Phase plane analysis solutions

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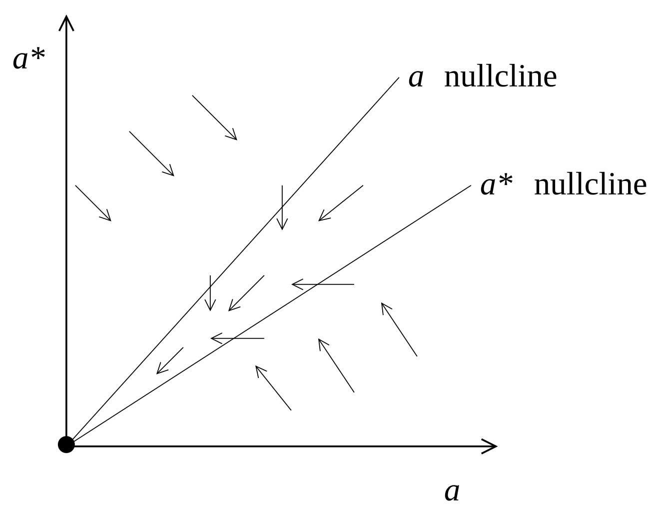
1. The concentration of X is constant, so we just have two variables, a and a^*. The rate equations are

$$\begin{aligned}\frac{da}{dt} &= -k_1xa + k_{-1}xa^*,\\ \frac{da^*}{dt} &= k_1xa - k_{-1}xa^* - k_2a^*.\end{aligned}$$

   The equilibrium point is still (0,0). (Verify this for yourself.) The velocity vector $\mathbf{v} = (\dot{a}, \dot{a}^*)$ has the following qualitative pattern on the a axis: $(-,+)$. Along the a^* axis, $\mathbf{v} \sim (+,-)$. The two nullclines are

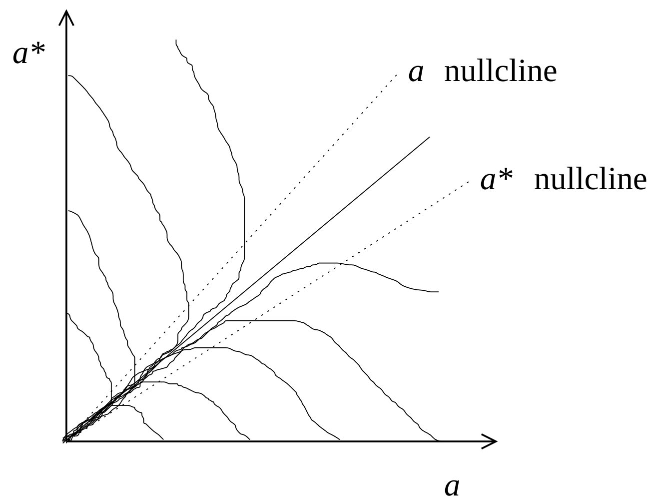
$$\begin{aligned}\tfrac{da}{dt} = 0 \quad &\Rightarrow \quad a^* = \tfrac{k_1}{k_{-1}}a,\\ \tfrac{da^*}{dt} = 0 \quad &\Rightarrow \quad a^* = \tfrac{k_1x}{k_{-1}x+k_2}a.\end{aligned}$$

   Both of the nullclines are straight lines passing through the origin. The a^* nullcline has a smaller slope. Above the a nullcline, $\dot{a} > 0$ while below it, this derivative is negative. Below the a^* nullcline, $\dot{a}^* > 0$, and negative above. The velocity field therefore has the following appearance:



The heavy dot marks the location of the equilibrium point.

We can now sketch the trajectories, shown as solid lines below:



2. (a)

$$\frac{d[O_3]}{dt} = k_0 - k_1[X][O_3] + k_{-1}[X][O_2][O] - k_2[O_3][O]$$
$$\frac{d[O]}{dt} = k_1[X][O_3] - k_{-1}[X][O_2][O] - k_2[O_3][O]$$

(b) I'll start by rewriting the rate equations, combining some of the constants:

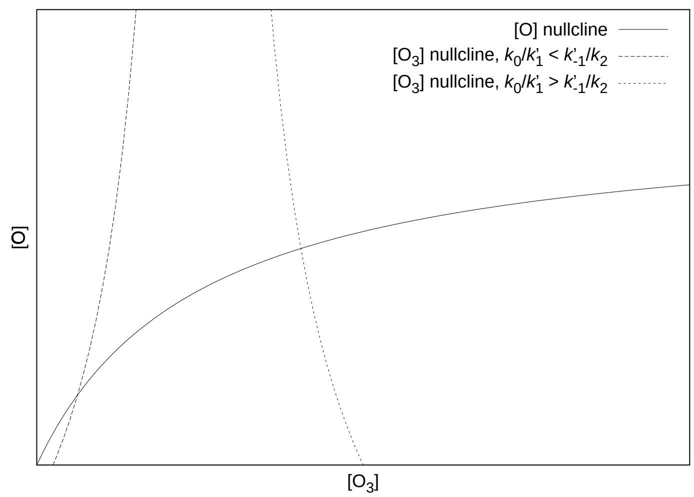
$$\frac{d[O_3]}{dt} = k_0 - k_1'[O_3] + k_{-1}'[O] - k_2[O_3][O] = 0, \quad (1)$$
$$\frac{d[O]}{dt} = k_1'[O_3] - k_{-1}'[O] - k_2[O_3][O] = 0. \quad (2)$$

In these equations, $k_1' = k_1[X]$ and $k_{-1}' = k_{-1}[X][O_2]$.
We find the nullclines by setting equations 1 and 2 to zero.

$$O_3 \text{ nullcline:} \quad [O] = \frac{k_0 - k_1'[O_3]}{k_2[O_3] - k_{-1}'}$$
$$O \text{ nullcline:} \quad [O] = \frac{k_1'[O_3]}{k_2[O_3] + k_{-1}'}$$

The [O] nullcline is easy to sketch. It passes through the origin (i.e. $[O] = 0$ when $[O_3] = 0$). At large values of $[O_3]$, it approaches the limit k_1'/k_2.

The $[O_3]$ nullcline is a little more complicated. It's easy to see that it has a negative value when $[O_3] = 0$ and also at very large values of $[O_3]$. It's positive when both the numerator and denominator are positive or when they're both negative. The numerator changes sign when $[O_3] = k_0/k_1'$ while the denominator changes sign when $[O_3] = k_{-1}'/k_2$. Exactly what the physically relevant part of the nullcline looks like depends on which of the numerator and denominator changes sign first, which just depends on the values of the rate constants and concentrations of O_2 and X. When the denominator changes sign, the value of [O] on the nullcline tends to infinity. The nullclines therefore have the following appearances:



Either way, there's just one equilibrium point (intersection of the [O] and $[O_3]$ nullclines), something which isn't guaranteed in an open system like this one.

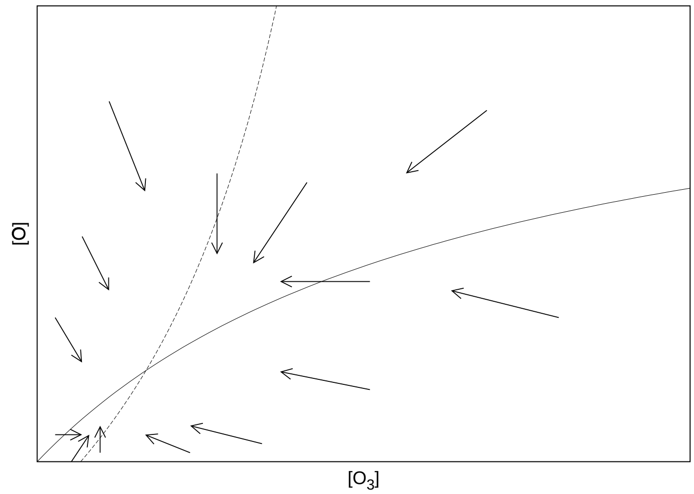
Now for the velocity field. Our velocity vector is $\mathbf{v} = \left(\frac{d[O_3]}{dt}, \frac{d[O]}{dt}\right)$. If $[O_3]$ is small and [O] is not too small (in the region above the [O] nullcline and between the $[O_3]$ nullcline and the [O] axis) $\frac{d[O_3]}{dt} > 0$ while $\frac{d[O]}{dt} < 0$. $d[O]/dt$ changes sign as we cross the [O] nullcline so in the region bounded by the $[O_3]$ axis and the two nullclines, $\frac{d[O_3]}{dt} > 0$ and $\frac{d[O]}{dt} > 0$. If we increase $[O_3]$, $\frac{d[O_3]}{dt}$ changes sign so in the region to the right of the $[O_3]$ nullcline and below the [O] nullcline, $\frac{d[O_3]}{dt} < 0$ and $\frac{d[O]}{dt} > 0$. That just leaves the region to the right of the $[O_3]$ nullcline and above the [O] nullcline where we must have $\frac{d[O_3]}{dt} < 0$ and $\frac{d[O]}{dt} < 0$.

Before we start to draw our velocity fields, let's consider the divergence of the field. The divergence is

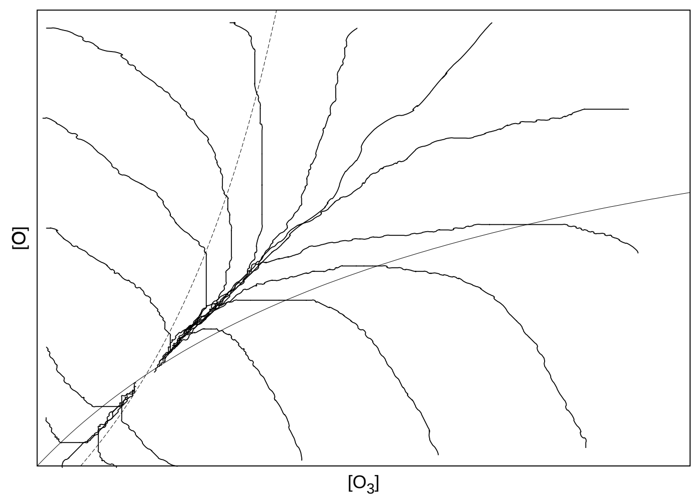
$$\operatorname{div}\mathbf{v} = -k_1' - k_2[O] - k_{-1}' - k_2[O_3] < 0$$

so the trajectories pinch towards each other everywhere.

Although the above description of the velocity field applies to both cases, we will see that we get different pictures because of the different shapes of the $[O_3]$ nullcline. Let's start with the case $k_0/k_1' < k_{-1}'/k_2$. The velocity field, shown with the nullclines, looks like

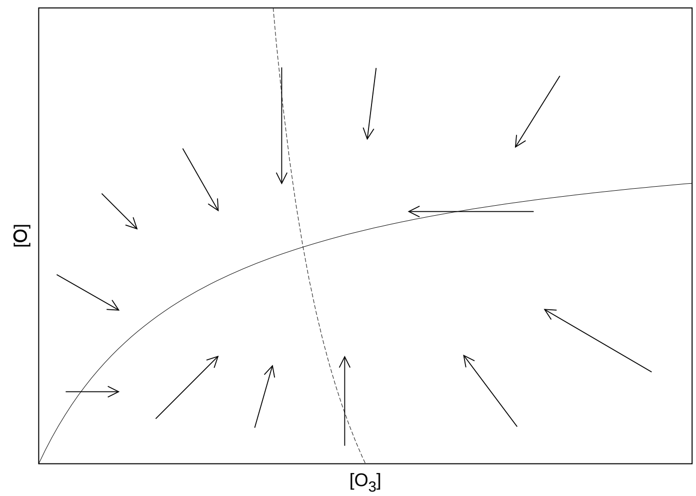


The velocity field in turn implies the following trajectories:

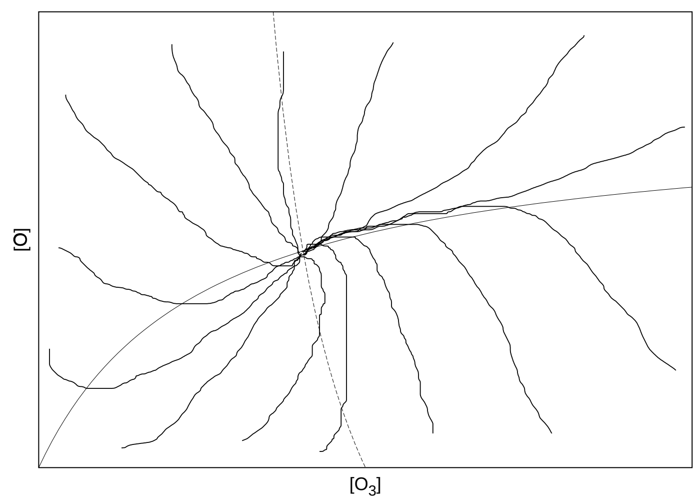


In this case, it certainly looks like we should see a slow manifold. We get the same kind of nullcline funnel as we have seen in other mechanisms, although in a sense there are now two funnels, one to either side of the equilibrium point.

The case $k_0/k_1' > k_{-1}'/k_2$ is a bit different. Here are the nullclines and velocity field:



Note that in this case, the velocity field doesn't force the trajectories between into a funnel. Each of the four regions created by the nullclines has both arrows pointing into it and arrows pointing out. If you now sketch some trajectories, you get the following:



It's not as clear that we'll get a slow manifold in this case. In fact, I would argue that we don't, except at large values of $[O_3]$ where at least the trajectories approaching from below are more or less forced to follow the [O] nullcline. (They cross this nullcline horizontally, and the velocity vector then points down and to the left, but the nullcline is fairly flat at large $[O_3]$ so the trajectories have to parallel this nullcline pretty closely on the way to the equilibrium point.)

The moral of this story is that we should be able to use something like the EA or SSA for this mechanism when $k_0/k_1' < k_{-1}'/k_2$, but probably not when $k_0/k_1' > k_{-1}'/k_2$ unless only interested in experiments where the initial O_3 pressure is very large.