Chemistry 4010 Fall 2019 Assignment 2 Solutions

1. The rate equations are

$$\begin{aligned}\frac{dx}{dt} &= v,\\ \frac{dv}{dt} &= (-kx - \mu v)/m.\end{aligned}$$

The Jacobian is the constant matrix

$$\mathbf{J} = \begin{bmatrix} 0 & 1 \\ -k/m & -\mu/m \end{bmatrix}.$$

The characteristic polynomial is found by solving $|\lambda\mathbf{I} - \mathbf{J}| = 0$.

$$\begin{aligned}|\lambda\mathbf{I} - \mathbf{J}| &= \begin{vmatrix} \lambda & -1 \\ k/m & \lambda + \mu/m \end{vmatrix}\\ &= \lambda(\lambda + \mu/m) + k/m = 0.\end{aligned}$$

All the coefficients of this quadratic polynomial are positive. By a theorem seen in class, the eigenvalues must therefore have negative real parts.

If you want to go further than this, you can write down the solution to the quadratic equation:

$$\begin{aligned}\lambda_\pm &= \frac{1}{2}\left\{-\frac{\mu}{m} \pm \sqrt{\left(\frac{\mu}{m}\right)^2 - 4\frac{k}{m}}\right\}\\ &= \frac{1}{2m}\left\{-\mu \pm \sqrt{\mu^2 - 4km}\right\}.\end{aligned}$$

If $\mu^2 > 4km$, then we have two real, negative eigenvalues. Physicists call this the *overdamped case*. On the other hand, if $\mu^2 < 4km$, we have two complex eigenvalues with negative real parts. This is the *underdamped case*.

2. (a) The rate equations for [A] and [X] are

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{X}]^2,$$
$$\frac{d[\mathrm{X}]}{dt} = 2k_1[\mathrm{A}] - 2k_{-1}[\mathrm{X}]^2 - k_2[\mathrm{X}].$$

Dimensions of the variables and parameters:

[A], [X]:	M
t:	s
k_1, k_2:	s^{-1}
k_{-1}:	$\mathrm{M}^{-1}\mathrm{s}^{-1}$

I arbitrarily choose the following dimensionless variables:

$$a = k_{-1}[\mathrm{A}]/k_1, \qquad x = k_{-1}[\mathrm{X}]/k_1, \qquad \tau = k_2 t.$$

Substituting into the first rate equation, we have

$$\frac{k_1 k_2}{k_{-1}} \frac{da}{d\tau} = -\frac{k_1^2}{k_{-1}} a + k_{-1}\left(\frac{k_1}{k_{-1}}\right)^2 x^2.$$
$$\therefore \dot{a} = -\frac{k_1}{k_2} a + \frac{k_1}{k_2} x^2.$$

Define

$$\alpha = k_1/k_2.$$
$$\therefore \dot{a} = \alpha(x^2 - a).$$

Similarly,

$$\dot{x} = 2\alpha a - 2\alpha x^2 - x.$$

(b) There is only one equilibrium point, namely $(0,0)$. The Jacobian is

$$\mathbf{J} = \begin{bmatrix} -\alpha & 2\alpha x \\ 2\alpha & -4\alpha x - 1 \end{bmatrix}.$$

Evaluated at the equilibrium point:

$$\mathbf{J}^* = \begin{bmatrix} -\alpha & 0 \\ 2\alpha & -1 \end{bmatrix}.$$

The characteristic equation is

$$
\begin{aligned}
|\lambda \mathbf{I} - \mathbf{J}^*| &= \begin{vmatrix} \lambda + \alpha & 0 \\ -2\alpha & \lambda + 1 \end{vmatrix} \\
&= (\lambda + \alpha)(\lambda + 1) = 0.
\end{aligned}
$$

The eigenvalues are therefore $-\alpha$ and -1. Both are negative, so the equilibrium point is stable.

3. (a) A naive approach would first try to find equilibrium points by setting $d\theta/dt = dr/dt = 0$. However, since $d\theta/dt$ is constant, there are no such points. We would be stuck if we tried to proceed this way. The problem is that the equilibrium point is the origin of the coordinate system, where the angle is undefined.

   (b) The only equilibrium point is $r^* = 0$. The Jacobian is $\partial \dot{r}/\partial r = -a$. Thus, $|\lambda \mathbf{I} - \mathbf{J}| = \det(\lambda + a) = \lambda + a$. Setting $\lambda + a = 0$, we conclude that $\lambda = -a$, so the equilibrium point at $r = 0$ is stable.

   We see here why, in geometric terms, we can neglect the θ equation: The angle is quite irrelevant at $r = 0$. If r was in equilibrium at a non-zero value, then we would not in fact have an equilibrium point in the classical sense. We could still talk about stability along the radial direction by analyzing the r equation however.

   (c) If $V(r, \theta)$ is a Lyapunov function, then the following should hold:

   - $V(r^*, \theta) = 0$. Since $r^* = 0$, this is in fact true.
   - $V(r, \theta) > 0$ for $r \neq 0$. Since $V(r, \theta) = r^2$ and $r^2 > 0$ for any $r \neq 0$, this is also true.
   - $\dot{V} < 0$ everywhere except at the origin.

$$
\begin{aligned}
\dot{V} &= \frac{dV}{dr}\frac{dr}{dt} \\
&= (2r)(-ar) = -2ar^2.
\end{aligned}
$$

   Since $a > 0$, this is clearly negative for any $r \neq 0$.

   The following three properties make $V(r, \theta)$ a Lyapunov function for the equilibrium at $r = 0$. This proves that $r = 0$ is approached asymptotically from any initial conditions in the plane.