Chemistry 4010 Fall 2019 Assignment 5 solutions

1.

$$\frac{d[\text{NO}]}{dt} = -2k_1[\text{NO}]^2 + 2k_{-1}[\text{N}_2\text{O}_2] \tag{1a}$$
$$\frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2] - k_2[\text{N}_2\text{O}_2][\text{O}_2] \tag{1b}$$
$$\frac{d[\text{O}_2]}{dt} = -k_2[\text{N}_2\text{O}_2][\text{O}_2] \tag{1c}$$
$$\frac{d[\text{NO}_2]}{dt} = 2k_2[\text{N}_2\text{O}_2][\text{O}_2] \tag{1d}$$
$$\tag{1e}$$

2. The following equations were obtained by counting the number of atoms of each kind in each chemical species, and then summing to get the total number of atoms. Technically, you then have to divide by the volume to get a concentration, but since all the chemical species are in a common volume, this doesn't change the relationships.

$$N_{\text{tot}} = [\text{NO}] + 2[\text{N}_2\text{O}_2] + [\text{NO}_2] \tag{2a}$$
$$O_{\text{tot}} = [\text{NO}] + 2[\text{N}_2\text{O}_2] + 2[\text{NO}_2] + 2[\text{O}_2] \tag{2b}$$

Note that I could prove these relationships by taking appropriate combinations of the rate equations. The rate equations can also be used to find other relationships, but any of these would be linear combinations of equations (2a) and (2b).

3. If we multiply equation (2a) by two and then substract equation (2b), we get

$$2N_{\text{tot}} - O_{\text{tot}} = c = [\text{NO}] + 2[\text{N}_2\text{O}_2] - 2[\text{O}_2]. \tag{3}$$

Note that we could have done the subtraction the other way. If you do this, your value of c will just be the negative of mine. This will reverse all of the interpretations below.

4. At $t = 0$, we get

$$c = [\text{NO}]_0 - 2[\text{O}_2]_0.$$

From the stoichiometry of the reaction, we need two equivalents of NO for every equivalent of O_2. Thus, when $c = 0$, we have exactly enough NO for the amount of O_2. If $c > 0$, then NO is in excess. If $c < 0$, O_2 is in excess.

5.

$$[\text{N}_2\text{O}_2] = \frac{1}{2}\left(c - [\text{NO}] + 2[\text{O}_2]\right).$$
$$\therefore \frac{d[\text{NO}]}{dt} = -2k_1[\text{NO}]^2 + k_{-1}\left(c - [\text{NO}] + 2[\text{O}_2]\right),$$
$$\frac{d[\text{O}_2]}{dt} = -\frac{1}{2}k_2[\text{O}_2]\left(c - [\text{NO}] + 2[\text{O}_2]\right).$$

6. We need to solve the equations

$$-2k_1[\mathrm{NO}]^2 + k_{-1}\left(c - [\mathrm{NO}] + 2[\mathrm{O}_2]\right) = 0, \tag{4a}$$

$$-\frac{1}{2}k_2[\mathrm{O}_2]\left(c - [\mathrm{NO}] + 2[\mathrm{O}_2]\right) = 0. \tag{4b}$$

The second equation has two solutions:

$c - [\mathrm{NO}] + 2[\mathrm{O}_2] = 0$: If we substitute this directly into equation (4a), we immediately get $[\mathrm{NO}] = 0$. Thus, $c + 2[\mathrm{O}_2] = 0$, i.e. $[\mathrm{O}_2] = -c/2$. I will call this equilibrium point P_1.

$[\mathrm{O}_2] = 0$: Substituting this into equation (4a), we get the quadratic equation

$$2k_1[\mathrm{NO}]^2 + k_{-1}[\mathrm{NO}] - k_{-1}c = 0.$$

This equation has solutions

$$[\mathrm{NO}]_\pm = \frac{-k_{-1} \pm \sqrt{k_{-1}^2 + 8k_1k_{-1}c}}{4k_1}. \tag{5}$$

I will call P_2 the equilibrium point $([\mathrm{NO}], [\mathrm{O}_2]) = ([\mathrm{NO}]_+, 0)$, and P_3 the equilibrium point $([\mathrm{NO}], [\mathrm{O}_2]) = ([\mathrm{NO}]_-, 0)$.

7. $[\mathrm{NO}]_-$ is always either a negative real number or a complex number, regardless of the value of c, and so P_3 is uninteresting to us.

   If $c < 0$, then P_1 is physically realizable while P_2 has a negative [NO] value.

   If $c > 0$, then P_2 is physically realizable while P_1 has a negative $[\mathrm{O}_2]$ value.

   It is not too hard to see that if $c = 0$, $P_1 = P_2 = (0, 0)$. In other words, the two equilibria cross at $c = 0$.

   Summary table:

Condition	Realizable equilibrium
$c \leq 0$	P_1
$c \geq 0$	P_2

8. We will need the Jacobian:

$$\mathbf{J} = \begin{bmatrix} -4k_1[\mathrm{NO}] - k_{-1} & 2k_{-1} \\ \frac{1}{2}k_2[\mathrm{O}_2] & -\frac{1}{2}k_2\left(c - [\mathrm{NO}] + 2[\mathrm{O}_2]\right) - k_2[\mathrm{O}_2] \end{bmatrix}$$

Stability analysis of P_1: The Jacobian at P_1 is

$$\mathbf{J}_1 = \begin{bmatrix} -k_{-1} & 2k_{-1} \\ -\frac{1}{4}k_2c & \frac{1}{2}k_2c \end{bmatrix}.$$

To find the eigenvalues:

$$
\begin{aligned}
|\lambda \mathbf{I} - \mathbf{J}_1| &= \begin{vmatrix} \lambda + k_{-1} & -2k_{-1} \\ \frac{1}{4}k_2 c & \lambda - \frac{1}{2}k_2 c \end{vmatrix} \\
&= (\lambda + k_{-1})(\lambda - \frac{1}{2}k_2 c) + \frac{1}{2}k_{-1}k_2 c \\
&= \lambda^2 + \lambda\left(k_{-1} - \frac{1}{2}k_2 c\right) \\
&= \lambda\left(\lambda + k_{-1} - \frac{1}{2}k_2 c\right) = 0. \\
\therefore \lambda &= 0 \\
\text{or} \quad \lambda &= \frac{1}{2}k_2 c - k_{-1}.
\end{aligned}
$$

If $c > 2k_{-1}/k_2$, then the second eigenvalue is positive and the equilibrium point is definitely unstable. On the other hand, if $c \leq 2k_{-1}/k_2$, the second eigenvalue is negative but the zero eigenvalue makes stability undecidable by linear stability analysis alone. Note that the latter condition includes negative values of c at which P_1 is physically realizable.

Stability analysis of P_2: Using the hint about not substituting in the equilibrium value of [NO], the Jacobian becomes

$$
\mathbf{J}_2 = \begin{bmatrix} -4k_1[\text{NO}] - k_{-1} & 2k_{-1} \\ 0 & -\frac{1}{2}k_2\left(c - [\text{NO}]\right) \end{bmatrix}
$$

The eigenvalues can be read off the diagonal of this triangular matrix:

$$
\begin{aligned}
\lambda &= -4k_1[\text{NO}] - k_{-1}, \\
\text{or} \quad \lambda &= -\frac{1}{2}k_2\left(c - [\text{NO}]\right).
\end{aligned}
$$

The first eigenvalue is negative when $[\text{NO}] > -k_{-1}/4k_1$. Considering equation (5), we see that $[\text{NO}]_+$ satisfies this inequality for any $c > -k_{-1}/8k_1$. (If c is smaller than this, $[\text{NO}]_+$ is no longer real-valued.) In particular, this eigenvalue will be negative whenever $[\text{NO}] > 0$, i.e. when P_2 is physically realizable. The second eigenvalue is a bit trickier. From equation (3) and given the equilibrium value of $[\text{O}_2] = 0$, we have

$$
c - [\text{NO}] = 2[\text{N}_2\text{O}_2].
$$

At equilibrium, equation (1a) implies that

$$
[\text{N}_2\text{O}_2] = k_1[\text{NO}]^2/k_1 > 0.
$$

Therefore $c - [\text{NO}] > 0$, so the second eigenvalue is always negative when P_2 exists. Putting these results together, we find that P_2 exists and is linearly stable whenever $c > -k_{-1}/8k_1$, which includes negative values of c where this point is not physically realizable.

9. (a) We found previously that P_1 had one negative and one zero eigenvalue if $c \leq 2k_{-1}/k_2$. To find the eigenvector that defines the centre eigenspace, we solve the equation

$$(\mathbf{J}_1 - \lambda\mathbf{I})\,\mathbf{v}^{(0)} = \mathbf{J}_1\mathbf{v}^{(0)} = \mathbf{0}.$$

$$\therefore \begin{bmatrix} -k_{-1} & 2k_{-1} \\ -\frac{1}{4}k_2c & \frac{1}{2}k_2c \end{bmatrix} \begin{bmatrix} v_1^{(0)} \\ v_2^{(0)} \end{bmatrix} = \mathbf{0}.$$

$$\therefore \begin{bmatrix} -k_{-1}v_1^{(0)} + 2k_{-1}v_2^{(0)} \\ -\frac{1}{4}k_2cv_1^{(0)} + \frac{1}{2}k_2cv_2^{(0)} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}.$$

Both of these equations give the same relationship between the two eigenvector components:

$$v_2^{(0)} = \frac{1}{2}v_1^{(0)}.$$

For example, $(2, 1)$ would be a possible eigenvector corresponding to the zero eigenvalue.

(b) P_1 is the point $[\mathrm{NO}] = 0$, $[\mathrm{O}_2] = -c/2$. Substituting these values into the Taylor series we get $a_0 = -c/2$.

The slope of the centre manifold at P_1 can be related to the Taylor series as follows:

$$\frac{d[\mathrm{O}_2]_{\mathrm{CM}}}{d[\mathrm{NO}]} = a_1 + 2a_2[\mathrm{NO}] + O([\mathrm{NO}]^2)$$

$$\therefore \left.\frac{d[\mathrm{O}_2]_{\mathrm{CM}}}{d[\mathrm{NO}]}\right|_{[\mathrm{NO}]=0} = a_1.$$

From our calculation of the eigenvector, we know that this slope is $a_1 = \frac{1}{2}$.

(c) $$\frac{d[\mathrm{O}_2]}{dt} = \frac{d[\mathrm{O}_2]_{\mathrm{CM}}}{d[\mathrm{NO}]}\frac{d[\mathrm{NO}]}{dt}$$

(d) Before we start substituting into the invariance equation, note the repeated term of $2[\mathrm{N}_2\mathrm{O}_2] = c - [\mathrm{NO}] + 2[\mathrm{O}_2]$ appearing in the rate equations. We can substitute $[\mathrm{O}_2]_{\mathrm{CM}}([\mathrm{NO}])$ into this expression and simplify this before we plod ahead.

$$\begin{aligned} 2[\mathrm{N}_2\mathrm{O}_2] &= c - [\mathrm{NO}] + 2\left(-\frac{c}{2} + \frac{1}{2}[\mathrm{NO}] + a_2[\mathrm{NO}]^2 + O([\mathrm{NO}]^3)\right) \\ &= 2a_2[\mathrm{NO}]^2 + O([\mathrm{NO}]^3). \end{aligned}$$

Now we can substitute into the invariance equation:

$$\begin{aligned} &-\frac{1}{2}k_2\left(-\frac{c}{2} + \frac{1}{2}[\mathrm{NO}] + a_2[\mathrm{NO}]^2 + O([\mathrm{NO}]^3)\right)\left(2a_2[\mathrm{NO}]^2 + O([\mathrm{NO}]^3)\right) \\ &\quad = \left(\frac{1}{2} + 2a_2[\mathrm{NO}] + O([\mathrm{NO}]^2)\right)\left[-2k_1[\mathrm{NO}]^2 + k_{-1}\left(2a_2[\mathrm{NO}]^2 + O([\mathrm{NO}]^3)\right)\right] \end{aligned}$$

The lowest-order terms on both sides of this equation are terms in $[\text{NO}]^2$. If we extract these terms and equate them, we get

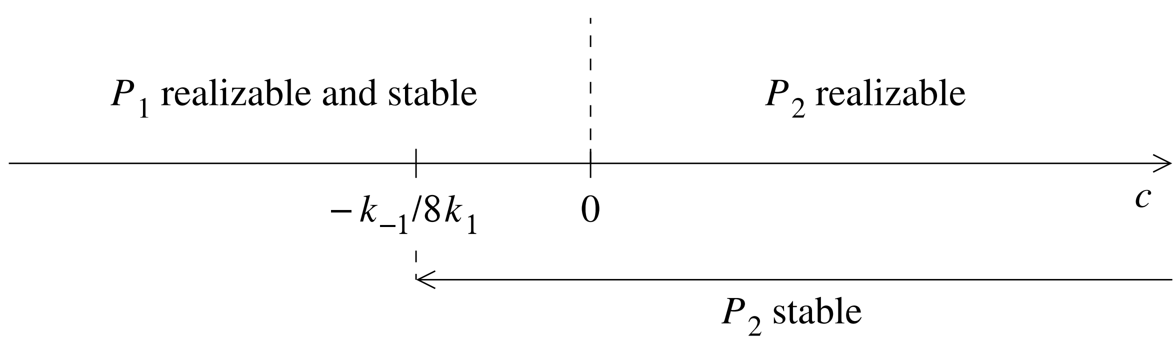
$$\frac{k_2 c}{2} a_2 = \frac{1}{2}\left(-2k_1 + 2k_{-1}a_2\right).$$
$$\therefore a_2 \left(\frac{k_2 c}{2} - k_{-1}\right) = -k_1.$$
$$\therefore a_2 = \frac{2k_1}{2k_{-1} - k_2 c}.$$

(e)

$$\begin{aligned} \left.\frac{d[\text{NO}]}{dt}\right|_{\text{CM}} &= -2k_1[\text{NO}]^2 + k_{-1}\left(2\frac{2k_1}{2k_{-1} - k_2 c}[\text{NO}]^2 + O([\text{NO}]^3)\right) \\ &= \frac{2k_1 k_2 c}{2k_{-1} - k_2 c}[\text{NO}]^2 + O([\text{NO}]^3). \end{aligned} \tag{6}$$

(f) We already know that P_1 is linearly unstable if $c > 2k_{-1}/k_2$. We therefore only need concern ourselves with the case $c < 2k_{-1}/k_2$. (The case $c = 2k_{-1}/k_2$ is complicated because at that value of c, the centre manifold is the entire phase plane. We will neglect this case, which only happens for one very special value of c and would therefore never occur in practice.) Note that if $c < 2k_{-1}/k_2$, from our linear stability analysis, P_1 has one negative and one zero eigenvalue. The centre-manifold theorem therefore applies, which means that we just need to figure out what happens on the centre manifold to determine the stability. Given the form of $d[\text{NO}]/dt$ on the centre manifold, we need the coefficient of $[\text{NO}]^2$ to be negative for (semi)stability. Note also that for $c < 2k_{-1}/k_2$, the denominator of this coefficient is positive. For stability, we must therefore have $c < 0$.

10. I have summarized my results in an illustration:



Interestingly, P_2 is stable outside of the range where it is physically realizable. Of course, this is local stability. Because trajectories started inside the physically realizable region cannot leave it, only the physically realizable equilibrium point is relevant for any given value of c. A stable, unphysical equilibrium can only attract trajectories in the unphysical part of the phase space.