Chemistry 4010 Fall 2019 Assignment 6 Solutions

We will be working with the following rate equations:

$$\frac{dA}{dt} = -k_1A^2 + k_{-1}AB,$$
$$\frac{dB}{dt} = k_1A^2 - k_{-1}AB - k_2B.$$

1. At a maximum of B, $dB/dt = 0$. Therefore,

   $$k_1A^2 - k_{-1}AB - k_2B = 0.$$

   Solving for B, we get

   $$B = \frac{k_1A^2}{k_{-1}A + k_2}.$$

   If the steady-state approximation is to be applicable, then the maximum in B must be reached early in the reaction when $A \approx A_0$, where A_0 is the initial concentration of A. Therefore

   $$B_{\mathrm{me}} \approx \frac{k_1A_0^2}{k_{-1}A_0 + k_2}.$$

   (The subscript 'me' is intended to mean 'maximum, estimated'. The fact that B_{me} can be read phonetically as 'be me' is just a fun coincidence.)

2. We start by rescaling the concentrations so that they are O(1) quantities. The following rescalings achieve this:

   $$a = A/A_0, \tag{1a}$$
   $$b = B/B_{\mathrm{me}}. \tag{1b}$$

   Substituting these quantities into dA/dt, we get

   $$A_0\frac{da}{dt} = -k_1A_0^2a^2 + k_{-1}A_0B_{\mathrm{me}}ab;$$
   $$\therefore \frac{da}{dt} = -k_1A_0a^2 + ab\frac{k_1k_{-1}A_0^2}{k_{-1}A_0 + k_2}$$
   $$= k_1A_0\left(-a^2 + ab\frac{k_{-1}A_0}{k_{-1}A_0 + k_2}\right).$$

You can easily verify that the fractional term in the above equation (a) is dimensionless, and (b) has a value in the interval $(0, 1)$ (assuming nonzero rate constants and initial concentration of A).Therefore, define

$$\beta = \frac{k_{-1}A_0}{k_{-1}A_0 + k_2}.$$

We therefore have

$$\frac{da}{dt} = k_1 A_0 \left(-a^2 + \beta ab\right). \tag{2}$$

We now susbstitute our scaled variables into dB/dt:

$$\begin{aligned} B_{\mathrm{me}}\frac{db}{dt} &= k_1 A_0^2 a^2 - k_{-1}A_0 B_{\mathrm{me}} ab - k_2 B_{\mathrm{me}} b; \\ \therefore \frac{db}{dt} &= \frac{k_1 A_0^2}{B_{\mathrm{me}}} a^2 - k_{-1}A_0 ab - k_2 b \\ &= a^2 \left(k_{-1}A_0 + k_2\right) - k_{-1}A_0 ab - k_2 b \\ &= \left(k_{-1}A_0 + k_2\right)\left[a^2 - \beta ab - (1-\beta)b\right], \end{aligned}$$

using the fact that

$$1 - \beta = \frac{k_2}{k_{-1}A_0 + k_2}.$$

We now need to pick a scaling for time. The typical assumption leading to the steady-state approximation would be that the intermediate is highly reactive, so that the slow time scale would be associated with the initial step of the reaction. Inspecting equation (2), we find a convenient term with units of $[t]^{-1}$ that is associated with the slow step. We therefore choose

$$\tau = k_1 A_0 t.$$

Substituting this quantity into the rate equations, we get

$$\frac{da}{d\tau} = -a^2 + \beta ab, \tag{3a}$$

$$\epsilon\frac{db}{d\tau} = a^2 - \beta ab - (1-\beta)b, \tag{3b}$$

where

$$\epsilon = \frac{k_1 A_0}{k_{-1}A_0 + k_2}.$$

The rate equations are now in the singular perturbation form, with small parameter ϵ. If either the deenergization reaction (with rate constant k_{-1}) or the product forming step (rate constant k_2) is fast compared to energization of the reactant (rate constant k_1), then ϵ will be small. Since the energized reactant (B) is supposed to be highly reactive, this small parameter is the correct one for this problem.

According to Tikhonov's theorem, the steady-state approximation will be valid when $\epsilon \ll 1$, i.e. when

$$k_1 A_0 \ll k_{-1} A_0 + k_2.$$

This will be true if either $k_1 \ll k_{-1}$ or $k_1 A_0 \ll k_2$.

3. The steady-state approximation is the $\epsilon \to 0$ limit of equation (3b), i.e.

$$b = \frac{a^2}{\beta a + 1 - \beta}. \tag{4}$$

Substituting this equation into equation (3a), we get

$$\frac{da}{d\tau} = -a^2 + \frac{\beta a^3}{\beta a + 1 - \beta} = \frac{-a^2(1-\beta)}{\beta a + 1 - \beta}.$$

We can solve this differential equation by separation of variables:

$$\begin{aligned} d\tau &= -da \frac{\beta a + 1 - \beta}{a^2(1-\beta)} \\ &= -da \left(\frac{\beta}{1-\beta} \frac{1}{a} + \frac{1}{a^2} \right). \end{aligned}$$

Note that because of the definition (1a), $a(0) = 1$.

$$\therefore \int_0^\tau du = -\int_1^a dv \left(\frac{\beta}{1-\beta} \frac{1}{v} + \frac{1}{v^2} \right)$$

(u and v are dummy variables of integration.)

$$\begin{aligned} \therefore \tau &= -\left[\frac{\beta}{1-\beta} \ln v - \frac{1}{v} \right]_1^a \\ &= -\frac{\beta}{1-\beta} \ln a + \frac{1}{a} - 1. \end{aligned} \tag{5}$$

4. (a) i. The trick is to define a new time variable θ related to τ by

$$\tau = \epsilon\theta.$$

Then we have

$$\begin{aligned}\frac{da}{d\theta} &= \epsilon\left(-a^2 + \beta ab\right),\\ \frac{db}{d\theta} &= a^2 - \beta ab - (1-\beta)b,\end{aligned}$$

ii. For very small ϵ, $da/d\theta \approx 0$, therefore $a \approx 1$. This reduces $db/d\theta$ to

$$\begin{aligned}\frac{db}{d\theta} &= 1 - \beta b - (1-\beta)b = 1 - b.\\ \therefore d\theta &= \frac{db}{1-b},\\ \therefore \int_0^\theta du &= \int_0^b \frac{dv}{1-v}.\\ \therefore \theta &= \int_0^b \frac{dv}{1-v}.\end{aligned}$$

With the substitution $w = 1 - v$, the integral becomes

$$\begin{aligned}\theta &= \int_1^{1-b} \frac{-dw}{w}\\ &= -\ln(1-b).\\ \therefore 1 - b &= e^{-\theta}.\\ \therefore b &= 1 - e^{-\theta}.\end{aligned}$$

iii. To obtain the global solution, we add the inner and outer solutions, and subtract their common part. The inner solution is valid at short times. As $\theta \to \infty$, it tends to $b \to 1$. The outer solution on the other hand is valid over the slow time scale. If we take $\tau \to 0$, we get $a \to 1$ which, from (4), also gives $b \to 1$. Thus, the common part is 1, and the global solution is

$$b(\tau) = 1 - e^{-\tau/\epsilon} + \frac{a(\tau)^2}{\beta a(\tau) + 1 - \beta} - 1$$
$$= \frac{a(\tau)^2}{\beta a(\tau) + 1 - \beta} - e^{-\tau/\epsilon}.$$

To use this formula, we calculate $a(\tau)$ from equation (5).

iv. My Maple worksheet to solve this problem appears at the end of the solutions.

(b) The slow manifold $b = b_{\mathrm{CM}}(a)$ satisfies the invariance equation:

$$\frac{db}{d\tau} = \frac{db_{\mathrm{CM}}}{da}\frac{da}{d\tau}.$$

Expand the slow manifold in a power series in ϵ:

$$b_{\mathrm{CM}}(a) = \phi_0(a) + \epsilon\phi_1(a) + O(\epsilon^2).$$
$$\therefore \frac{db_{\mathrm{CM}}}{da} = \frac{d\phi_0}{da} + \epsilon\frac{d\phi_1}{da} + O(\epsilon^2).$$

We can now substitute into the invariance equation:

$$\frac{1}{\epsilon}\left\{a^2 - \left[\phi_0 + \epsilon\phi_1 + O(\epsilon^2)\right](\beta a + 1 - \beta)\right\}$$
$$= \left[\frac{d\phi_0}{da} + \epsilon\frac{d\phi_1}{da} + O(\epsilon^2)\right]\left\{-a^2 + \beta a\left[\phi_0(a) + \epsilon\phi_1(a) + O(\epsilon^2)\right]\right\}.$$

$$\therefore a^2 - \left[\phi_0 + \epsilon\phi_1 + O(\epsilon^2)\right](\beta a + 1 - \beta)$$
$$= \epsilon\left[\frac{d\phi_0}{da} + \epsilon\frac{d\phi_1}{da} + O(\epsilon^2)\right]\left\{-a^2 + \beta a\left[\phi_0 + \epsilon\phi_1 + O(\epsilon^2)\right]\right\}.$$

We now collect terms in equal powers of ϵ on both sides of the equation.

ϵ^0:

$$a^2 - \phi_0(\beta a + 1 - \beta) = 0.$$
$$\therefore \phi_0 = \frac{a^2}{\beta a + 1 - \beta}.$$

This is no great surprise: the zero-order term is just the steady-state approximation. [Compare equation (4).]

ϵ^1**:**

$$-\phi_1\left(\beta a+1-\beta\right)=\frac{d\phi_0}{da}\left(-a^2+\beta a\phi_0\right).$$
$$\therefore \phi_1=-\frac{d\phi_0}{da}\,\frac{-a^2+\beta a\phi_0}{\beta a+1-\beta}$$

Having obtained this equation, it's easiest to use Maple to compute and simplify this function. See my Maple worksheet for details. The result is

$$\phi_1=\frac{a^3(1-\beta)\left[\beta a+2(1-\beta)\right]}{\left[\beta a+1-\beta\right]^4}.$$

The first-order expansion of the slow manifold is therefore

$$b_{\mathrm{CM}}\approx\frac{a^2}{\beta a+1-\beta}+\epsilon\frac{a^3(1-\beta)\left[\beta a+2(1-\beta)\right]}{\left[\beta a+1-\beta\right]^4}.$$

Question 4(a)iv

Set the rate constants and calculate the dimensionless parameters:

> $k1 := 1$

$$k1 := 1 \quad (1)$$

> $km1 := 100$

$$km1 := 100 \quad (2)$$

> $k2 := 2$

$$k2 := 2 \quad (3)$$

> $A0 := 0.01$

$$A0 := 0.01 \quad (4)$$

> $\text{beta} := \dfrac{km1 \cdot A0}{(km1 \cdot A0 + k2)}$

$$\beta := 0.3333333333 \quad (5)$$

> $\text{epsilon} := \dfrac{k1 \cdot A0}{(km1 \cdot A0 + k2)}$

$$\epsilon := 0.003333333333 \quad (6)$$

Note the small value of epsilon.

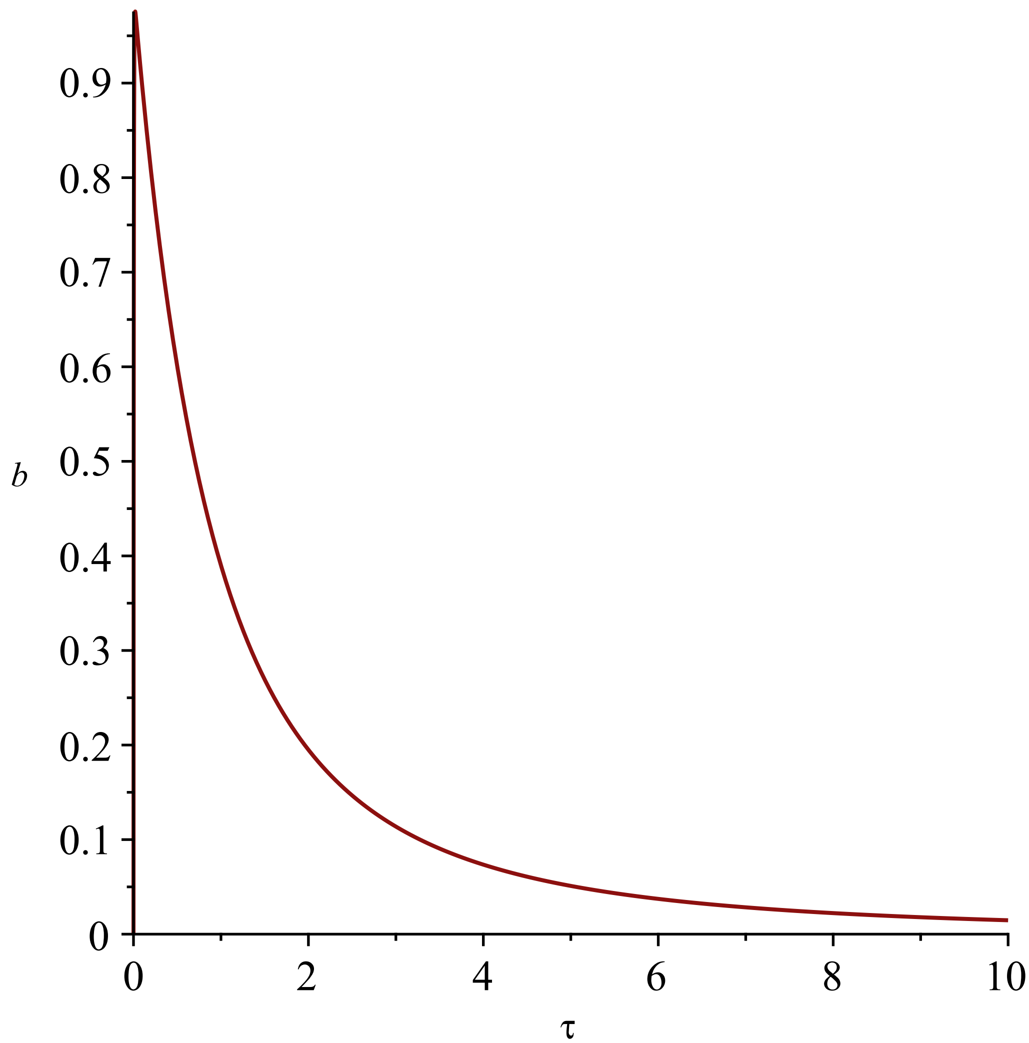
Now define a function to calculate b(tau):

> $b := \textbf{proc}(\text{tau})\ \textbf{global}\ \text{epsilon, beta};\ \textbf{local}\ a;$
> $a := fsolve\left(\text{tau} = -\dfrac{\text{beta}}{1-\text{beta}} \cdot \ln(a) + \dfrac{1}{a} - 1\right):$
> $\dfrac{a^2}{\text{beta} \cdot a + 1 - \text{beta}} - \exp\left(-\dfrac{\text{tau}}{\text{epsilon}}\right)$
> **end**

```
b := proc(tau)                                                    (7)
    local a;
    global epsilon, beta;
    a := fsolve(tau = -beta*ln(a)/(1 - beta) + 1/a - 1);
    a^2/(beta*a + 1 - beta) - exp(-tau/epsilon)
end proc
```

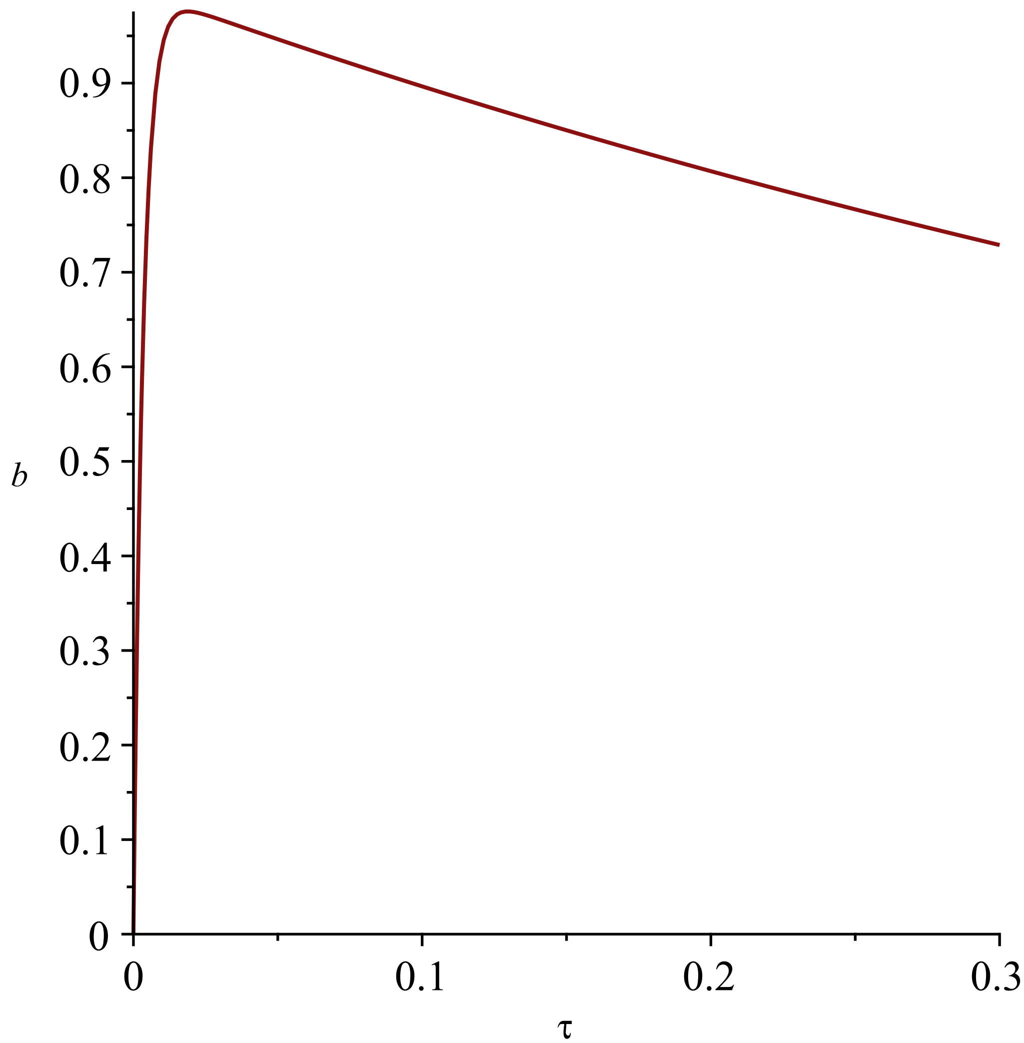
I experimented a bit to find a range of tau values that show clearly the shape of the function:

> $plot(b, 0\,..10, labels = [\text{tau}, b])$



If you want to see the rapid initial rise in b, you have to zoom in on the initial portion of the curve:

> $plot(b, 0\,..0.3, labels = [\text{tau}, b])$



Question 4(b) calculation

First, clear the value of beta (or reset the worksheet):

> beta := 'beta'

$$\beta := \beta \quad (8)$$

> $phi0 := \dfrac{a^2}{\text{beta}\cdot a + 1 - \text{beta}}$

$$\phi 0 := \frac{a^2}{\beta\, a - \beta + 1} \quad (9)$$

Possible intermediate result:

> $simplify(diff(phi0, a))$

$$\frac{(2 + (a-2)\,\beta)\, a}{(1 + (a-1)\,\beta)^2} \quad (10)$$

> $phi1 := \dfrac{-diff(phi0, a)\cdot\left(-a^2 + \text{beta}\cdot a\cdot phi0\right)}{\text{beta}\cdot a + 1 - \text{beta}}$

$$\phi 1 := -\frac{\left(\frac{2\,a}{\beta\,a-\beta+1}-\frac{a^2\,\beta}{(\beta\,a-\beta+1)^2}\right)\left(\frac{a^3\,\beta}{\beta\,a-\beta+1}-a^2\right)}{\beta\,a-\beta+1} \tag{11}$$

> *simplify*(*phi1*)

$$-\frac{(\beta-1)\,(2+(a-2)\,\beta)\,a^3}{(1+(a-1)\,\beta)^4} \tag{12}$$

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