# Singular perturbation treatment of the decomposition of ozone
1. Scaling and conditions for the validity of the steady-state approximation

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The natural decomposition of ozone in the atmosphere proceeds by a number of pathways, one of which is the following:

$$M + O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O + M$$

$$O + O_3 \xrightarrow{k_2} 2\,O_2$$
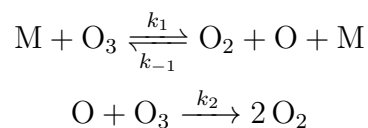
M represents any of a number of stable molecules from which ozone can gain enough energy in a collision to dissociate. We assume an experiment that replicates atmospheric conditions, in which O_2 would be in large excess so that its concentration can be treated as constant. We therefore obtain the following pair of rate equations:

$$\frac{d[O_3]}{dt} = -k_1[M][O_3] + k_{-1}[M][O_2][O] - k_2[O_3][O]$$

$$\frac{d[O]}{dt} = k_1[M][O_3] - k_{-1}[M][O_2][O] - k_2[O_3][O]$$

In classical chemical kinetics, we would obtain an expression for the rate of reaction that did not involve the intermediate [O] by applying the steady-state approximation. Specifically, we would set $d[O]/dt = 0$, and then use this

equation to eliminate [O]. We would justify this by saying that the oxygen atoms that appear as intermediates react fast once made. We would therefore expect that, after a short time, the rate or production would closely match the rate of removal of these atoms. In other words, the net rate of change of [O] is small. But mathematically, what does this mean? Small compared to what?

Questions of relative smallness of terms in equations are resolved using a mathematical procedure known as **scaling**. This is a special case of transformation to dimensionless variables in which we attempt to find transformations that make our variables $O(1)$.

Typically, the scaling of a reactant like ozone is easy: We use the initial concentration to transform the concentration:

$$x = [O_3]/[O_3]_0.$$

x is clearly $O(1)$ until very late stages of the reaction when most of the ozone has been consumed. Intermediates are trickier. Because they tend to be highly reactive, their maximal concentrations are governed by the dynamics of the system, and not by simple stoichiometric considerations. However, we do know how $[O_3]$ and $[O]$ are related when $[O]$ reaches its maximum: At a maximum of $[O]$, $d[O]/dt = 0$, so

$$k_1[M][O_3] - k_{-1}[M][O_2][O] - k_2[O_3][O] = 0,$$

or

$$[O]_{\text{max}} = \frac{k_1[M][O_3]}{k_{-1}[M][O_2] + k_2[O_3]}.$$

The problem is that we don't know the value of $[O_3]$ at which $[O]$ reaches its maximum. However, if oxygen atoms are very reactive, you would expect that maximum to be reached early, before much ozone has reacted. Thus, we would expect that $[O_3] \approx [O_3]_0$ when $[O]$ reaches its maximum value. Consequently,

$$[O]_{\text{max,est}} \approx \frac{k_1[M][O_3]_0}{k_{-1}[M][O_2] + k_2[O_3]_0}.$$

For scaling purposes, we don't need to know the maximum value very precisely. We just need a decent estimate that is of the correct order of magnitude. This is what we have just obtained. We therefore define the dimensionless variable

$$y = [O]/[O]_{\text{max,est}} = [O]\frac{k_{-1}[M][O_2] + k_2[O_3]_0}{k_1[M][O_3]_0}.$$

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We will defer the choice of a scaling for time. For now, we will just substitute our new dimensionless variables into the rate equations. If we do this and rearrange a bit, we get

$$\frac{dx}{dt} = k_1[\text{M}] \left(-x + \frac{k_{-1}[\text{M}][\text{O}_2]}{k_{-1}[\text{M}][\text{O}_2] + k_2[\text{O}_3]_0} y - \frac{k_2[\text{O}_3]_0}{k_{-1}[\text{M}][\text{O}_2] + k_2[\text{O}_3]_0} xy \right),$$

$$\frac{dy}{dt} = (k_{-1}[\text{M}][\text{O}_2] + k_2[\text{O}_3]_0)$$
$$\times \left(x - \frac{k_{-1}[\text{M}][\text{O}_2]}{k_{-1}[\text{M}][\text{O}_2] + k_2[\text{O}_3]_0} y - \frac{k_2[\text{O}_3]_0}{k_{-1}[\text{M}][\text{O}_2] + k_2[\text{O}_3]_0} xy \right).$$

The dimensionless parameter

$$\alpha = \frac{k_{-1}[\text{M}][\text{O}_2]}{k_{-1}[\text{M}][\text{O}_2] + k_2[\text{O}_3]_0}$$

appears repeatedly in these equations. Note that $0 < \alpha < 1$. Using this definition, we have

$$\frac{dx}{dt} = k_1[\text{M}] \left[-x + \alpha y - (1 - \alpha)xy \right],$$
$$\frac{dy}{dt} = (k_{-1}[\text{M}][\text{O}_2] + k_2[\text{O}_3]_0) \left[x - \alpha y - (1 - \alpha)xy \right].$$

We still haven't picked a scaling for time. The idea now is that the reactant (O_3) evolves on a slow time scale. Its equation should therefore consist largely of O(1) terms. This can be achieved if $(k_1[\text{M}])^{-1}$ represents the slow time scale. In other words, we should define a dimensionless time

$$\tau = (k_1[\text{M}])t.$$

Doing this, we get

$$\frac{dx}{d\tau} = -x + \alpha y - (1 - \alpha)xy, \tag{1a}$$

$$\epsilon \frac{dy}{d\tau} = x - \alpha y - (1 - \alpha)xy, \tag{1b}$$

with

$$\epsilon = \frac{k_1[\text{M}]}{k_{-1}[\text{M}][\text{O}_2] + k_2[\text{O}_3]_0}. \tag{1c}$$

The equations are now in the Tikhonov singular perturbation form. The first thing to do is to check the stability of the adjoined system. In other words, if we treat x as a fixed quantity, we need to find out if
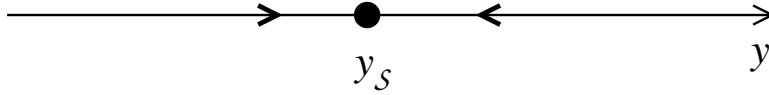
$$y_\mathcal{S} = \frac{x}{\alpha + (1 - \alpha)x}$$

is a stable solution of

$$\frac{dy}{d\tau} = x - \alpha y - (1 - \alpha)xy.$$

This is a one-dimensional dynamical system in y. Note that if $y < y_\mathcal{S}$, we have

$$y < \frac{x}{\alpha + (1 - \alpha)x}$$
$$\therefore y\left[\alpha + (1 - \alpha)x\right] < x$$
$$\therefore x - y\left[\alpha + (1 - \alpha)x\right] = \frac{dy}{d\tau} > 0.$$

We can similarly show that if $y > y_\mathcal{S}$, $dy/d\tau < 0$. The flow implied by the adjoined system is therefore

This proves that $y = y_\mathcal{S}(x)$ is a stable solution of the adjoined system.

We can conclude that if ϵ is sufficiently small, it should be possible to approximate the system (1) by

$$\frac{dx}{d\tau} = -x + \alpha y - (1 - \alpha)xy,$$
$$y \approx y_\mathcal{S}(x) = \frac{x}{\alpha + (1 - \alpha)x},$$

i.e. the steady-state approximation. ϵ is small if either

$$k_1 \ll k_{-1}[O_2]$$

or

$$k_1[M] \ll k_2[O_3]_0.$$

Either of these conditions is sufficient for the steady-state approximation to be valid.