Furnace reaction analysis

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FURNACE-REACTION ANALYSIS

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FURNACE REACTION ANALYSIS

by

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Abstract

One technique for analysing the properties of a given chemical sample is to heat it continuously in a furnace to a temperature at which a reaction takes place, and to compare the temperature profile in the sample with that of the furnace. From practice typical profiles are available, which can be used to determine the constants which describe the reaction, namely the heat of reaction, its activation energy and the rate constant. In chapter one of this paper we present a simple mathematical model, by which we can predict the temperature profile observed in practice, and in addition we show how the above constants can be computed from the temperature profile. In chapter two we discuss the phenomenon of self-ignition. In this case the heat due to the chemical reaction cannot be absorbed by the surroundings.

1. Furnace reaction analysis

§1.1. The model

Let us consider a rectangular sample, inserted in a furnace and heated from the sides (see figure below)
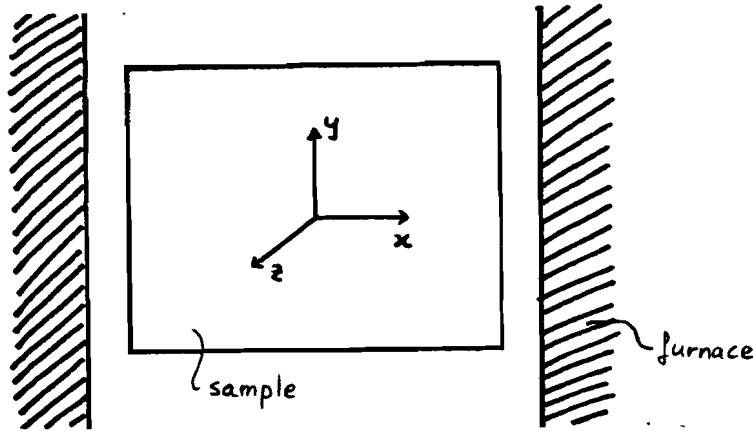
Fig. (1.1) Chemical sample in a furnace

The temperature of the furnace T_F [K] can be regulated. We consider a problem in which the furnace is heated at a uniform (and known) rate β [Ks^{-1}], so that

(1.1) $T_F(t) = T_0 + \beta t$

where T_0 [K] is the temperature of the environment.

If the y- and z-dimensions are much larger than L, then the temperature depends only on x and t, so

(1.2) $T = T(x,t)$.

In other words, we only consider a one-dimensional model, that is the sample is an infinite block of width $2L$, heated from both sides, with no heat transfer parallel to its sides (see figure 1.2).

Fig. (1.2) A chemical sample in a furnace (one-dimensional model)

With aid of a thermo-couple in the center of the sample (at $x = 0$) we can measure the temperature at $x = 0$ $T(0,t)$. We now can find some information about the chemical reaction by using the

difference between the temperature of the furnace $T_F(t)$ and the temperature of the sample at $x = 0$ $T(0,t)$. A typical temperature profile, which is observed in practice, is depicted in figure (1.3).
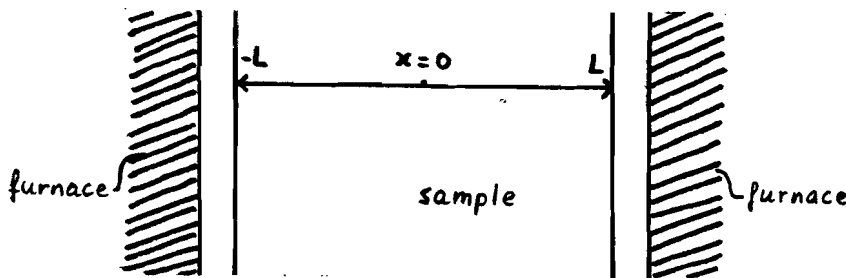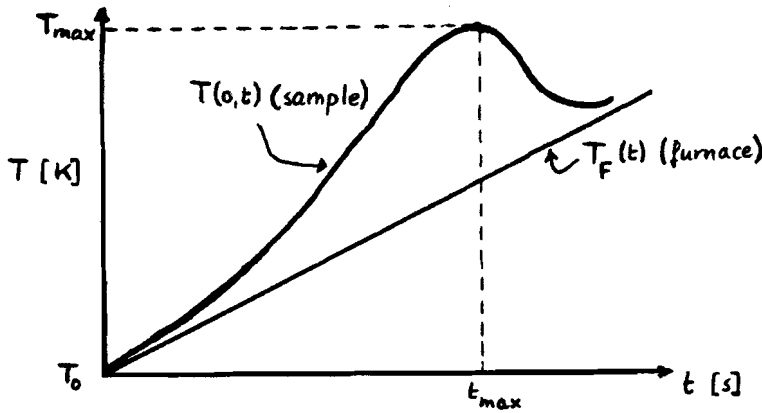

Fig. (1.3) A typical temperature profile

In the above picture t_{max}, T_{max}, and the area Q between the curves of $T(0,t)$ and $T_F(t)$ can easily be measured from the experimental evidence. We now present a simple mathematical model, by which we can predict the temperature profile as given in figure (1.3). Also we show how t_{max}, T_{max} and Q can be used to determine the constants which describe the reaction.

§1.2. The temperature distribution of the chemical sample

We assume the sample to be at rest. Therefore the convection term in the heat equation for the sample will be absent, i.e. it reduces to

$$(1.3) \qquad \rho c \, \frac{\partial T}{\partial t} = \lambda \, \frac{\partial^2 T}{\partial x^2} + Q$$

with

$$(1.4) \qquad \begin{cases} \rho & \text{density } [kg \ m^{-3}] \\ c & \text{specific heat } [J \ kg^{-1} \ K^{-1}] \\ \lambda & \text{heat conductivity } [J \ m^{-1} \ s^{-1} \ K^{-1}] \\ Q & \text{production of heat per unit of volume} \\ & \text{and time, owing to the chemical} \\ & \text{reaction } [J \ m^{-3} \ s^{-1}] \\ T & \text{absolute temperature } [K] \end{cases}$$

Let $\alpha(t)$ be the mass-fraction of the active material (α is dimensionless) an let μ $[J \ kg^{-1}]$ be the heat of (the present) reaction. Now, the production of heat per unit of volume and time Q will be proportional to the speed of the reaction $\dfrac{d\alpha}{dt}$, and since $\dfrac{d\alpha}{dt}$ is negative and Q is positive, we find

(we assume ρ remains constant)

$$(1.5) \qquad Q = -\rho\mu \, \frac{d\alpha}{dt}.$$

For simplicity we consider only a single first-order reaction with one rate-constant $\overline{A}$ $[s^{-1}]$. Then, because of the classical Arrhenius law, we have the following rate-equation

$$(1.6) \qquad \frac{d\alpha}{dt} = -\overline{A} \, \alpha \, e^{-E/RT}$$

with

$$(1.7) \qquad \left\{ \begin{array}{l} E \text{ activation energy (needed to get} \\ \quad \text{the reaction started)} \; [J \; kg^{-1}] \\ R \text{ universal gas constant per unit} \\ \quad \text{of mass } [J \; kg^{-1} \; K^{-1}]. \end{array} \right.$$

Combining (1.6) and (1.5) we derive for Q:

$$(1.8) \qquad Q = \rho \, \mu \, \overline{A} \, \alpha(t) \, e^{-E/RT(x,t)}.$$

In the above expression for Q, the parameters $\overline{A}$, E and μ are the unknown parameters which describe the reaction. Further on in this paper we will outline a method for obtaining these (that is, their non-dimensional versions) out of fig. (1.3).

If we substitute (1.5) into (1.3), we get, together with (1.6)

$$(1.9) \qquad \rho c \, \frac{\partial T}{\partial t} = \lambda \, \frac{\partial^2 T}{\partial x^2} - \rho\mu \, \frac{\partial \alpha}{\partial t} \quad \text{(heat balance)}$$

$$(1.10) \qquad \frac{\partial \alpha}{\partial t} = -\overline{A} \, \alpha(t) \, e^{-E/RT} \quad \text{(Arrhenius law)}.$$

In order to solve (1.9) and (1.10) we need 4 boundary conditions, 3 for T and 1 for α. Since no reaction has taken place at $t = 0$ we have

$$(1.11) \qquad \alpha(0) = 1.$$

Because of symmetry-considerations we have

$$(1.12) \qquad \frac{\partial T}{\partial x}(0,t) = 0 \quad (t \geq 0).$$

Furthermore, since the furnace is off for $t \leq 0$ we assume

$$(1.13) \qquad T(x,0) = T_0 \quad -L \leq x \leq L$$

where T_0 is the temperature of the environment. For the heating due to the furnace at $x = \pm L$ we assume the heat flux to be proportional to the difference of the temperature at the end of the sample $T(x,L)$ and the temperature of the furnace $T_F(t)$

(1.14) $\dfrac{\partial T}{\partial x}(L,t) = -H(T - T_F(t))$ $(t \ge 0)$

with H $[J\,m^{-2}\,s^{-1}\,K^{-1}]$ a known heat transfer coefficient. If we substitute (1.1) in (1.14) we derive

(1.15) $\dfrac{\partial T}{\partial x}(L,t) = -H(T - T_0 - \beta t).$

§1.3. The non-dimensional equations

Before solving the problem (1.9) and (1.10), together with the boundary-conditions (1.11)-(1.15), we first normalize the problem, scaling the variables x with L, t with conduction time $\dfrac{L^2 \rho c}{\lambda}$ and

$T - T_0$ with $\dfrac{\mu}{c}$. We then get the non-dimensional versions of (1.9)-(1.15) (without ambiguity the same symbols have been used)

(1.16) $\dfrac{\partial T}{\partial t} = \dfrac{\partial^2 T}{\partial x^2} - \dfrac{\partial \alpha}{\partial t}$ $0 < x < 1$, $t > 0$ (heat equation)

(1.17) $\dfrac{\partial \alpha}{\partial t} = -A^*\,\alpha\,\exp[-\{\varepsilon(1 + \delta T)\}^{-1}]$ $(t > 0)$ (Arrhenius law)

(1.18) $\alpha(0) = 1$

(1.19) $T(x,0) = 0$ $0 \le x \le 1$

(1.20) $\dfrac{\partial T}{\partial x}(0,t) = 0$ $t \ge 0$

(1.21) $\dfrac{\partial T}{\partial x}(1,t) = -h(T - \omega t)$ $t \ge 0$

where

(1.22) $\begin{cases} A^* = \dfrac{L^2 \rho c \bar{A}}{\lambda} \\[2ex] \varepsilon = \dfrac{R T_0}{E} \\[2ex] \delta = \dfrac{\mu}{T_0 c} \\[2ex] h = \dfrac{HL}{\lambda} \\[2ex] \omega = \dfrac{\rho c^2 L^2 \beta}{\mu \lambda}. \end{cases}$

In stead of the 11 dimensional parameters $\rho, c, \lambda, \mu, \bar{A}, E, R, H, \beta, T_0$ and L we now only have 5

non-dimensional parameters $A^*, \varepsilon, \delta, h$ and ω. These parameters are the so called essential parameters of the problem. Since $\rho, c, \lambda, R, H, \beta, L$ and T_0 are known, $\mu, \bar{A}$ and E unknown (for these parameters had to be determined) parameters, h is a known, whereas A^*, ε and δ are unknown parameters. However, if we are able to determine A^*, ε and δ, then we also by (1.22) have determined $\bar{A}, \varepsilon$ and μ. It is our task now to determine the parameters A^*, ε and δ. The remaining parameter ω is a unknown parameter, but also a function of β. Since we can influence the temperature T_F of the furnace, we can vary the parameter β and make it, and therefore also ω, as small as we want, say $\omega \to 0$. We now consider the implications of a situation in which $\omega \ll 1$, that is, the furnace is only slowly heated compared with the conduction time $\dfrac{L^2 \rho c}{\lambda}$.

For the furnace heating term to appear the equations in the limit $\omega \to 0$ (cf. 1.21), time has to be rescaled so we finally write $\tau = \omega t$ to obtain the following boundary value problem

$$(1.23) \qquad \frac{\partial^2 T}{\partial x^2} = \omega \left[\frac{\partial T}{\partial \tau} + \frac{\partial \alpha}{\partial \tau} \right] \quad 0 < x < 1, \; \tau > 0$$

$$(1.24) \qquad \frac{\partial \alpha}{\partial \tau} = -\bar{A} \, \alpha \exp[-\{\varepsilon(1 + \delta T)\}^{-1}] \quad \tau > 0$$

$$(1.25) \qquad \alpha(0) = 1$$

$$(1.26) \qquad T(x, 0) = 0 \quad 0 \le x \le 1$$

$$(1.27) \qquad \frac{\partial T}{\partial x}(0, \tau) = 0 \quad t \ge 0$$

$$(1.28) \qquad \frac{\partial T}{\partial x}(1, \tau) = -h(T - \tau) \quad \tau \ge 0$$

where

$$(1.29) \qquad \bar{A} = A^* / \omega.$$

To retain a non-trivial solution for α, we require that $\bar{A}$ is $O(1)$, i.e. because ω is small, A^* is small (if $\bar{A} \gg 1$ then $\dfrac{d\alpha}{d\tau} \ll 0$, that is, the reaction is too fast and if $\bar{A} \ll 1$, then $\dfrac{d\alpha}{d\tau} \cong 0$, together with (1.25) which implies that there is no reaction at all).

§1.4. Regular asymptotic expansions

We now exploit the smallness of ω by writing T and α in a regular asymptotic expansion. That is, we write

$$(1.30) \qquad T = T_0(x, \tau) + \omega T_1(x, \tau) + O(\omega^2)$$

and

(1.31) $\alpha = \alpha_0(\tau) + O(\omega)$.

We substitute (1.30) and (1.31) in (1.23)-(1.28) and by equating powers of ω, we get relations for T_0, T_1 and α_0.

For $T_0(x, \tau)$ we find:

(1.32) $\dfrac{\partial^2 T_0}{\partial x^2} = 0$ $0 < x < 1$

(1.33) $T_0(x, 0) = 0$ $0 \leq x \leq 1$

(1.34) $\dfrac{\partial T_0}{\partial x}(0, \tau) = 0$ $\tau \geq 0$

(1.35) $\dfrac{\partial T_0}{\partial x}(1, \tau) = -h(T_0 - \tau)$ $\tau \geq 0$.

Hence

(1.36) $T_0(x, \tau) = \tau$.

Since

$$\exp\left[-1/\varepsilon(1 + \delta(T_0 + \omega T_1))\right] = \exp\left[-\{\varepsilon(1 + \delta T_0)\}^{-1}\right] + O(\omega)$$

we find for α_0

(1.37) $\dfrac{\partial \alpha_0}{\partial \tau} = -\bar{A}\, \alpha_0 \exp\{-1/\varepsilon(1 + \delta\tau)\}$

(1.38) $\alpha_0(0) = 1$.

Hence

(1.39) $\alpha_0(\tau) = \exp\{-\bar{A} \int\limits_0^\tau \exp\{-1/\varepsilon(1 + \delta\tau'))\}\, d\tau'\}$.

For T_1 we derive

(1.40) $\dfrac{\partial^2 T_1}{\partial x^2} = 1 - \bar{A}\, \alpha_0 \exp\{-1/\varepsilon(1 + \delta\tau)\}$

(1.41) $\dfrac{\partial T_1}{\partial x}(0, \tau) = 0$ $(\tau \geq 0)$

(1.42) $\dfrac{\partial T_1}{\partial x}(1, \tau) = -h\, T_1(1, \tau)$ $\tau \geq 0$

(1.43) $T_1(x, 0) = 0$ $0 \leq x \leq 1$.

However, we are not able to find a solution that satisfies (1.40)-(1.43). If we drop (1.43) we find the following expression for T_1

$$(1.44) \qquad T_1(x,\tau) = 1 - \bar{A}\ \alpha_0(\tau)\ \exp\{-[\varepsilon(1+\delta\tau)]^{-1}\} \left\{ \frac{x^2-1}{2} - \frac{1}{h} \right\}.$$

As already said, near $\tau = 0$ the boundary condition $T_1 = 0$ has not been satisfied. It is however not of great interest since, for small τ, the reaction has hardly started. The question of interest is whether equation (1.44) gives indeed a curve for T at $x = 0$ of the general form shown in fig. 1.3. Set

$$(1.45) \qquad f(\tau) = T(0,\tau) - \tau$$

$$(1.46) \qquad F(\tau) = 1 - \bar{A}\ \alpha_0(\tau)\ \exp\{-1/\varepsilon(1+\delta\tau)\}.$$

Then

$$(1.47) \qquad f(\tau) = -\omega \left[\frac{1}{2} + \frac{1}{h} \right] F(\tau).$$

Define

$$(1.48) \qquad \psi(\tau) = \frac{\delta}{\varepsilon}\ (1+\delta\tau)^{-2}$$

$$(1.49) \qquad \phi(\tau) = \bar{A}\ \exp\{-1/\varepsilon(1+\delta\tau)\}.$$

So, ψ is strictly decreasing and ϕ is strictly increasing.
We now have the following relationship between ψ, ϕ and f'

$$(1.50) \qquad \mathrm{sgn}(f'(\tau)) = \mathrm{sgn}(\psi(\tau) - \phi(\tau)).$$

So, if $\phi(0) \geq \psi(0)$, $f'(\tau) \leq 0$ for all τ, that is, $f(\tau)$ strictly decreasing: the curve for T at $x = 0$ is not of the general form shown in fig. 1.3. Therefore, $\phi(0) < \psi(0)$, that is

$$(1.51) \qquad \bar{A} < \frac{\delta}{\varepsilon} \exp\left[\frac{1}{\varepsilon} \right].$$

Now, there is exactly one $\tau^* \geq 0$, so that $f'(\tau^*) = 0$ and

$$(1.52) \qquad \begin{cases} f'(\tau) > 0 \ , \ 0 \leq \tau < \tau^* \\ f'(\tau) < 0 \ , \ \tau > \tau^* \end{cases}$$

so that $f(\tau)$ is maximal for $\tau = \tau^*$, that is

$$(1.53) \qquad \forall \tau \geq 0 \ [T(0,\tau) - \tau \leq T(0,\tau^*) - \tau^*].$$

In order to obtain fig. 1.3 $f(0)$ should be non-negative, that is

$$\bar{A} \geq \exp\left[\frac{1}{\varepsilon} \right].$$

Together with (1.51) we thus have

$(1.54) \qquad \exp\left[\dfrac{1}{\varepsilon}\right] \le \bar{A} < \dfrac{\delta}{\varepsilon}\exp\left[\dfrac{1}{\varepsilon}\right].$

Therefore

$(1.55) \qquad \delta > \varepsilon.$

Furthermore, $f(\infty)$ should be non-negative, that is

$(1.56) \qquad \bar{A}\,\exp[-\bar{A}\displaystyle\int_0^\infty \exp\left[-\dfrac{1}{\varepsilon(1+\delta u)}\right]\,du] \ge 1.$

So if, $\bar{A}$, δ and ε are chosen so that they satisfy (1.54)-(1.56), we obtain the non-dimensional version of the derived temperature profile at $x = 0$. Now, given the dimensional temperature profile of fig. 1.3, how can we gather from it its non-dimensional version? We set to work in the following way: To make a distinction between the dimensionful and non-dimensional temperatures we indicate the dimensionless temperature of the sample by $\theta(\xi,\tau)$ and the temperature of the furnace by $\theta_F(\tau)$, where $\xi = \dfrac{x}{L}$ and $\tau = \dfrac{\omega\lambda}{L^2\rho c}\,t$.

Between $T(x,t)$ and $\theta(\xi,\tau)$, $T_F(t)$ and $\theta_F(t)$ we now have the following relationship

$(1.57) \qquad \theta(\xi,\tau) = \dfrac{c}{\mu}\,(T(L\,\xi,\,\dfrac{L^2\rho c\,\tau}{\omega\lambda}) - T_0)$

$(1.58) \qquad \theta_F(\tau) = \dfrac{c}{\mu}\,(T_F\left[\dfrac{L^2\rho c\,\tau}{\omega\lambda}\right] - T_0) = \tau.$

So, if we have at our disposal figure (1.3) we transform it into its non-dimensional version, by substituting the straight line $\theta_F(\tau) = \tau$ for the straight line $T_F(t) = T_0 + \beta$ and by substituting $\theta(0,\tau) = \dfrac{c}{\mu}\,\{T(0,\dfrac{L^2\rho c\,\tau}{\omega\lambda}) - T_0\}$ for the curve $T(0,t)$. Further on t_{max} corresponds with $\tau_{max} = t_{max}\dfrac{L^2\rho c}{\omega L}$ and T_{max} agrees with $\theta_{max} = \theta(0,\tau_{max}) = \dfrac{c}{\mu}\,(T(0,t_{max}\dfrac{L^2\rho c}{\omega\lambda}) - T_0)$.

§1.5. The identification of the parameters $\bar{A}$, E and μ

Given the non-dimensional version of fig. (1.3), we now show how we can use it to determine the unknown constants $\bar{A}$, δ and ε. See also fig. (1.4).

Since $\tau^* = \tau_{max}$, we have, since $f'(\tau^*) = 0$, $\psi(\tau_{max}) = \phi(\tau_{max})$, that is

$(1.59) \qquad \dfrac{\delta}{\varepsilon}\,(1+\delta\,\tau_{max})^{-2} = \bar{A}\,\exp\{-[\varepsilon(1+\delta\tau_{max})]^{-1}\}.$
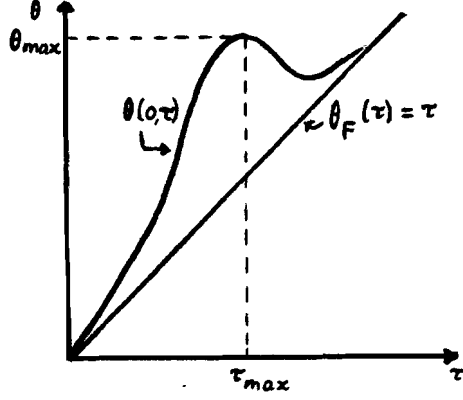
Fig. (1.4). The non-dimensional temperature profile of fig. 1.3.

Next, since $f(\tau)$ is maximal for $\tau = \tau_{max}$ we have

$$(1.60) \qquad -\omega \left[\frac{1}{2} + \frac{1}{h} \right] (1 - \bar{A}\ \alpha_0(\tau_{max})\ \exp\{-[\varepsilon(1 + \delta\tau_{max})]^{-1}\} = \theta_{max} - \tau_{max}$$

where

$$(1.61) \qquad \alpha_0(\tau_{max}) = \exp\{-\bar{A} \int_0^{\tau_{max}} \exp\{-[\varepsilon(1 + \delta u)]^{-1}\}\ du\ \}.$$

Finally, we can use the surface O between $\theta(0,\tau)$ and $\theta_F = \tau$ to get a third relation, connecting $\bar{A}$, ε and δ. We derive

$$(1.62) \qquad O = \int_0^\infty f(\tau)\ d\tau = -\omega \left[\frac{1}{2} + \frac{1}{h} \right] \int_0^\infty [1 - \bar{A}\ \alpha_0(\tau)\ \exp\{-[\varepsilon(1 + \delta\tau)]^{-1}\}\ d\tau$$

where

$$(1.63) \qquad O = \int_0^\infty \{\theta(0,\tau) - \tau\}\ d\tau.$$

If we have solved δ, ε and $\bar{A}$ out of (1.59), (1.60) and (1.62) then we derive for μ, E and $\bar{A}$

$$(1.64) \qquad \bar{A} = \frac{A^* \lambda}{L^2 \rho c} = \frac{\omega \bar{A} \lambda}{L^2 \rho c}$$

$$(1.65) \qquad E = \frac{RT_0}{\varepsilon}$$

$$(1.66) \qquad \mu = T_0\, c\, \delta.$$

Let us now return to expression (1.39). The relation for $\alpha_0(\tau)$ and hence the relation for $T_1(x,t)$ in (1.44) can be simplified (in such a way that T at $x = 0$ still will have the desired profile), in the case of a large activation energy E and heat of reaction μ, that is, ε and δ both small. Since

(1.67) $\int_0^\tau \exp[-1/\varepsilon(1+\delta u)]\, du = \frac{\varepsilon}{\delta} \exp\left[-\frac{1}{\varepsilon}\right] \{\exp\left[\frac{\delta}{\varepsilon}\tau\right] - 1\} \{1 + O\left[\frac{\delta^2}{\varepsilon}\right]\}$

we find

(1.68) $\alpha_0(\tau) \cong \exp[-\bar{A} \exp\left[-\frac{1}{\varepsilon}\right] \frac{\varepsilon}{\delta} \{\exp\left[\frac{\delta\tau}{\varepsilon}\right] - 1\}]$.

Analogously to (1.47) we derive

(1.69) $T(0,\tau) - \tau = \omega\left[\frac{1}{2} + \frac{1}{h}\right] - f(\tau)$

where

(1.70) $f(\tau) = \bar{A}\, \alpha_0 \exp(-1/\varepsilon(1+\delta\tau)) - 1$.

Differentiating (1.70) we get

(1.71) $f'(\tau) = \bar{A} \exp(-1/\varepsilon(1+\delta\tau))\, g(\tau)$

where

(1.72) $g(\tau) = \alpha_0'(\tau) + \delta/\varepsilon(1+\delta\tau)^{-2}\, \alpha_0(\tau)$.

Substituting expression (1.37) in (1.72) we derive

(1.73) $g(\tau) = \alpha_0(\tau)\, h(\tau)$

where

(1.74) $h(\tau) = -\bar{A} \exp(-1/\varepsilon(1+\delta\tau)) + \delta/\varepsilon(1+\delta\tau)^{-2}$.

Since

(1.75) $\exp(-1/\varepsilon(1+\delta\tau)) = \exp(-1/\varepsilon(1-\delta\tau+O(\delta^2)))$

$$= \exp(-1/\varepsilon) \exp\left[\frac{\delta\tau}{\varepsilon}\right] (1+O\left[\frac{\delta^2}{\varepsilon}\right])$$

and

(1.76) $\frac{\delta}{\varepsilon}(1+\delta\tau)^2 = \frac{\delta}{\varepsilon}(1+O(\delta))^2 = \frac{\delta}{\varepsilon}(1+O(\delta)) = \frac{\delta}{\varepsilon} + O\left[\frac{\delta^2}{\varepsilon}\right]$

for $h(\tau)$ we derive:

(1.77) $h(\tau) = -\bar{A} \exp(-1/\varepsilon) \exp\left[\frac{\delta\tau}{\varepsilon}\right] + \frac{\delta}{\varepsilon} + O\left[\frac{\delta^2}{\varepsilon}\right]$

Set

(1.78) $\phi(\tau) = \bar{A} \exp(-1/\varepsilon) \exp\left[\dfrac{\delta\tau}{\varepsilon}\right].$

Substituting (1.78) into (1.77) we get

(1.79) $h(\tau) \equiv \dfrac{\delta}{\varepsilon} - \phi(\tau).$

Furthermore

(1.80) $\operatorname{sgn}\{\dfrac{d}{d\tau}(T(0,\tau) - \tau)\} = \operatorname{sgn}\left[\dfrac{\delta}{\varepsilon} - \phi(\tau)\right].$

Note that ϕ is an increasing function of τ. So if $\phi(0) \geq \dfrac{\delta}{\varepsilon}$, then $\operatorname{sgn}\{\dfrac{d}{d\tau}(T(0,\tau) - \tau)\} \leq 0$ for all $\tau \geq 0$, that is $T(0,\tau) - \tau$ is a decreasing function of τ, and therefore $T(0,\tau) - \tau$ cannot have the desired profile.

Therefore we derive:

(1.81) $\phi(0) < \dfrac{\delta}{\varepsilon}.$

or, by using $\bar{A}$, δ and ε:

(1.82) $\bar{A} < \dfrac{\delta}{\varepsilon} \exp\left[\dfrac{1}{\varepsilon}\right]$ (cf. 1.51).

In this case, since

(1.83) $\lim_{\tau \to \infty} \phi(\tau) = 0$

we have

(1.84) $\exists!\, \tau_0 > 0\ [\forall \tau < \tau_0\ \{\dfrac{d}{d\tau}(T(0,\tau) - tau)\} > 0\ \wedge\ \forall t > \tau_0\ \{\dfrac{d}{d\tau}(T(0,\tau) - \tau)\} < 0]$

and therefore $T(0,\tau) - \tau$ is maximal for $\tau = \tau_0$. In this case τ_0 corresponds with τ_{max}, and by (1.80) we have:

(1.85) $\bar{A} \exp(-1/\varepsilon)\varepsilon \exp\left[\dfrac{\delta\tau_{max}}{\varepsilon}\right] = \delta.$

So, for τ_{max} we find

(1.86) $\tau_{max} = \dfrac{\varepsilon}{\delta} \ln\left[\dfrac{\delta}{\varepsilon A\, e^{-1/\varepsilon}}\right] = \dfrac{\varepsilon}{\delta} \ln \dfrac{\delta}{A\varepsilon} + \dfrac{1}{\delta}.$

Analogously to (1.60) we get

(1.87) $\omega\left[\dfrac{1}{2}+\dfrac{1}{h}\right]\ \{\bar{A}\ \alpha_0(\tau_{max})\ \exp\left[-\dfrac{1}{\varepsilon}\right]\ \exp\left[\dfrac{\delta\tau_{max}}{\varepsilon}\right]\ -1\}=\theta_{max}-\tau_{max}$

where

(1.88) $\alpha_0(\tau_{max})\cong\exp[-\bar{A}\ \exp\left[-\dfrac{1}{\varepsilon}\right]\ \dfrac{\varepsilon}{\delta}\ \{\exp\left[\dfrac{\delta\tau_{max}}{\varepsilon}\right]\ -1\}].$

Finally, analogously to (1.62) we get:

(1.89) $\omega\left[\dfrac{1}{2}+\dfrac{1}{h}\right]\ \displaystyle\int_0^\infty\ \{\bar{A}\ \alpha_0(\tau)\ \exp\left[-\dfrac{1}{\varepsilon}\right]\ \exp\left[\dfrac{\delta\tau}{\varepsilon}\right]\ -1\}\ d\tau=\int_0^\infty\ \{\theta(0,\tau)-\tau\}\ d\tau.$

So, if $\delta\ll 1$ and $\varepsilon\ll 1$ we have the relations (1.86)-(1.89), by which $\bar{A}$, δ and ε can be obtained.

2. The phenomenon of self-ignition

§2.1. Introduction

In the last section we considered the temperature distribution $T(x,t)$ satisfying

$$(2.1) \qquad \rho c \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \rho \mu \bar{A} \, \alpha(t) \, e^{-E/RT}.$$

If $T = T_0 + T_1$ with T_0 a constant and $|T_1| \ll T_0$ then

$$(2.2) \qquad -\frac{E}{RT} \sim -\frac{E}{RT_0} + \frac{ET_1}{RT_0^2}$$

hence,

$$(2.3) \qquad e^{-E/RT} \sim e^{-E/RT_0} \, e^{ET_1/RT_0^2}.$$

Now, if α changes very slowly, then (2.1) is approximately equal to

$$(2.4) \qquad \rho c \frac{\partial T_1}{\partial t} = \lambda \frac{\partial^2 T_1}{\partial x^2} + \bar{A} \, e^{\bar{b} T_1},$$

form some constants $\bar{A}, \bar{b}$.

This situation (i.e. $T = T_0 + T_1$ with $|T_1| \ll T_0$) can be compared with the storage of grain. The grain, at an approximately constant temperature, reacts very slowly but sometimes starts burning. This phenomenon of self-ignition will be considered in this section.

§2.2. Heat equation

Instead of considering a furnace that is heated at a uniform rate β so that $T_f(t) = T_0 + \beta t$, where β is known and can be varied, we now consider a furnace in which the temperature T_f of the furnace is constant at both ends (see figure 2.1).
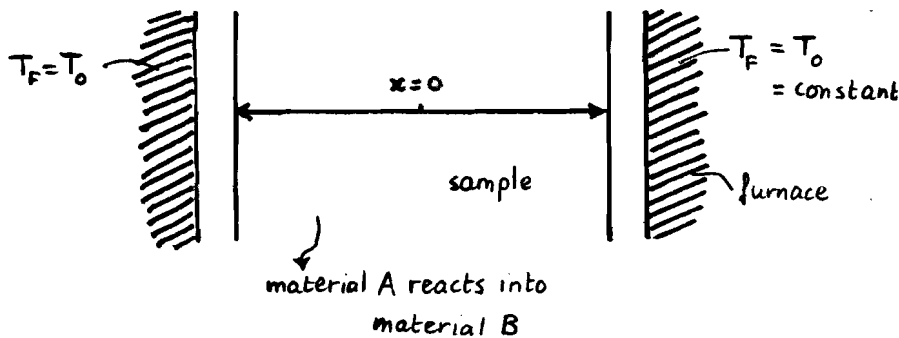

material A reacts into
material B

Fig. (2.1)

By the following heat equation we describe the temperature of the chemical sample

(2.5) $\quad \rho c \dfrac{\partial T}{\partial t} = \lambda \dfrac{\partial^2 T}{\partial x^2} + Q$

where Q represents the heat from the reaction.

We consider the case that Q is given by

(2.6) $\quad Q = -\rho \mu \dfrac{d\alpha}{dt}$

where ρ is the density, μ is the reaction heat and $\alpha = \alpha(t)$ is the fraction of material A that remains. Initially, $\alpha(0) = 1$ and finally $\alpha(\infty) = 0$.

Now, instead of Arrhenius law, we model the rate equation as follows

(2.7) $\quad \dfrac{\partial \alpha}{\partial t} = -A\, e^{bT}$

where A is the rate constant and b is a constant. Hence

(2.8) $\quad \rho c \dfrac{\partial T}{\partial t} = \lambda \dfrac{\partial^2 T}{\partial x^2} + \rho \mu A\, e^{bT}$

with boundary conditions

$$T(L,t) = T_0 , \quad T(x,0) = T_0 , \quad \dfrac{\partial T}{\partial x}(0,t) = 0.$$

Scaling to get a non-dimensional form we put

$$x = L x^* , \quad T = T_0 + \dfrac{1}{b}\theta , \quad t = L^2 \dfrac{\rho c}{\lambda} t^*$$

$$c^2 = \dfrac{L^2 \rho \mu A b}{\lambda} e^{bT_0}.$$

Dropping $*$, we get the following non-dimensional heat-equation

(2.9) $\quad \dfrac{\partial \theta}{\partial t} = \dfrac{\partial^2 \theta}{\partial x^2} + c^2 e^{\theta} \quad , \theta = \theta(x,t)$

with boundary conditions

$$\theta(1,t) = 0 , \quad \theta(x,0) = 0 , \quad \dfrac{\partial \theta}{\partial x}(0,t) = 0.$$

Instead of solving equation (2.9), we are interested in the steady-state solutions of equation (2.9).

§2.3. Steady-state temperature

The steady-state temperature distribution satisfies

(2.10) $\theta''(x) + c^2 e^{\theta(x)} = 0$

with boundary conditions $\theta(1) = \theta'(0) = 0$.

We shall first show that if $\theta(0) = \theta_0$ and $s_0^2 = e^{\theta_0}$, s_0 satisfies

(2.11) $s_0 = \cosh\left[\dfrac{c\,s_0}{\sqrt{2}}\right]$.

Proof: Notice that $\theta''(x) < 0$ on $[0,1]$, so $\theta(x)$ is concave, and

$$\theta'(x) = \theta'(0) + \int_0^x \theta''(\xi)\,d\xi = -c^2 \int_0^x e^{\theta(\xi)}\,d\xi < 0 \quad \text{on } [0,1]\,,$$

hence $\theta(x)$ is decreasing on $[0,1]$.

Multiplying on both sides with θ', integration yields

(2.12) $(\theta'(x))^2 = 2\,c^2(s_0^2 - e^{\theta(x)})$.

We know that $\theta'(x) < 0$ on $[0,1]$. Hence

$$\theta'(x) = -c \cdot \sqrt{2}\ \sqrt{s_0^2 - e^{\theta(x)}}$$

and by separation of variables we obtain:

(2.13) $\displaystyle \int_0^{\theta_0} \frac{d\theta}{\sqrt{s_0^2 - e^{\theta}}} = c\sqrt{2}$.

Writing $s^2 = e^{\theta}$ and so $d\theta = \dfrac{2}{s}\,ds$ and substituting this into (2.12) we obtain:

$$\int_1^{s_0} \frac{ds}{s\sqrt{s_0^2 - s^2}} = \frac{c}{\sqrt{2}}$$

$$\Leftrightarrow \frac{1}{s_0}\,[\ln(s_0 + \sqrt{s_0^2 - 1}\,)] = \frac{c}{\sqrt{2}}$$

$$\Leftrightarrow \ln(s_0 + \sqrt{s_0^2 - 1}\,) = \frac{c s_0}{\sqrt{2}}$$

$$\Leftrightarrow \operatorname{arccosh} s_0 = \frac{c s_0}{\sqrt{2}}$$

$$\Leftrightarrow \quad s_0 = \cosh\left[\frac{cs_0}{\sqrt{2}}\right].$$

□

Now, look at the equation (2.11). Define (for $c > 0$):

$$f_c : \mathbb{R} \to \mathbb{R}, \quad f_c(\eta) = \cosh(\eta) - \frac{\sqrt{2}}{c}\,\eta.$$

As can be seen in figure 2.2, there is a unique c^* for which f_c has exactly one zero, say η^*. These c^*, η^* are determined by

$$\begin{cases} \cosh(\eta^*) - \dfrac{\sqrt{2}}{c^*}\,\eta^* = 0 \\[2mm] \sinh(\eta^*) - \dfrac{\sqrt{2}}{c^*} = 0. \end{cases}$$

By eliminating c^*, $\eta^*\tanh\eta^* = 1$ and one may verify that $\eta^* \approx 1.198$, hence $c^* \approx 0.939$
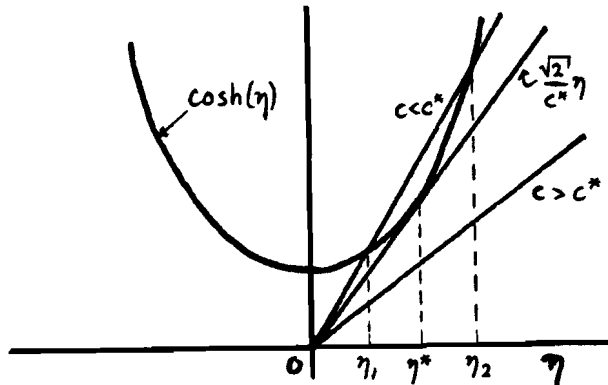

Fig. (2.2)

For $0 < c < c^*$, f_c has two zeros say η_1, η_2 where $0 < \eta_1 < \eta^* < \eta_2$. This means that for $0 < c < c^*$ there are two steady-state solutions (with different θ_0). We shall look at this problem in §2.4 and in the appendix.

For $c > c^*$ we have no steady-state solution. Let us look at the partial differential equation (2.9), when $c > c^*$. The following may give a physical interpretation what will happen in this area and so may explain why a steady-state solution does not exist for large c. In equation (2.9) the term $\dfrac{\partial^2\theta}{\partial x^2}$ represents the amount of heat discharged to the surroundings.

The second term on the right represents the heat from the reaction when material A turns into material B. When $c > c^*$ it means that $\dfrac{\partial\theta}{\partial t} > 0$, that is, there will be more heat produced then

there is heat discharged. Hence the temperature will increase and the reaction will be faster, with the result that the temperature increases further and the reaction gets an explosive character. We call this effect self-ignition.

§2.4. Stability of steady-state solutions

In this paragraph we shall look at the steady-state solutions for $c < c^*$. When $c < c^*$ we already mentioned that there are two steady-state solutions for which $s_0 = \cosh\left[\dfrac{cs_0}{\sqrt{2}}\right]$ with $s_0 = e^{\theta(0)}$.

It is interesting to know whether these solutions are stable or not.

First we shall derive an explicit formula of a steady-state solution $\theta(x)$. As we have seen

$$\theta'(x) = -c\sqrt{2} \cdot \sqrt{s_0^2 - e^{\theta(x)}}.$$

Separation of variables yields

$$\int_{\theta}^{\theta_0} \frac{1}{\sqrt{s^2 - e^{\phi}}}\, d\phi = c\sqrt{2}\, x.$$

Put $s^2 = e^{\phi}$, $d\phi = \dfrac{2}{s}\, ds$. Then

$$\int_{e^{\theta/2}}^{s} \frac{1}{s\sqrt{s_0 - s^2}}\, ds = \frac{cx}{\sqrt{2}}$$

$$\Longleftrightarrow \ln\left[\frac{s_0 + \sqrt{s_0^2 - e^{\theta}}}{e^{\theta/2}}\right] = \frac{cs_0 x}{\sqrt{2}}$$

$$(2.14) \qquad \Rightarrow \theta(x) = -2\ln\left[\frac{1}{s_0}\cosh\left[\frac{cs_0 x}{\sqrt{2}}\right]\right]$$

with boundary conditions $\theta(0) = \theta_0$, $\theta(1) = 0$, $\theta'(0) = 0$.

In general, one wants to know whether a chemical reaction has an explosive character or not. It is therefore interesting to know under what conditions the reaction will be stable. An unstable reaction is useless and is a great waste of money. We will now investigate stability of $\theta(x,t)$.
Write

$$(2.15) \qquad \theta(x,t) = \psi(x) + \varepsilon \cdot f(x,t), \quad \text{with } |\varepsilon| \ll 1$$

where $\psi(x)$ is a steady-state solution.
Putting $\theta(x,t)$ into equation (2.9) gives the linearized equation for $f(x,t)$:

(2.16) $\dfrac{\partial f}{\partial t} = c^2 f e^{\psi} + \dfrac{\partial^2 f}{\partial x^2}$

where $f = f(x,t)$ and $\psi = \psi(x)$.
The boundary conditions are

$$f(1,t) = 0, \quad f(x,0) = f_0(x), \quad \dfrac{\partial f}{\partial x}(0,t) = 0.$$

Writing $f(x,t) = g(x)\, h(t)$ gives

(2.17) $\dfrac{h'}{h} = c^2 e^{\psi} + \dfrac{g''}{g}.$

Now, observe that the left-hand side of (2.17) is a function of t only, while the right-hand side of (2.17) is a function of x only. This implies that

$$\dfrac{h'}{h} = -\lambda \quad \text{and} \quad c^2 e^{\psi} + \dfrac{g''}{g} = -\lambda$$

for some constant λ.
Hence

$$h(t) = c_1 e^{-\lambda t}$$

(2.18) $g''(x) + (c^2 e^{\psi(x)} + \lambda)\, g(x) = 0, \quad g(1) = g'(0) = 0.$

At this point, the constant λ is arbitrary. However, we look for a nontrivial solution $g(x)$ of the boundary-value problem (2.18). In fact, (2.18) is a self-adjoint eigenvalue problem (a Sturm-Liouville problem) and there exists a countable sequence of real eigenvalues λ_n.
If $\lambda_n > 0$ for all n then the steady-state solution will be asymptotically stable in L_2-norm. (See also appendix.)

We will look closer at the equation

(2.19) $-g''(x) + w(x)\, g(x) = \lambda\, g(x)$

where $w(x) = -\left[\dfrac{c s_0}{\cosh(\dfrac{c s_0 x}{\sqrt{2}})} \right]^2$, $g(1) = g'(0) = 0.$

Note $(f,g) = \displaystyle\int_0^1 f(x)\, g(x)\, dx.$

Multiplying (2.19) on both sides with g we get:

$$-g g'' + w g^2 = \lambda g^2 \;\Rightarrow\; (g', g') + (wg, g) = \lambda(g,g)$$

$$g(x) = -\int_x^1 g'(\eta)\, d\eta \quad \Rightarrow \quad g^2(x) = [\int_x^1 g'(\eta)\, d\eta]^2.$$

With Cauchy-Schwarz we get

$$g^2(x) \le (1-x)\int_x^1 (g'(\eta))^2\, d\eta \le (1-x)\, (g',g')$$

$$\Rightarrow \quad wg^2 \ge w(1-x)\, (g',g').$$

It follows

$$\lambda = \frac{1}{(g,g)}\, [(g',g') + (wg,g)] \ge \frac{(g',g')}{(g,g)}\, [1 + \int_0^1 w(x)\,(1-x)\, dx].$$

Define

$$K := -\int_0^1 w(x)\,(1-x)\, dx \quad \Rightarrow \quad \lambda \ge 2(1-K).$$

The steady-state solution is stable if $\lambda > 0$, hence $K < 1$.
We notice that

$$K = \int_0^1 \left[\frac{cs_0}{\cosh(\frac{cs_0 x}{\sqrt{2}})} \right]^2 (x-1)\, dx = 2\ln[\cosh\left[\frac{cs_0}{\sqrt{2}}\right]]$$

(with the aid of partial integration and the fact that $\int \tanh(z)\, dz = \ln[\cosh(z)]$).
Define

$$\bar{K} : [0,\infty) \to [0,\infty), \quad \bar{K}(\eta) = 2\ln[\cosh(\eta)].$$

It is easily verified that $\bar{K}$ is a positive, monotone non-decreasing function and that $\bar{K}(\eta) < 1$ for $\eta < \ln(\sqrt{e} + \sqrt{e-1}) := \bar{\eta}$.

Now looking again at figure 2.2 in §2.3 and using the same notation, we notice that for $\bar{c} := \frac{\sqrt{2}}{e^{1/2}}\, \bar{\eta}$, $\eta_1 = \bar{\eta}$. So, for all $c < \bar{c}$, $\eta_1 < \bar{\eta}$.

Finally, we conclude that for all c, $0 < c < \bar{c} = \frac{\sqrt{2}}{e^{1/2}}\, \bar{\eta}$, $\bar{c} \approx 0.93 < c^*$ the steady-state solution with θ_0 corresponding to η_1 is asymptotically stable for the linearized equation (2.16).

It remains to prove that stability of the linearized equation implies stability of the non-linearized equation under certain conditions.
A more precise approach of stability for $c_1 < c^*$ and instability for $c_2 > c^*$ will be given in the appendix.

3. Recommendations on further research

The reader may have noticed that no numerical results appear in this paper.

Some interesting work that might be done is:

* the identification of the parameters mentioned in chapter one

* a numerical solution of the reaction equation itself

* using the latter result to test the former: choose parameter values, solve the reaction equation (verifying that $T(0,t)$ has the desired form), then recover the parameters.

The last suggestion might indicate how far the small-ω asymptotics can be pushed.

Appendix

In order to prove asymptotic stability of a steady-state solution in §2.4, we encountered the eigenvalue-problem

$$(A1) \quad \begin{cases} g'' + w(x)g = -\lambda g \\ g(1) = g'(0) = 0 \end{cases}$$

$$\left(w(x) = (cs_0)^2 \cosh^{-2} \left[\frac{cs_0 x}{\sqrt{2}} \right] \right)$$

and we gave a condition for $\lambda_1, \lambda_2,...$ to be positive. In this appendix we present a way to determine the sign of each eigenvalue λ_i of the problem (A1).

We look for a solution $g(x,\lambda)$ of

$$(A2) \quad \begin{cases} \dfrac{\partial^2 g}{\partial x^2} + (w(x) + \lambda)g = 0 \\ g(0,\lambda) = 1, \quad \dfrac{\partial g}{\partial x}(0,\lambda) = 0. \end{cases}$$

We notice that λ is an eigenvalue of (A1) if and only if $g(x,\lambda)$ satisfies $g(1,\lambda) = 0$.

Using [Coddington & Levinson], page 212, 213 one can prove the following result:

- if $g(x,0)$ has no zeros in $(0,1]$, then there is no $\lambda < 0$ with $g(1,\lambda) = 0$

- if $g(x,0)$ has k zeros in $(0,1]$, then there exist exactly k values of λ, $\lambda_1 < \cdots < \lambda_k \leq 0$ with

$$g(1,\lambda_1) = \cdots = g(1,\lambda_k) = 0.$$

This means that the number of eigenvalues $\lambda_i \leq 0$ of (A1) is exactly the number of zeros of $g(x,0)$ in $(0,1]$.

In our case $g(x,0)$ satisfies (writing $\gamma := \dfrac{cs_0}{\sqrt{2}}$)

$$(A3) \quad \begin{cases} g'' + \dfrac{2\gamma^2}{\cosh^2(\gamma x)} g = 0 \\ g(0,0) = 1, \quad g'(0,0) = 0. \end{cases}$$

Putting $\bar{g}(t) := g(\tanh(\gamma x), 0)$ leads to

$$(A4) \quad \begin{cases} \dfrac{d}{dt}[(1 - t^2)\dfrac{d\bar{g}}{dt}] + 2\bar{g} = 0 \quad \text{(Legendre--equation)} \\ \bar{g}(0) = 1, \quad \bar{g}'(0) = 0 \end{cases}$$

and one may easily verify that $\bar{g}(t) = 1 - \frac{1}{2} \log \dfrac{1+t}{1-t}$, so $g(x,0) = 1 - \gamma x \tanh(\gamma x)$.

We notice that $g(1,0) = 1 - \gamma\tanh\gamma$, $x \mapsto x\tanh x$ is a monotonically increasing function on $[0,\infty)$, so we conclude that the eigenvalues λ_i of the eigenvalue problem (A1) satisfy

$$\begin{cases} 0 < \lambda_1 < \lambda_2 \cdots & \text{if } \gamma < \gamma^* \\ \lambda_1 < 0 < \lambda \cdots & \text{if } \gamma > \gamma^* \\ \text{where } \gamma^* \tanh\gamma^* = 1. \end{cases}$$

Finally, we notice that $\gamma^* = \eta^*$ (see §2.3), so the steady-state solution with θ_0 corresponding to η_1 is asymptotically stable while the steady-state solution with θ_0 corresponding to η_2 is unstable.

Ref.: [Coddington & Levinson]: E. Coddington and N. Levinson, *Theory of ordinary differential equations*, New York 1955.

Acknowledgement