\delta\to 1}\sigma(\theta) &= \lim_{\delta\to 1}\frac{\ln\left(\frac{\theta(\delta-1)}{\delta} + 1\right)}{\delta - 1} \\
&\overset{\text{L'H}}{=} \lim_{\delta\to 1}\frac{\frac{\theta}{\delta^2}}{\frac{\theta(\delta-1)}{\delta} + 1} \\
&= \theta
\end{aligned} \tag{8}
$$

4.2 Late Solutions

Clearly, the late solutions differ for explosions and fizzles (see Figure 1). First, we will approximate the late solution for the fizzle. Notice that the late solution asymptotes horizontally i.e., the slope of the curve approaches 0. Using this observation, we have:

$$\begin{aligned} \frac{d\theta}{d\sigma} &\approx 0 \\ \implies \delta e^{\theta} &\approx \theta \end{aligned} \tag{9}$$

We now have a root finding problem. Note that this is a different problem than we saw earlier in Section 3. Earlier, we were solving for δ. Here, for a fixed δ, we need to find θ_{fiz} that solves Equation (9). This gives us the late solution (the horizontal asymptote), $\theta(\sigma) = \theta_{fiz}$.

For the explosion, from Figure 1, notice that the exponential term (rate of reaction) dominates the linear term (heat loss) in Equation (4). And as $\sigma \to \sigma_{exp}$, $\theta \to \infty$ where σ_{exp} is the explosion time. We now have the following new initial value problem for the late solution:

$$\frac{d\theta}{d\sigma} \approx \delta e^{\theta} \quad , \quad \theta(\sigma_{exp}) \to \infty$$

Solving this problem gives us the late solution described in Equation (10).

$$\sigma(\theta) = \sigma_{exp} - \frac{1}{\delta e^{\theta}} \tag{10}$$

This gives birth to a new issue – we have no prior knowledge about the exact value of σ_{exp}. We can approximate the value of σ_{exp} by integrating Equation (5). This approximation is described in Equation (11).

$$\begin{aligned} \int_0^{\infty} \frac{d\sigma}{d\theta} d\theta &= \int_0^{\infty} \frac{d\theta}{\delta e^{\theta} - \theta} \\ \implies \sigma(\infty) - \sigma(0) &= \int_0^{\infty} \frac{d\theta}{\delta e^{\theta} - \theta} \\ \implies \sigma_{exp} &= \int_0^{\infty} \frac{d\theta}{\delta e^{\theta} - \theta} \end{aligned} \tag{11}$$

We can use integration techniques such as Simpson's 1/3 Rule or the Gaussian Quadrature method to approximate the value of σ_{exp}. Note that we do not actually have to evaluate the integral to infinity, because after a certain point, changes in value of the integral are insignificant as the integrand is an exponentially decaying function.

Now that we have a good idea of what our solutions should look like, we can proceed to use a fourth-order Runge-Kutta scheme to numerically find the solutions to explosions and fizzles.

5 Results

From then on, when anything went wrong with a computer, we said it had bugs in it.

– Grace Hopper

5.1 Fizzle

Using $\delta = 1/3$, we numerically integrated and solved the initial value problem described in Equation (4). With step size $h = 0.05$, we integrated from $0 \leq \sigma \leq 20$ using fourth-order Runge-Kutta scheme. A few of the numerical values are shown in Table 1. The solid grey line in Figure 3 traces the numerical solutions.

We saw in Section 4.1 that the early solution for a fizzle can be approximated using Equation (6). This curve is traced by the dashed blue-green line in Figure 3 for $0 \leq \sigma \leq 2.5$.

In Section 4.2, we saw that the late solution (the horizontal asymptote) for a fizzle is the root of Equation (9). With $\delta = 1/3$, the root is, $\theta_{fiz} = 0.6190613$. We calculated this using the Newton-Raphson root finding scheme[1]. This late solution is traced by the dashed orange line in Figure 3 for $5.5 \leq \sigma \leq 20$. Therefore, from the transformation we made in Section 3, we can expect the asymptotic temperature in a fizzle to be $T \approx T_0(1 + 0.6191\frac{RT_0}{E})$.

From Figure 3, we can see that our numerical solution closely follows the short term approximation during early times, and approaches the long term approximation during later times. Both observations individually verify that our numerical solution for the fizzle is correct (or at least is on the right track).

In the case of a fizzle, we know that the heat loss is greater than the rate at which energy is generated by the reaction. By following the numerical solution we graphed in Figure 3, we can gain more insights behind the physics of a fizzle. Observe that during early times, there

Note: All simulations and visualizations were developed in Python using NumPy [1] and Matplotlib [2] libraries respectively.

[1] See Appendix A for details

σ	θ
0.00	0.0000000
0.05	0.0163927
0.10	0.0322523
0.15	0.0476004
0.20	0.0624573
0.25	0.0768426
0.30	0.0907748
0.35	0.1042716
0.40	0.1173499
0.45	0.1300256
0.50	0.1423142
$\vdots$	$\vdots$
19.85	0.6188410
19.90	0.6188451
19.95	0.6188492
20.00	0.6188532

Table 1: *A few numerical values obtained from solving the Fizzle problem, with $\delta = 1/3$, described in Equation (4). These values were calculated using fourth-order Runge-Kutta scheme with step size $h = 0.05$ for $0 \leq \sigma \leq 20$.*

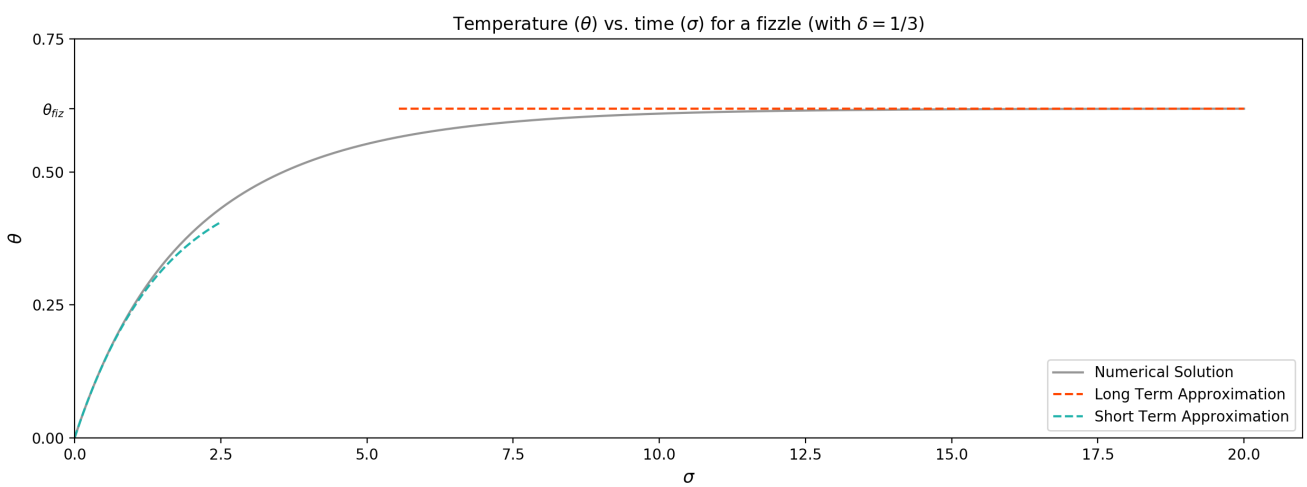

Figure 3: *Curves obtained by numerically integrating the Fizzle problem (described in Equation (4)) along with short term (early solution) and long term (late solution) approximations. The solid grey line traces the numerical solution. The dashed blue-green line shows the short term approximation. The dashed orange line shows the long term approximation.*

is a gradual temperature increase. This can explained by the fact that during this period, the energy generated by the reaction is faster than the heat loss. We know, from Newton's Law of Cooling, that heat loss is faster when there is a larger temperature gradient. As the temperature inside the poorly insulated box increases (due to forward reaction), so does the temperature gradient. This leads to a greater heat loss. After a long time, the rate of heat loss slowly becomes equal to the rate of thermal energy generated by the reaction. This leads to an almost constant temperature inside the box, which is signified by the horizontal asymptote.

5.2 Explosion

Using $\delta = 1$, we numerically integrated and solved the initial value problem described in Equation (5). With step size $h = 0.01$, we integrated from $0 \leq \theta \leq 10$ using fourth-order Runge-Kutta scheme. A few of the numerical values are shown in Table 2. The solid grey line in Figure 3 traces the numerical solutions.

We saw in Section 4.1 that the early solution for an explosion can be approximated using Equation (7). For $\delta = 1$, we calculated the limit of Equation (7) to obtain the approximation described in Equation (8). This curve is traced by the dashed blue-green line in Figure 4 for $0 \leq \theta \leq 0.8$.

In Section 4.2, we saw that the late solution for an explosion is approximated by Equation (10). To calculate σ_{exp}, we had to numerically integrate Equation (11). With $\delta = 1$, we obtain $\sigma_{exp} = 1.3590983$. We calculated this using Simpson's 1/3 Rule[2]. This late solution is traced by the dashed orange line in Figure 4 for $1.35 \leq \theta \leq 10$. Therefore, we can expect the explosion to occur when $t \approx 1.3591 t_{ref}$ from the transformation we made in Section 3.

Once again, from Figure 4, we can see that our numerical solution closely follows the short term approximations during early times, and approaches the long term approximation during later times. These observations individually verify that our numerical solution for the explosion is correct.

In the case of an explosion, we know that the rate at which energy is generated by the reaction is greater than the heat loss. By following the numerical solution we graphed in Figure 4, we can gain insights behind the physics of an explosion. Observe that during early times, there is a gradual temperature increase. This is an almost linear increase as demonstrated by our short term approximation. This can explained by the fact that during this period, the energy generated by the reaction is faster than the heat loss. Unlike in a fizzle where, after a certain point, heat loss and energy generation by the reaction become equal, in an explosion, the heat loss is always small. This is because of a large δ (here, $\delta = 1$), which corresponds to a

[2]See Appendix B for details

θ	σ
0.00	0.0000000
0.01	0.0099998
0.02	0.0199987
0.03	0.0299955
0.04	0.0399892
0.05	0.0499789
0.06	0.0599635
0.07	0.0699419
0.08	0.0799131
0.09	0.0898760
0.10	0.0998296
$\vdots$	$\vdots$
9.97	1.3590515
9.98	1.3590519
9.99	1.3590524
10.00	1.3590529

Table 2: *A few numerical values obtained from solving the Explosion problem, with $\delta = 1$, described in Equation (5). These values were calculated using fourth-order Runge-Kutta scheme with step size $h = 0.01$ for $0 \leq \theta \leq 10$.*

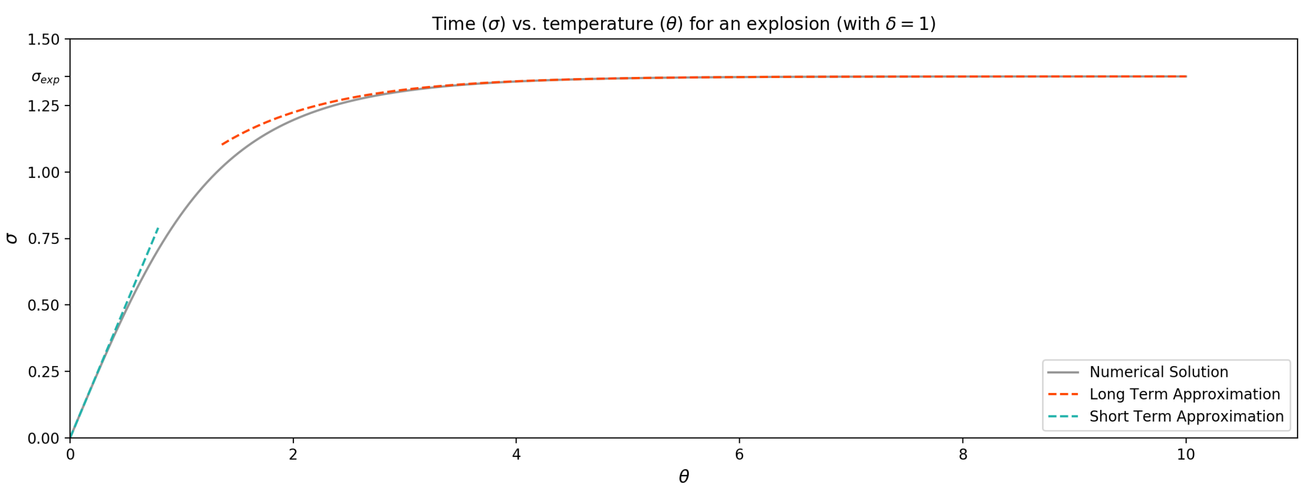

Figure 4: *Curves obtained by numerically integrating the Explosion problem (described in Equation (5)) along with short term (early solution) and long term (late solution) approximations. The solid grey line traces the numerical solution. The dashed blue-green line shows the short term approximation. The dashed orange line shows the long term approximation.*

small convective heat transfer coefficient i.e., the material is a very good insulator. Therefore, the heat loss term plays only a very small role.

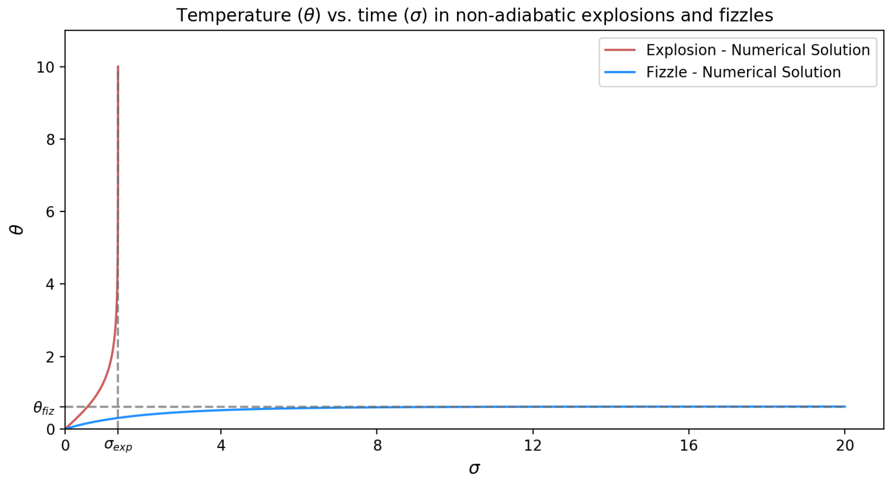

Figure 5: *Curves obtained by numerically integrating the Explosion problem (described in Equation (5)) and the Fizzle problem (described in Equation (4). The red curve shows the explosion. The blue line shows the fizzle. The dashed grey lines show the asymptotes.*

After temperature increases to a certain point (the explosion time), a spontaneous explosion happens. In a very small time, temperature increases rapidly to a very large values. If we plot this on a temperature vs. time graph, this corresponds to a horizontal asymptote at the explosion time. Our intuition of the physics correctly correlates to the results seen in Figure 4.

Both results, explosion and fizzle, are plotted together in Figure 5. The red curve shows the explosion. The blue line shows the fizzle. The dashed grey lines show the asymptotes. The horizontal asymptote shows θ_{fiz} – the temperature where heat loss and energy generated by reaction reach same values. The vertical asymptote shows σ_{exp} – the time when the insulated box explodes.

6 Conclusion

Don't worry about people stealing an idea.
If it's original, you will have to ram it down their throats.

– Howard Aiken

We have shown that given enough time, a fuel exposed to an oxidizer with mitigated heat loss will eventually explode. We discovered that in the non-dimensionalized problem described in Equation (2), an explosion occurs when $\delta > 1/e$ and a fizzle occurs when $\delta < 1/e$. This is because $\delta = 1/e$ corresponds to the scenario where the effects of energy gain and heat loss cancel each other, and δ is inversely proportional to the convective heat transfer coefficient of the boundary of the system.

In the case of the fuel and oxidizer combination provided to us, it will take $t \approx 1.3591 t_{ref}$ time for the system to explode when $\delta = 1$. This measure is based on t_{ref} because when we transformed the system, we scaled time by t_{ref}. Here, $\sigma_{exp} = 1.3590983$.

On the other hand, when heat loss is too great for there to be a net energy gain in the system, a fizzle occurs. In this scenario, the temperature increases steadily over time, eventually asymptotically approaching a constant temperature $T \approx T_0(1 + 0.6191 \frac{RT_0}{E})$ when $\delta = 1/3$. Here, $\theta_{fiz} = 0.6190613$. This is the equilibrium temperature, where the reaction is proceeding at the same rate as the poorly insulated box transfers heat into the surroundings.

The θ vs. σ (temperature vs. time) plots for the explosion (when $\delta = 1$) and the fizzle (when $\delta = 1/3$) is shown in Figure 5.

Our findings have a few interesting purposes. The most obvious of those are guidelines to keeping a fuel in storage for long periods of time. Proper storage should consist of keeping the fuel sealed from the oxidizer. This means having the fuel in an otherwise vacuum compartment. Another option is to store in normal conditions, but allowing sufficient heat to leave the the storage (system). Hopefully, since t_{ref} is usually measured on the order of thousands of years, the fuel being stored will be consumed before causing a runaway reaction.

Another interesting application is to use these results to carefully bury a cache of fuel and oxidizer far enough underground such that it is properly insulated. The only purpose this would serve is to create noise or maybe a small crater which will frighten future humans or wildlife – a blast from the past, quite literally. However, such a system would require infinite amount of fuel and oxidizer. Therefore, there is no way of knowing if this magnificent 10,000 year time bomb will be witnessed by any life . . .

References

[1] T. E. Oliphant, *Guide to NumPy*, vol. 1. Dec 2006.

[2] J. D. Hunter, "Matplotlib: A 2D graphics environment," *Computing In Science & Engineering*, vol. 9, no. 3, pp. 90–95, 2007.

[3] R. L. Burden and J. D. Faires, *Numerical Analysis*. Cengage Learning, 9 ed., Aug 2010.

A Estimating θ_{fiz}

To estimate θ_{fiz}, we have to find the root of Equation (12), which is a rearranged version of the original problem described in Equation (9). Here, $\delta = 1/3$.

$$f(\theta) = e^{\theta} - \frac{\theta}{\delta} \tag{12}$$
$$\implies f'(\theta) = e^{\theta} - \frac{1}{\delta} \tag{13}$$

With initial guess $\theta_0 = 0.5$, we used Newton-Raphson method to estimate the root of Equation (12). We used the "x-ratio test" with a tolerance $= 10^{-4}$ to test for convergence i.e., we declared convergence when $\frac{\theta_{n+1} - \theta_n}{\theta_n} < 10^{-4}$ where θ_n is the root estimate in the n-th iteration. The Newton-Raphson algorithm converged in just 4 iterations. The values are described in Table 3.

Therefore, we have $\theta_{fiz} \approx 0.6190613$.

Iteration (i)	θ_i
0	0.5000000
1	0.6100597
2	0.6189968
3	0.6190613
4	0.6190613

Table 3: *Root estimates of Equation (12), with $\delta = 1/3$, obtained by using Newton-Raphson root finding technique with $\theta_0 = 0.5$.*

B Estimating σ_{exp}

To estimate σ_{exp}, we have to numerically integrate Equation (11). In practice, we do not have to integrate with an upper limit of ∞. Since the integrand is an exponentially decaying function, it is going to quickly approach 0. Therefore, beyond a certain point, increasing the upper limit of the integral will only make insignificant changes to σ_{exp}. So, we just need to evaluate Equation (14).

$$\sigma_{exp} = \int_0^a \frac{d\theta}{\delta e^\theta - \theta} \tag{14}$$

Depending on our required we are free to choose the upper bound, a, in Equation (14). Here, we are only interested in the first 8 decimal places. Using Simpson's 1/3 Rule with step size $h = 0.01$, we found that σ_{exp} does not change after $a = 19$. A few of the values of σ_{exp} for various a are outlined in Table 4.

a	σ_{exp}
1	0.84307889
2	1.19499148
3	1.30445050
4	1.33998684
5	1.35223249
6	1.35659935
7	1.35818326
8	1.35876234
⋮	⋮
17	1.35909824
18	1.35909826
19	1.35909827
20	1.35909828
21	1.35909828
22	1.35909828
23	1.35909828

Table 4: *Various estimates of σ_{exp} corresponding to different values of a in Equation (14). Here, we used Simpson's 1/3 Rule with step size $h = 0.01$ to evaluate the integral. Also, we are only interested in the first 8 decimal places of σ_{exp}.*