Combustion

Lighting a match is an everyday experience, but an understanding of why it occurs is less obvious. As the match is lit, a reaction starts to occur, which is exothermic, i. e., it releases heat. The amount of heat released is proportional to the rate of reaction, and this itself increases with temperature (coal burns when hot, but not at room temperature). The heat released is given by the Arrhenius expression $A\exp(-E/RT)$, where E is the activation, R is the gas constant, T is the absolute temperature, and we take A as constant (it actually depends on reactant concentration). A simple model for the match temperature is then

$$c\frac{dT}{dt} = -k(T - T_0) + A\exp(-E/RT), \tag{1}$$

where ε is a suitable specific heat capacity, k is a cooling rate coefficient, and T_0 is ambient (e. g., room) temperature. The terms on the right represent the source term due to the reactive heat release, and a Newtonian cooling term (cooling rate proportional to temperature excess over the surroundings).

We can solve (1) as a quadrature, but it is much simpler to look at the problem graphically. Bearing in mind that T is absolute temperature, the source and sink terms typically have the form shown in figure 1, and we can see that there are three equilibria, and the lowest and highest ones are stable. Of course, one could have only the low equilibrium (for example, if k is large or T_0 is low) or the high equilibrium (if k is small or T_0 is high). The low equilibrium corresponds to the quiescent state — the match in the matchbox; the high one is the match alight. If we vary T_0, then the equilibrium excess temperature Δ $(= T - T_0)$ varies as shown in figure 2: the upper and lower branches are stable.

We can model lighting a match as a local perturbation to Δ; the heat of friction in striking a match raises the temperature excess from near zero to a value above the unstable equilibrium on the middle branch, and Δ then migrates to the stable upper branch, where the reaction (like that of a coal fire) is self-perpetuating. Figure 2 also explains why it is difficult to light a wet match, but a match will spontaneously light if held at some distance above a lighted candle.

Figure 2 exhibits a form of hysteresis, meaning non-reversibility. Suppose we place a (very large, so it will not burn out) match in an oven, and we slowly raise the ambient temperature from a very low value to a very high value, and then lower it once again. Because the variation is slow, the excess temperature will follow the equilibrium curve in figure 2. At the value T_+, Δ suddenly jumps (spontaneous combusion) to the hot branch, and remains on this if T_0 is increased further. Now if T_0 is decreased, Δ remains on the hot branch until $T_0 = T_-$, below which it suddenly drops to the cool branch again (extinction).[1] The path traced out in the $(T_0, \Delta T)$ plane is not reversible (it is not an arc but a closed curve).

[1]We can understand why T follows the equilibrium curve as follows. We can write (1) in terms of suitable dimensionless variables as $\dot{\Delta} = T_0 - g(\Delta)$, where $g(\Delta)$ is a cubic-like curve similar to the function $T_0(\Delta)$ depicted in figure 2. if T_0 is slowly varying, then $T_0 = T_0(\varepsilon t)$ where $\varepsilon \ll 1$, and putting $\tau = \varepsilon t$, we have $\varepsilon d\Delta/d\tau = T_0(\tau) - g(\Delta)$; thus on the slow time scale τ, Δ will tend rapidly to a (quasi-equilibrium) zero of the right hand side.

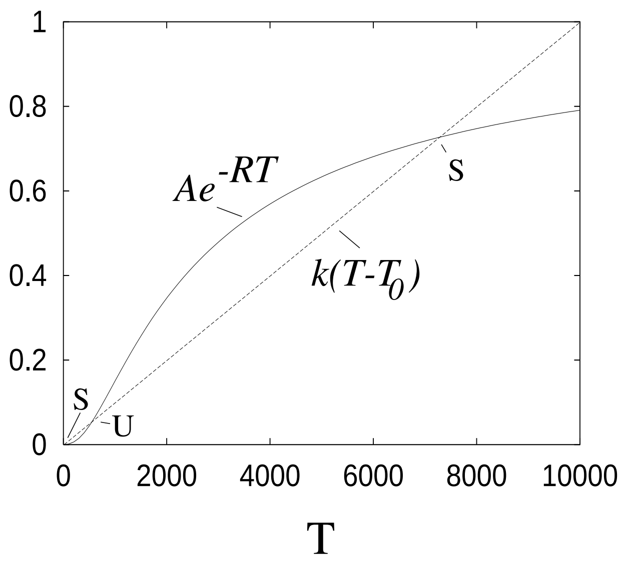

Figure 1: Plots of the functions $A\exp[-E/R(T+T_m)]$ and $k(T-T_0)$ using values $T_m = 273$ (so T is measured in centigrade), with values $A = 1$, $E = 20,000$, $R = 8.3$, $k = 10^{-4}$, $T_0 = 15^\circ$ C.

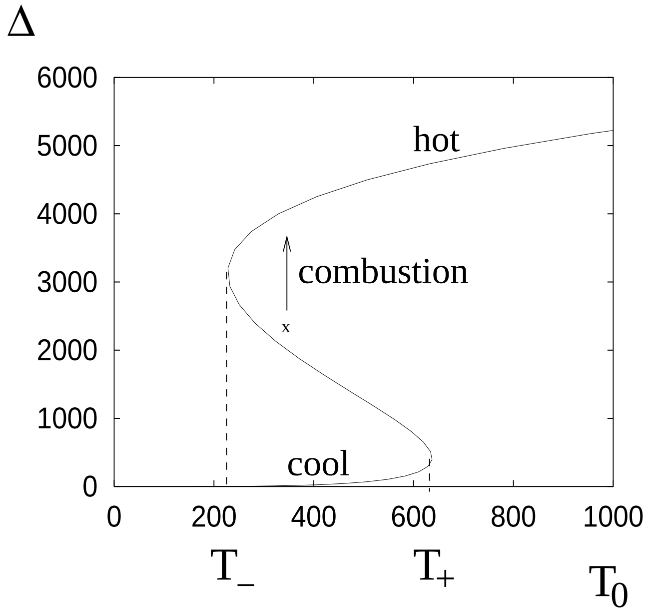

Figure 2: Equlibrium curve for Δ_0 as a function of T_0, parameters as for figure 1, but $E = 35,000$. An initial condition above the unstable middle branch leads to combustion.

The reason the multiple equilibria exist (at least for matches) is that for many reactions, E/R is very large and also A is very large. This just says that it is possible that $Ae^{-E/RT}$ is very small near T_0 but jumps rapidly at higher T to a large asymptote. To be more specific, we non-dimensionalise (1) by putting

$$T = T_0 + (\Delta T)\theta, \quad t = [t]t^*, \tag{2}$$

and in fact we choose the cooling time scale $[t] = c/k$. Then we have, dropping the asterisk, and after some simplification,

$$\dot{\theta} = -\theta + \frac{A}{k\Delta T}\exp\left(-\frac{E}{RT_0}\right)\exp\left[\frac{E\Delta T}{RT_0^2}\frac{\theta}{1+\varepsilon\theta}\right], \tag{3}$$

where $\varepsilon = \Delta T/T_0$. The temperature rise scale ΔT has to be chosen, and there are two natural choices: to set the exponent coefficient $E\Delta T/RT_0^2$ to one, or the pre-multiplicative constant to one. In one way, the latter seems the better choice: it seems to balance the source with the sink. But because E/R is large, we might then find $E\Delta T/RT_0^2$ to be large, which would ruin the intention. So we choose (but it does not really matter)

$$\Delta T = \frac{RT_0^2}{E}, \tag{4}$$

so that

$$\dot{\theta} = -\theta + \lambda\exp\left[\frac{\theta}{1+\varepsilon\theta}\right], \tag{5}$$

where

$$\lambda = \frac{EA}{kRT_0^2}\exp\left(-\frac{E}{RT_0}\right), \quad \varepsilon = \frac{RT_0}{E}. \tag{6}$$

If typical values are $T_0 = 300$ K, $E/R = 10,000$ K, we see that $\varepsilon \ll 1$, and also, since

$$\lambda = \frac{\lambda_0}{\varepsilon^2}\exp\left(-\frac{1}{\varepsilon}\right), \quad \lambda_0 = \frac{A}{kE}, \tag{7}$$

λ is extremely sensitive to ε and thus T_0.

So long as $\theta = O(1)$, or at least $\theta \ll 1/\varepsilon$ (i.e. $T - T_0 \ll T_0$), we can neglect the $\varepsilon\theta$ term, so that

$$\dot{\theta} \approx -\theta + \lambda e^{\theta}. \tag{8}$$

This gives the lower part of the S-shaped curve in figure 2, and the equilibria are given by $\theta e^{-\theta} = \lambda$, and these coalesce and disappear if $\lambda > e^{-1}$. This corresponds to the value of $T_0 = T_+$ in figure 2, and implies

$$\frac{E}{RT_+} \approx 1 + \ln\lambda_0 + 2\ln\left(\frac{E}{RT_+}\right). \tag{9}$$

There are two roots to this, but only one has $E/RT_+ \gg 1$. Further, since $x \gg 2\ln x$ if $x \gg 1$, we have, approximately,

$$T_+ \approx \frac{E}{R[1 + \ln\lambda_0 + 2\ln\{1+\ln\lambda_0\}]}. \tag{10}$$

If $E/R \gg T_0$, then the fact that one can light matches at room temperature suggests that λ_0 is large, and specifically $\ln \lambda_0 \sim E/RT_0$. (Note that this does not imply $\lambda = O(1)$.)

Carrying on in this vein, let us suppose that we define a temperature T_q by

$$\lambda_0 = \exp\left[\frac{E}{RT_q}\right], \tag{11}$$

and we suppose $T_q \sim T_0$. It follows that $T_+ \approx T_q$, or more precisely,

$$T_+ \approx \frac{T_q}{1+\varepsilon_q\{1+2\ln(1+\varepsilon_q^{-1})\}}, \tag{12}$$

where $\varepsilon_q = RT_q/E$. The stable cool branch and unstable middle branch are then the roots of

$$\theta e^{-\theta} \approx \lambda = \frac{1}{\varepsilon^2}\exp\left[-\frac{1}{\varepsilon}\left(1-\frac{T_0}{T_q}\right)\right], \tag{13}$$

and in general $\lambda \ll 1$ (if $T_0 < T_q$), so that we find the stable cool branch (when $\theta \ll 1$)

$$\theta \approx \lambda \approx \left(\frac{E}{RT_0}\right)^2 \exp\left[\frac{E}{R}\left(\frac{1}{T_+}-\frac{1}{T_0}\right)\right], \tag{14}$$

and the unstable middle branch (where $\theta \gg 1$),

$$\theta \approx \frac{1}{\varepsilon}\left(1-\frac{T_0}{T_q}\right) \approx \frac{E}{R}\left(\frac{1}{T_0}-\frac{1}{T_+}\right). \tag{15}$$

Evidently θ becomes $O(1/\varepsilon)$ on the middle branch, and to allow for this, we put

$$\theta = \Theta/\varepsilon, \tag{16}$$

and (5) becomes

$$\dot{\theta} = -\Theta + \frac{1}{\varepsilon}\exp\left[\frac{1}{\varepsilon}\left\{\frac{\Theta}{1+\Theta} - \left(1-\frac{T_0}{T_q}\right)\right\}\right]. \tag{17}$$

Equating the right hand side to zero gives the approximate equilibria

$$\theta \approx \frac{T_+ - T_0 + \varepsilon T_+ \ln\left(\frac{T_+-T_0}{T_0}\right)}{T_0 - \varepsilon T_+ \ln\left(\frac{T_+-T_0}{T_0}\right)} \tag{18}$$

and Θ tends to infinity as $T_0 \to 0$. The hot branch is recovered for even higher values of Θ, so that $\Theta \gg 1$, in which case equilibria of (16) are given by

$$\Theta \approx \frac{1}{\varepsilon}\exp\left[\frac{T_0}{\varepsilon T_q}\right], \tag{19}$$

and increase again with T_0.

The critical value of T is that on the unstable middle branch, as this gives the necessary temperature which must be generated in order for combustion to occur. From (17) (ignoring terms in ε), this can be written dimensionally in the simple approximate form

$$T \approx T_+, \tag{20}$$

where T_+ is the critical temperature at the nose of the curve in figure 2. The fact that T is approximately constant on the unstable branch is due to the steepness of the exponential curve in figure 1, which is in turn due to the large value of E/R. In terms of the parameters of the problem, the critical (ignition) temperature is

$$T_+ \approx \frac{E}{R \ln\left(\frac{A}{kE}\right)}. \tag{21}$$