Modelling of critical phenomena for ignition of metal particles

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Abstract. The singularly perturbed system of differential equations describing metal particle ignition is analyzed. Two general types of combustion reactions are recognized, namely subcritical and supercritical. It is shown that there exists a so-called critical regime, which separates domains of subcritical and supercritical regimes. The critical regime is modelled by the special phase trajectory of the system, which includes the repulsive part with slow variation of the temperature of a metal particle and the thickness of the oxide film. The asymptotic formulae for the calculation of critical values of the modified Semenov number are obtained in the cases of parabolic and cubic laws of oxidation kinetics.

1. Introduction
The paper is devoted to the investigation of critical phenomena for ignition of metal particles. Dynamics of heating, ignition, and combustion of metal particles has been widely studied over the past 50 years, and has been reviewed in [5, 16, 17], among others, and more recently in [18]. Ignition and combustion of metal particles are the issues important for various applications, including aerospace and chemical technologies, ground transportation, and industrial safety [1, 8, 10].

The use of metals as high–energy fuel additives is generally compromised by the formation of an oxide film that covers the fuel surface. This film prevents direct interaction between the metal and the gaseous oxidant. Hence, the kinetics laws of metal oxidation are different from the kinetics laws of heterogeneous reactions and depend on the physical properties and the thickness of the oxide film build-up on the metal surface [8, 17, 19]. Heat released on metal oxidation may causes fast self–heating of the metal particles at high temperature. Thus, metal ignition, and therefore the explosion, occurs as a result of thermal self–acceleration of the chemical reaction [4, 13]. In some cases, the heat released at oxidation of particles has time to be removed into the surroundings, and the ignition does not take place. Then the particle temperature reaches a maximum and decays to reach the initial gas temperature (subcritical regime). In other cases, heat released in the particle causes self–acceleration of the oxidation reaction, which leads to a rapid increase in particle temperature, thus causing ignition (supercritical regime) [3].

In this paper the existence of the critical regime, separating the domain of subcritical regimes from the domain of supercritical ones, is shown. Using the special asymptotic formulae [11] the conditions under which the critical regime takes place in the chemical system are obtained. That approach was applied in [2, 6, 7, 9] to model thermal explosion of gaseous reactants.
2. Mathematical model

Taking into consideration a uniform temperature distribution in a particle, a constant particle size and the constant physical properties of both gas and particle, the known dimensionless model of the process has the following form [8]:

\[
\gamma \frac{d\theta}{d\tau} = \varphi(\eta) \exp\left( \frac{\theta}{1 + \beta \theta} \right) - \frac{\theta}{\kappa},
\]

\[
\frac{d\eta}{d\tau} = \varphi(\eta) \exp\left( \frac{\theta}{1 + \theta \beta} \right),
\]

with initial conditions:

\(\eta(0) = 0, \quad \theta(0) = -\theta_i\).

Here \(\theta\) is the dimensionless temperature of a metal particle and

\[
\theta = \frac{(T - T_0)E}{RT_0^2},
\]

where \(T\) is the temperature of a metal particle, \(T_0\) is the gas temperature, \(E\) is the Arrhenius activation energy, \(R\) is the universal gas constant; \(\eta\) is the dimensionless related growth of the thickness of the oxide film and

\[
\eta = \frac{\delta - \delta_{in}}{\delta},
\]

where \(\delta\) is the oxide film thickness, \(\delta_{in}\) is the initial thickness of the film; \(\tau\) is dimensionless time; the parameters \(\beta\) and \(\gamma\) reflect the temperature sensitivity and the exothermicity of the reaction; \(\kappa\) is a modified Semenov number related to convection heat transfer; \(\varphi(\eta)\) is the kinetic function. This paper examines two forms of oxidation kinetics:

\[
\varphi(\eta) = (\eta + 1)^{-n}, \quad n = 1, 2,
\]

corresponding to the cases of parabolic and cubic laws, respectively.

The initial temperature of a metal particle is either lower than the gas temperature or equal to it. In the first case, corresponding to cold particles, we have \(\theta(0) = -\theta_i < 0\), and in the second one, when the metal particles and the gas are heated simultaneously during a very short time, \(\theta(0) = 0\).

The chemically relevant phase space \(\Delta\) of the system (1) is defined by

\[
\Delta := \{(\theta, \eta) \in \mathbb{R}^2 : \theta \geq -\theta_i, \eta \geq 0\}.
\]

It should be noted that the system (1) is similar to the dimensionless model of the thermal explosion of a gas [4, 13, 16, 19]. But in the thermal explosion theory the kinetic function is usually \(\varphi(\eta) = (\eta + 1)^n\), and \(\eta\) reflects the depth of a gas conversion.

In the case of very small particle size and significant initial thickness of the oxide film the parameter \(\gamma\) is small [8] and, hence, the system (1) is singularly perturbed [12, 15]. Thus, it is possible to apply the mathematical apparatus of singular perturbations for the investigation of the critical conditions for ignition of a metal particle in this case.
3. Case of parabolic law

In the case of a parabolic law of oxidation kinetics the system (1) has the form

\[ \gamma \frac{d\theta}{d\tau} = (\eta + 1)^{-1} \exp \left( \frac{\theta}{1 + \beta \theta} \right) - \frac{\theta}{\kappa}, \]

(2)

\[ \frac{d\eta}{d\tau} = (\eta + 1)^{-1} \exp \left( \frac{\theta}{1 + \theta \beta} \right), \]

with initial conditions

\[ \eta(0) = 0, \quad \theta(0) = -\theta_i. \]

(3)

If we put \( \gamma = 0 \) in the first equation of (2) we get the degenerate equation

\[ F(\eta, \theta, \kappa) = (\eta + 1)^{-1} \exp \left( \frac{\theta}{1 + \beta \theta} \right) - \frac{\theta}{\kappa} = 0 \]

(4)

which describes the slow curve

\[ S = \left\{ (\theta, \eta) : (\eta + 1)^{-1} \exp \left( \frac{\theta}{1 + \beta \theta} \right) - \frac{\theta}{\kappa} = 0 \right\} \]

of the system (2) (see, for example, [14]). The subset \( S^s \) (\( S^u \)) of \( S \) with

\[ \frac{\partial}{\partial \theta} F(\eta, \theta, \kappa) < 0 \ (> 0) \]

(5)

is called the attractive (repulsive) part of \( S \). A point \( A \) on \( S \) in which \( \partial F / \partial \theta = 0 \) is called the jump point [11, 14].

![Figure 1](image_url)

**Figure 1.** The form of the slow curve of the system (2): (a) for \( \kappa < \kappa_0 \), (b) for \( \kappa > \kappa_0 \), where \( \kappa_0 = (1 + \beta) / e, \ e = \exp(1) \).

We take \( \kappa \) as the control parameter with fixed \( \beta, \gamma \). For all \( \kappa \) the slow curve of the system (2) consists of two branches, which are separated by the asymptote \( \eta = -1 \), see Figure 1. Hence, the lower branch of \( S \) in \( (\theta, \eta) \)–plane is outside \( \Delta \). The second one has two jump points \( A_1 \) and \( A_2 \) with coordinates \( (\eta_1, \theta_1) \) and \( (\eta_2, \theta_2) \), respectively, where \( \theta_1, \theta_2 \) are the roots of the equation

\[ \theta - (1 + \beta \theta)^2 = 0, \]
i.e.,

\[
\theta_1 = \frac{1 - 2\beta - \sqrt{1 - 4\beta}}{2\beta^2}, \quad \theta_2 = \frac{1 - 2\beta + \sqrt{1 - 4\beta}}{2\beta^2},
\]

and

\[
\eta_1 = \frac{\kappa}{\theta_1} \exp\left(\frac{\theta_1}{1 + \beta\theta_1}\right) - 1, \quad \eta_2 = \frac{\kappa}{\theta_2} \exp\left(\frac{\theta_2}{1 + \beta\theta_2}\right) - 1.
\]

Hence, according to (4)–(7), the upper branch of the slow curve \(S\) consists of two attractive parts \(S^s_1\) and \(S^s_2\) and the repulsive one \(S^u\), where

\[
\begin{align*}
S^s_1 & := \{ (\theta, \eta) \in S : \eta > -1, \ 0 < \theta < \theta_1 \}, \\
S^s_2 & := \{ (\theta, \eta) \in S : \eta > -1, \ \theta > \theta_2 \}, \\
S^u & := \{ (\theta, \eta) \in S : \eta > -1, \ \theta_1 < \theta < \theta_2 \}.
\end{align*}
\]

Since the parameter \(\beta\) is small (for real chemical systems, see, for example, [8, 19]), from (6) we have \(\theta_1 = 1 + 2\beta + O(\beta^2), \theta_2 = \beta^{-2} (1 - 2\beta + O(\beta^2))\) as \(\beta \to 0\). Hence, the part \(S^s_2\) corresponds to a very high values of the metal temperature and this means in practice the destruction of the reactant vessel. So, to analyze the behavior of the system (2), we will concentrate our attention on \(S^s_1\) and \(S^u\) only.

![Figure 2. The slow curve of the system (2) for \(\beta = 0.01, \kappa = 0.2 < \kappa_0, \theta < 5\).](image-url)

In the case \(\kappa < \kappa_0 = (1 + \beta)/e\), where \(e = \exp(1)\), some part of set \(S^s_1\) of the slow curve lies below the \(\eta\)-axis, see Figures 1(a) and 2. The trajectory of the system starting from the initial point rapidly tends to \(S^s_1\) and then follows the attractive set \(S^s_1\) at the tempo of the slow variable, see Figure 3. This behavior corresponds to the slow regime with low temperatures (subcritical regime).

In the case \(\kappa > \kappa_0\) the branch of the slow curve with \(\eta > 0\) is situated above the \(\theta\)-axis entirely, see Figures 1(b) and 4. The trajectory of the system in this case, starting from the initial point, passes by the slow curve at the tempo of the fast variable. Theoretically the trajectory of (2) reaches the attractive set \(S^s_2\) of the slow curve and then follows it at the tempo of the slow variable up to the point \(A_2\). After this moment the trajectory loses its connection
Figure 3. (a) The slow curve (the thin line) and the trajectory (the thick line) of the system (2) for $\beta = 0.01$, $\gamma = 0.01$, $\kappa = 0.2$, $\theta_i = 0$. (b) The $\eta$– and $\theta$–components of the solution in the case of the slow regime for $\beta = 0.01$, $\gamma = 0.01$, $\kappa = 0.2$, $\theta_i = 0$.

Figure 4. The slow curve of the system (2) for $\beta = 0.01$, $\kappa = 0.5 > \kappa_0$, $\theta < 4$.

with the slow curve: a jump of the trajectory of the slow curve occurs. Then the trajectory rapidly tends to the attractive set $S^*_1$. However, due to a very high temperature the explosion causes long before the trajectory reaches $S^*_2$, see Figure 5. This behavior corresponds to the ignition (supercritical regime).

In the case $\kappa = \kappa_0$ we have $\eta_1 = 0$, see Figure 6. In a neighborhood of $\kappa_0$ it is possible to find the value $\kappa = \kappa^*$ corresponding to the critical regime. The trajectory of the system with $\kappa = \kappa^*$ starting from the initial point rapidly tends to a very small vicinity of the point $A_1$ and then follows the repulsive part $S^u$ of the slow curve, up to a point $J$ from which the solution “jumps” towards the attractive component $S^*_1$ and then follows it, see Figure 7(a).
Figure 5. (a) The trajectory of the system (2) for $\beta = 0.01$, $\gamma = 0.01$, $\kappa = 0.5$, $\theta_i = 0$. (b) The $\eta$– and $\theta$–components of the solution in the case of the ignition for $\beta = 0.01$, $\gamma = 0.01$, $\kappa = 0.5$, $\theta_i = 0$.

Figure 6. The slow curve of the system (2) for $\beta = 0.01$, $\kappa = \kappa_0 = 0.3716$, $\theta < 4$.

To find the value $\kappa = \kappa^*$, which corresponds to a trajectory modelling the critical regime in the chemical system, we use the techniques proposed in [11]. The idea of this approach consists of the following. If we reverse the time in the system (2) by $\tau = -t$, the repulsive part $S^u$ of slow curve becomes the attractive one for the system.
Figure 7. (a) The slow curve (the thin line) and the trajectory (the thick line) of the system (2) in the case of critical regime. (b) The $\eta$– and $\theta$–components of the solution in the case of the critical regime for $\beta = 0.01, \gamma = 0.01, \theta_i = 0, \kappa = \kappa^* \approx 0.41767$.

$$\gamma \frac{d\theta}{dt} = -(\eta + 1)^{-1} \exp \left( \frac{\theta}{1 + \beta \theta} \right) + \frac{\theta}{\kappa} = f(\eta, \theta),$$

$$\frac{d\eta}{dt} = -(\eta + 1)^{-1} \exp \left( \frac{\theta}{1 + \beta \theta} \right) = g(\eta, \theta)$$

with the new time $t$. A trajectory of the system (8) starting from any point in the basin of attraction of the set $S_u$, after a short time follows the attractive set $S_u$ at the tempo of the slow variable up to the point $A_1$, see Figure 8. This part of the trajectory is the part of slow motions and the trajectory here has the asymptotic representation [11]

$$\eta(\theta, \gamma) = h_0(\theta) + \gamma h_1(\theta) + O(\gamma^2).$$

When the trajectory reaches the point $A_1$, it jumps off the slow curve and rapidly tends to the final point. Note, that the final point of the system (8) corresponds to the initial point (3) of the system (2). This part of the trajectory is the part of fast motions and the trajectory here has the asymptotic representation [11]

$$\eta(\theta, \gamma) = \eta_1 + b_{0,0}^0 \Gamma^{2/3} \text{sign} g(\eta_1, \theta_1) \gamma^{2/3} + \frac{1}{3} b_{0,1}^1 \Gamma \text{sign} g(\eta_1, \theta_1) \gamma \ln \frac{1}{\gamma} + O(\gamma),$$

where

$$b_{0,0}^0 = \Omega_0 = 2.338107, \quad b_{0,1}^1 = \frac{\Gamma'}{\Gamma},$$

$$\Gamma = \sqrt{\frac{2}{|f_{\eta \eta}(\eta_1, \theta_1) f_{\eta}(\eta_1, \theta_1)| |g(\eta_1, \theta_1)|}},$$

$$\Gamma' = \frac{6 f_{\theta \eta}(\eta_1, \theta_1) g_\theta(\eta_1, \theta_1) - 2 f_{\theta \theta}(\eta_1, \theta_1) g(\eta_1, \theta_1)}{3 f_{\eta \eta}(\eta_1, \theta_1)}.$$
Recall, \( \eta_1 \) and \( \theta_1 \) here are the coordinates of the jump point \( A_1 \) and, using \( \beta \ll 1 \), we have from (6) and (7)

\[
\eta_1 = \kappa e(1 - \beta) - 1 + O(\beta^2), \quad \theta_1 = 1 + 2\beta + O(\beta^2).
\]

With this \( \eta_1, \theta_1 \) and (3), (8), (9) we obtain the equation for \( \kappa \):

\[
0 = \kappa e(1 - \beta) - 1 + \Omega_0(2\kappa e)^{1/3} (1 + \frac{5}{2}\beta)^{2/3} \gamma^{2/3} + \frac{4(1 + 6\beta)}{9} \gamma \ln \frac{1}{\gamma} + O(\gamma + \beta^2). \tag{10}
\]

From the equation (10) it follows that the critical value of the parameter \( \kappa \) can be found in the asymptotic representation

\[
\kappa = \kappa^* = \kappa_0 + \kappa_1 \gamma^{2/3} + \kappa_2 \gamma \ln \frac{1}{\gamma} + O(\gamma).
\]

By substituting this series into (10) and equating the coefficients we get

\[
\kappa^* = \frac{1}{\kappa_0} \left[ 1 + \beta - \Omega_0 \sqrt{2}(1 + 3\beta) \gamma^{2/3} - \frac{4}{9} (1 + 7\beta) \gamma \ln \frac{1}{\gamma} \right] + O(\gamma + \beta^2).
\]

The critical regime corresponding to \( \kappa = \kappa^* \) separates the region of slow regimes \( (\kappa < \kappa^*) \) which are characterized by low temperatures and the region of the ignition \( (\kappa > \kappa^*) \). During the critical regime the temperature attains a high value but without the ignition, at the tempo of slow variable of the system, see Figure 7(b).

4. Case of cubic law

In the case of a cubic law of oxidation kinetics the system (1) has the form

\[
\frac{d\theta}{d\tau} = (\eta + 1)^{-2} \exp \left( \frac{\theta}{1 + \beta \theta} \right) - \frac{\theta}{\kappa},
\]

\[
\frac{d\eta}{d\tau} = (\eta + 1)^{-2} \exp \left( \frac{\theta}{1 + \beta \theta} \right), \tag{11}
\]
with initial conditions
\[ \eta(0) = 0, \quad \theta(0) = -\theta_i. \] (12)

The degenerate equation
\[ F(\eta, \theta, \kappa) = (\eta + 1)^{-2} \exp \left( \frac{\theta}{1 + \beta \theta} \right) - \frac{\theta}{\kappa} = 0 \] (13)
describes the slow curve
\[ S = \{ (\theta, \eta) : (\eta + 1)^{-2} \exp \left( \frac{\theta}{1 + \beta \theta} \right) - \frac{\theta}{\kappa} = 0 \} \]
of the system (11).

\[ \begin{array}{cc}
\eta &\hline
S_1^s & S_1^u & S_2^s & S_2^u \\
A_1 & A_2 & A_1 & A_2 \\
\theta & \hline
\end{array} \]

(a) (b)

**Figure 9.** The form of the slow curve of the system (11): (a) for \( \kappa < \kappa_0 \), (b) for \( \kappa > \kappa_0 \), where \( \kappa_0 = (1 + \beta)/e, \ e = \exp(1) \).

As in previous section we take \( \kappa \) as a control parameter with fixed \( \beta, \gamma \). For all \( \kappa \) the slow curve of the system (11) consists of two branches which are described by the equations
\[ \eta = -1 + \sqrt{\frac{\kappa}{\theta} \exp \left( \frac{\theta}{1 + \beta \theta} \right)} \]
and
\[ \eta = -1 - \sqrt{\frac{\kappa}{\theta} \exp \left( \frac{\theta}{1 + \beta \theta} \right)}. \]

From the last equation it follows that one branch of \( S \) (namely, the lower one in \( (\theta, \eta) \)-plane) is outside \( \Delta \), see Figure 9. The upper branch of \( S \) has two jump points \( A_1 \) and \( A_2 \) with coordinates \( (\eta_1, \theta_1) \) and \( (\eta_2, \theta_2) \), respectively, where \( \theta_1 \) and \( \theta_2 \) are the roots of the equation
\[ \theta - (1 + \beta \theta)^2 = 0, \]
i.e.,
\[ \theta_1 = \frac{1 - 2\beta - \sqrt{1 - 4\beta}}{2\beta^2}, \quad \theta_2 = \frac{1 - 2\beta + \sqrt{1 - 4\beta}}{2\beta^2}. \] (14)

and
\[ \eta_1 = -1 + \sqrt{\frac{\kappa}{\theta_1} \exp \left( \frac{\theta_1}{1 + \beta \theta_1} \right)}, \quad \eta_2 = -1 + \sqrt{\frac{\kappa}{\theta_2} \exp \left( \frac{\theta_2}{1 + \beta \theta_2} \right)}. \] (15)
Hence, according to (5), (13)–(15), the upper branch of the slow curve $S$ consists of two attractive parts $S_s^1$ and $S_s^2$ and the repulsive $S_u$, where

$$
S_s^1 := \{ (\theta, \eta) \in S : \eta > -1, \ 0 < \theta < \theta_1 \},
$$
$$
S_s^2 := \{ (\theta, \eta) \in S : \eta > -1, \ \theta > \theta_2 \},
$$
$$
S_u := \{ (\theta, \eta) \in S : \eta > -1, \ \theta_1 < \theta < \theta_2 \}.
$$

**Figure 10.** The slow curve of the system (11) for $\beta = 0.01, \kappa = 0.27 < \kappa_0, \theta \leq 6$.

**Figure 11.** (a) The slow curve (the thin line) and the trajectory (the thick line) of the system (11) for $\beta = 0.01, \gamma = 0.01, \kappa = 0.27, \theta_i = 0$. (b) The $\eta$– and $\theta$–components of the solution in the case of the slow regime for $\beta = 0.01, \gamma = 0.01, \kappa = 0.27, \theta_i = 0$.

Taking into account that $\beta \ll 1$, from (14) we have $\theta_1 = 1 + 2\beta + O(\beta^2), \ \theta_2 = \beta^{-2} (1 - 2\beta + O(\beta^2))$ as $\beta \to 0$. By the foregoing, we confine our attention to the behavior of the solution of (11) near $S_s^1$ and $S_u$ only.
Similar to the case of parabolic law of oxidation kinetics, the form of $S$ depends on the value of the parameter $\kappa$ and, consequently, depending on its value the chemical reaction either changes to a slow regime with decay of the reaction, or goes into a regime of self–acceleration which leads to an ignition.

In the case $\kappa < \kappa_0$ some part of set $S^s_1$ of the slow curve lies below the $\eta$–axis, see Figures 9(a) and 10. After the part of the fast motion from the initial point up to $S^s_1$, which corresponds to the initial heating of the chemical system, the trajectory of the system follows the attractive set $S^u_1$ at the tempo of the slow variable, see Figure 11. This behavior corresponds to the slow regime with low temperatures (subcritical regime).

![Graph](https://example.com/graph1.png)

**Figure 12.** The slow curve of the system (11) for $\beta = 0.01, \kappa = 0.45 > \kappa_0, \theta < 5$.

![Graph](https://example.com/graph2.png)

**Figure 13.** (a) The trajectory of the system (11) for $\beta = 0.01, \gamma = 0.01, \kappa = 0.45, \theta_i = 0$.
(b) The $\eta$– and $\theta$–components of the solution in the case of the ignition for $\beta = 0.01, \gamma = 0.01, \kappa = 0.45, \theta_i = 0$. 
In the case $\kappa > \kappa_0$ the branch of the slow curve with $\eta > 0$ lies above the $\theta$–axis entirely, see Figures 9(b) and 12. The trajectory of the system in this case passes beyond the slow curve and then describes the fast regime. The trajectory of (11) reaches the attractive set $S^a_2$ and then follows it at the tempo of the slow variable up to the point $A_2$. After this moment the trajectory jumps off the slow curve and rapidly tends to the attractive set $S^s_1$, see Figure 13. This behavior corresponds to the ignition characterizing a very high temperature, see Figure 13.

Figure 14 shows the slow curve in the case $\kappa = \kappa_0$. In a neighborhood of $\kappa_0$ it is possible to find the value $\kappa = \kappa^*$ corresponding to the critical regime. In Figure 15(a) the trajectory of the system with $\kappa = \kappa^*$, starting from the initial point, rapidly tends to a very small vicinity of the point $A_1$ and then follows the repulsive part $S^u$ of the slow curve, up to a point $J$ from which the solution “jumps” towards the attractive component $S^s_1$ and then follows it.

To find the value $\kappa = \kappa^*$ which corresponds to a trajectory modelling the critical regime in the chemical system by Mishchenko–Rozov asymptotics we reverse the time in the system (11) by $\tau = -t$. As the result we obtain the system

\[
\begin{align*}
\gamma \frac{d\theta}{dt} &= -(\eta + 1)^{-2} \exp\left(\frac{\theta}{1 + \beta \theta}\right) + \frac{\theta}{\kappa} = f(\eta, \theta), \\
\frac{d\eta}{dt} &= -(\eta + 1)^{-2} \exp\left(\frac{\theta}{1 + \theta \beta}\right) = g(\eta, \theta).
\end{align*}
\]

The attractive set of the slow curve of the system (16) coincides with the repulsive $S^u$ of the system (11), and the repulsive set of $S$ of the system (16) coincides with $S^s$ of the system (11). Hence, a trajectory of the system (16) starting from any point from the basin of attraction of the set $S^u$, after a short time follows the attractive set $S^s$ at the tempo of the slow variable up to the point $A_1$. This part of the trajectory corresponds to the slow motions and the trajectory here has the asymptotic representation

\[\eta(\theta, \gamma) = h_0(\theta) + \gamma h_1(\theta) + O(\gamma^2).\]

When the trajectory reaches the point $A_1$, it jumps off the slow curve and rapidly tends to the final point with coordinates $\eta = 0$, $\theta = -\theta_i$. This part of the trajectory corresponds to
Figure 15. (a) The slow curve (the thin line) and the trajectory (the thick line) of the system (11) for $\beta = 0.01$, $\gamma = 0.01$, $\theta_0 = 0$, $\kappa = \kappa^* \approx 0.44720$. (b) The $\eta$– and $\theta$–components of the solution in the case of the critical regime for $\beta = 0.01$, $\gamma = 0.01$, $\theta_0 = 0$, $\kappa = \kappa^* \approx 0.44720$.

the part of fast motions and the trajectory here has the asymptotic representation (9) with the functions $f$ and $g$ from the system (16), and $\eta_1$ and $\theta_1$ given by (14), (15).

Using the fact that $\beta \ll 1$, from (14) and (15) we have

$$\eta_1 = \sqrt{\kappa e} \left(1 - \frac{\beta^2}{2}\right) - 1 + O(\beta^2), \quad \theta_1 = 1 + 2\beta + O(\beta^2).$$

Then from (9), (12), and (16) we obtain the equation

$$0 = \sqrt{\kappa e} \left(1 - \frac{\beta^2}{2}\right) - 1 + \Omega_0(\kappa e)^{1/6} \left(1 + \frac{11}{4}\beta\right)^{2/3} \gamma^{2/3} \gamma \ln \frac{1}{\gamma} + O(\gamma + \beta^2), \quad (17)$$

where $\kappa$ has the asymptotic representation

$$\kappa = \kappa^* = \kappa_0 + \kappa_1 \gamma^{2/3} + \kappa_2 \gamma \ln \frac{1}{\gamma} + O(\gamma).$$

By substituting this series into (17) and equating the coefficients we get the critical value of the parameter $\kappa$

$$\kappa^* = \frac{1}{e} \left[1 + \beta - 2\Omega_0(1 + 3\beta)\gamma^{2/3} - \frac{8}{9}(1 + 7\beta)\gamma \ln \frac{1}{\gamma}\right] + O(\gamma + \beta^2),$$

which corresponds to the critical regime in the chemical system in the case of cubic law of oxidation kinetics.

As in the previous case the critical regime separates the region of slow regimes ($\kappa < \kappa^*$) which are characterized by low temperatures and the region of the ignition ($\kappa > \kappa^*$). During the critical regime the temperature attains a high value but without ignition, at the tempo of slow variable of the system, see Figure 15(b).
5. Conclusion
A realistic time scale is used such that rapid motions of the temperature appear against a background of the slow changing of the related growth of the thickness of the oxide film. This clearly demonstrated the possibility of using the singular perturbation theory to investigate reactions of this sort.

For two form of oxidation kinetics (parabolic and cubic laws) the asymptotic formulae are obtained, specifying the critical value of the parameter $\kappa$ reflecting the convection heat transfer in the metal ignition model. The approach to the modelling of critical phenomena is suggested. The critical trajectory is identified with the trajectory passing along the unstable part of slow curve.

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