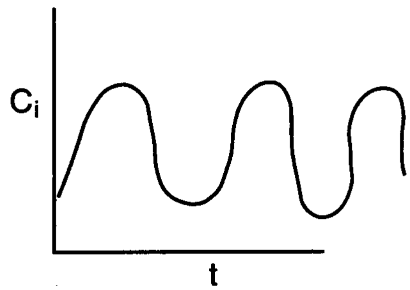
ChE 528

Oscillating Reactions



Even though an abbreviated form of the BZ reaction is given on the web below, it is still relatively complex. Consequently to illustrate how oscillating reactions occur we shall use the following relatively simple reaction sequences. Consider the following elementary multiple reactions

(1) $P \xrightarrow{k_0} A$ $\qquad k_0 = 0.001\ s^{-1} \qquad C_{P_0} = 0.1\ mol/dm^3$

(2) $A \xrightarrow{k_u} B$ $\qquad k_u = 0.01\ s^{-1}$

(3) $A + 2B \xrightarrow{k_1} 3B$ $\qquad k_1 = 2.5 \times 10^9\ dm^6/mol^3\ s^{-1}$

(4) $B \xrightarrow{k_2} C$ $\qquad k_2 = 1.0\ s^{-1}$

An example of these reactions could be the dissociation of $NaIO_3$ and subsequent reactions of IO_3^-

(1A) $NaIO_3 \longrightarrow Na^+ + IO_3^-$ $\qquad$ (1) $P \xrightarrow{k_0} A$

(2A) $IO_3^- \xrightarrow{X.S.\ AsO_3^{-3}} I^- + Prod.$ $\qquad$ (2) $A \xrightarrow{k_u} B$

$IO_3^- + 2I^- + 3AsO_3^{-3} \longrightarrow 3AsO_4^{-3} + 3I^-$

(3A)* $IO_3^- + 2I^- + \xrightarrow{X.S.\ AsO_3^-} 3I^-$ $\qquad$ (3) $A + 2B \xrightarrow{k_1} 3B$

$\left[IO_3^- + 5I^- + 6H^+(X.S.) \longrightarrow 3I_2 + 3H_2O\right]$

(4A) $I^- \xrightarrow{S} \frac{1}{2} I_2 + S^-(\text{Solvent Transfer})$ $\qquad$ (4) $B \xrightarrow{k_2} C$

Batch mole balances and combined rate laws

* [Note: a more rigorous version of this oxidation/reduction of iodine should include the reaction]

$$\frac{dC_P}{dt} = r_P = -k_0 C_P \quad (5)$$

$$\frac{dC_A}{dt} = r_A = k_0 C_P - k_1 C_A C_B^2 - k_u C_A \quad (6)$$

$$\frac{dC_B}{dt} = r_B = k_1 C_A C_B^2 + k_u C_A - k_2 C_B \quad (7)$$

The initial conditions are that when t = 0 then: $C_P = C_{P0}$ and $C_{A0} = C_{B0} = 0$

<u>Applying the PSSH</u>

$$\frac{dC_A}{dt} = \frac{dC_B}{dt} = 0$$

<u>Concentration</u>

(8) $$k_0 C_P - k_1 C_{A_{SS}} C_{B_{SS}}^2 - k_u C_{A_{SS}} = 0$$

(9) $$k_1 C_{A_{SS}} C_{B_{SS}}^2 + k_u C_{A_{SS}} - k_2 C_{B_{SS}} = 0$$

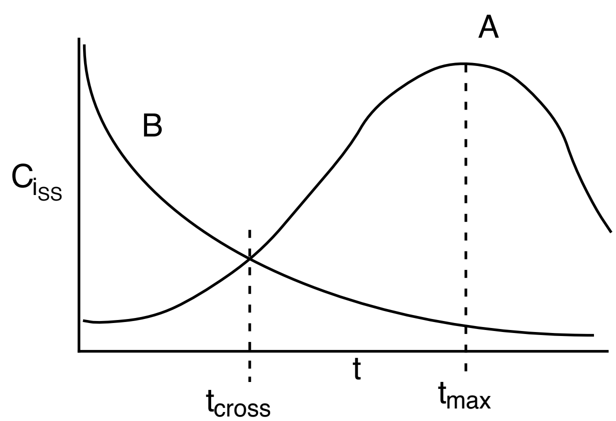
(10) $$C_P = C_{P_0} \; e^{-k_0 t}$$

Solving for the pseudo-steady state concentrations

(11) $$C_{B_{SS}} = \frac{k_0}{k_2} C_P$$

(12) $$C_{A_{SS}} = \frac{k_2^2 k_0 C_P}{\left(k_1 k_0^2 C_P^2 + k_2^2 k_u\right)}$$

(13) $$C_P = C_{P0} \; e^{-k_0 t}$$



<u>At t_{cross}</u>

In terms of concentration

(14) $$C_{A_{SS}} = C_{B_{SS}} = \left[\frac{k_2 - k_u}{k_1}\right]^{1/2}$$

(15) $$C_{P_{cross}} = \frac{k_2}{k_0}\left[\frac{k_2 - k_u}{k_1}\right]^{1/2}$$

(16) $$t_{cross} = k_0^{-1} \; \ln\left[\frac{k_0 k_1^{1/2} C_{P0}}{k_2 (k_2 - k_u)^{1/2}}\right]$$

At t_{max}

(17) $$C_{A_{SS}}\Big)_{max} = \frac{1}{2}\,\frac{k_2}{(k_1 k_u)^{1/2}}$$

(18) $$\boxed{t_{max} = \frac{1}{2}k_0^{-1}\ln\left[\frac{k_1 k_0^2 C_{P0}^2}{k_2^2 k_u}\right]}$$

Let

$$\varepsilon = \frac{k_0}{k_2}$$

$$\mu = \varepsilon\left(\frac{k_1}{k_2}\right)^{1/2} C_P \ , \ \alpha = \left(\frac{k_1}{k_2}\right)^{1/2} C_A \ , \ \beta = \left(\frac{k_1}{k_2}\right)^{1/2} C_B \ , \ \tau = k_2 t$$

then

$$\boxed{\begin{aligned} \frac{d\mu}{d\tau} &= -\varepsilon\mu \\ \frac{d\alpha}{d\tau} &= \mu - \alpha\beta^2 - \kappa_u\alpha \\ \frac{d\beta}{d\tau} &= \alpha\beta^2 + \kappa_u\alpha - \beta \end{aligned}}$$

where $\varepsilon = \frac{k_0}{k_2} = 10^{-3}$

$\kappa_u = \frac{k_u}{k_2} = 10^{-2}$

$\tau = 0: \quad \mu = \mu_0 = 5 \ , \ \alpha = \beta = 0$

$$\frac{d\alpha}{d\tau} = \mu - \alpha\beta^2 - \kappa_u\alpha$$

$$\boxed{\mu = \mu_0 \ e^{-\varepsilon\tau}}$$

$$C_P = \frac{C_{P_0}}{\mu_0}\mu$$

$$\mu_0 = \frac{k_0}{k_2}\left(\frac{k_1}{k_2}\right)^{1/2} C_{P_0}$$

(19) $$\mu = \mu_0 e^{-\varepsilon\tau}$$

(20) $$\frac{d\alpha}{d\tau} = \mu - \alpha\beta^2 - \kappa_u\alpha$$

(21) $$\frac{d\beta}{d\tau} = \alpha\beta^2 + \kappa_u\alpha - \beta$$

At Pseudo-steady state

$$\frac{d\alpha}{d\tau} = \frac{d\beta}{d\tau} = 0$$

Dimensionless

(22) $\mu - \alpha_{SS}\beta_{SS}^2 - \kappa_u\alpha_{SS} = 0$

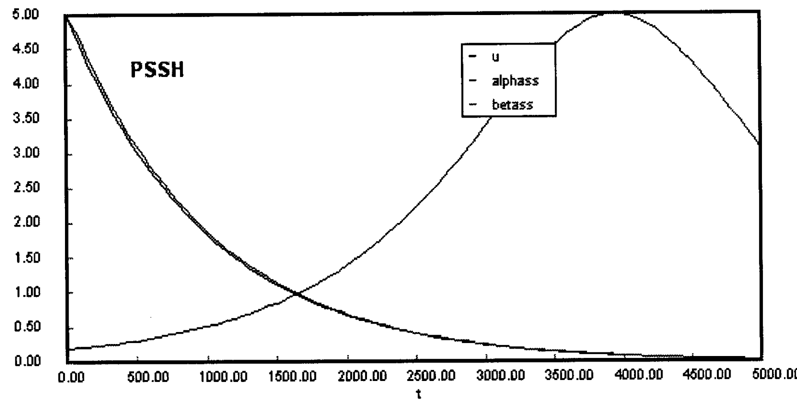
(23) $\alpha_{SS}\beta_{SS}^2 + \kappa_u\alpha_{SS} - \beta_{SS} = 0$

(24) $\mu = \mu_0 e^{-\varepsilon\tau}$

In terms of dimensionless variables

(25) $\alpha_{SS} = \dfrac{\mu}{\mu^2 + \kappa_u}$

(26) $\beta_{SS} = \mu$



At τ_{cross}

(27) $\alpha_{SS} = \beta_{SS} = (1-\kappa_u)^{1/2}$ and $\mu_c = (1-\kappa_u)^{1/2} = .995$

$$\mu = \mu_o \ e^{-\varepsilon\tau}$$

$$t = \frac{1}{\varepsilon}\ln\frac{\mu_o}{\mu}$$

$$t_c = \frac{1}{10^{-3}}\ln\frac{\mu_o}{\mu_c} = 1000\ln\frac{5}{.995}$$

$$t_c = 1614 \ \text{s}$$

At τ_{max}

$$\frac{d\alpha_{ss}}{d\tau} = 0 = \left[\frac{d\mu}{dt}\left(\mu^2 + \kappa u\right) - \mu 2\mu\frac{d\mu}{dt}\right]\Big/\left[\mu^2 + \kappa u\right]^2 = 0, \ \mu^2 + \kappa u - 2\mu = 0$$

$$\mu_m = (\kappa u)^{1/2}$$

(28) $\alpha_{SS})_{max} = \dfrac{1}{2}\ \kappa_u^{-1}$ and $\mu_m = \kappa_u^{1/2} = .1$

α_{SS} reaches a maximum at

$$t_m = \frac{1}{\varepsilon}\ln\frac{\mu_o}{\mu_m} = \frac{1}{10^{-3}}\ln\frac{5}{.1} = 3912 \ \text{S}$$

Dynamics of the Reactions

(20) $\dfrac{d\alpha}{d\tau} = \mu - \alpha\beta^2 - \kappa_u\alpha$

(21) $\dfrac{d\beta}{d\tau} = \alpha\beta^2 + \kappa_u\alpha - \beta$

(29) $$\frac{d\alpha}{d\tau} = f(\alpha,\beta)\ ,\quad f(\alpha,\beta) = \mu - \alpha\beta^2 - \kappa_u\alpha$$

(30) $$\frac{d\beta}{d\tau} = g(\alpha,\beta)\ ,\quad g(\alpha,\beta) = \alpha\beta^2 + \kappa_u\alpha - \beta$$

$$f(\alpha_{SS}\ ,\ \beta_{SS}) = 0$$

$$g(\alpha_{SS}\ ,\ \beta_{SS}) = 0$$

Let $\Delta\alpha$ and $\Delta\beta$ be perturbations from the pseudo-steady state.

$$\alpha = \alpha_{SS} + \Delta\alpha$$

$$\beta = \beta_{SS} + \Delta\beta$$

(31) $$\frac{d(\alpha_{SS} + \Delta\alpha)}{d\tau} = f(\alpha_{SS} + \Delta\alpha,\ \beta_{SS} + \Delta\beta)$$

$$= f(\alpha_{SS},\ \beta_{SS}) + \frac{\partial f}{\partial\alpha}(\alpha_{SS},\ \beta_{SS})\Delta\alpha + \frac{\partial f}{\partial\beta}(\alpha_{SS},\ \beta_{SS})\Delta\beta + \ldots.$$

$$\frac{d(\Delta\alpha)}{d\tau} = \frac{\partial f}{\partial\alpha}(\alpha_{SS},\ \beta_{SS})\Delta\alpha + \frac{\partial f}{\partial\beta}(\alpha_{SS},\ \beta_{SS})\cdot\Delta\beta$$

(32) $$\frac{d(\Delta\alpha)}{d\tau} = \left.\frac{\partial f}{\partial\alpha}\right)_{SS}\Delta\alpha + \left.\frac{\partial f}{\partial\beta}\right)_{SS}\Delta\beta$$

(33) $$\frac{d(\Delta\beta)}{d\tau} = \left.\frac{\partial g}{\partial\alpha}\right)_{SS}\Delta\alpha + \left.\frac{\partial g}{\partial\beta}\right)_{SS}\Delta\beta$$

$$\mathbf{F} = \begin{bmatrix} \left.\frac{\partial f}{\partial\alpha}\right)_{SS} & \left.\frac{\partial f}{\partial\beta}\right)_{SS} \\ \left.\frac{\partial g}{\partial\alpha}\right)_{SS} & \left.\frac{\partial g}{\partial\beta}\right)_{SS} \end{bmatrix}$$

$$\dot{\mathbf{X}} = \mathbf{F} \bullet \mathbf{X}$$

$$\begin{bmatrix} \frac{d\Delta\alpha}{d\tau} \\ \frac{d\Delta\beta}{d\tau} \end{bmatrix} = \mathbf{F} \bullet \begin{bmatrix} \Delta\alpha \\ \Delta\beta \end{bmatrix}$$

Two coupled ODEs

(34) $$\frac{dy}{d\tau} = ay + bx$$

(35) $$\frac{dx}{dt} = cy + dx$$

$$\mathbf{A} = \begin{bmatrix} a & b \\ c & d \end{bmatrix}$$

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$$\frac{dy}{dt} = ay + bx \qquad x = \frac{1}{b}\frac{dy}{dt} - \frac{a}{b}y$$

$$\frac{dx}{dt} = cy + dx$$

$$\frac{dy^2}{dt^2} = a\frac{dy}{dt} + b\frac{dx}{dt}$$

$$= a\frac{dy}{dt} + bcy + bdx$$

$$= a\frac{dy}{dt} + bcy + bd\left[\frac{1}{b}\frac{dy}{dt} - \frac{a}{b}y\right]$$

$$\frac{d^2y}{dt^2} - (a+d)\frac{dy}{dt} + (ad - bc)y = 0$$

$$y = K_1e^{\lambda_1 t} + K_2e^{\lambda_2 t}$$

$$X = K_3e^{\lambda_1 t} + K_4e^{\lambda_1 t}$$

$$\lambda_1, \lambda_2 = \frac{(a+d) \pm \sqrt{(a+d)^2 - 4[ad - bc]}}{2}$$

For which the solution is

(36) $$\boxed{\Delta\alpha = K_1e^{\lambda_1\tau} + K_2e^{\lambda_2\tau}}$$

(37) $$\boxed{\Delta\beta = K_3e^{\lambda_1\tau} + K_4e^{\lambda_2\tau}}$$

where

(38) $$\lambda_1, \lambda_2 = \frac{(a+d) \pm \sqrt{(a+d)^2 - 4(ad - bc)}}{2}$$

(39) $$\lambda_1, \lambda_2 = \frac{Tr[\mathbf{A}] \pm \sqrt{(Tr[\mathbf{A}])^2 - 4(Det(\mathbf{A}))}}{2}$$

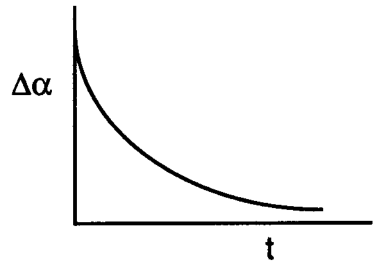
In general,

(40) $$\lambda_1, \lambda_2 = \frac{Tr(\mathbf{F}) \pm \sqrt{[Tr(\mathbf{F})]^2 - 4[Det(\mathbf{F})]}}{2}$$

<u>Determining the properties of the roots λ_1, λ_2</u>

1. If $Tr(\mathbf{F}) < 0$, $Det(\mathbf{F}) > 0$, $[Tr^2(\mathbf{F}) - 4\,Det(\mathbf{F})] > 0$
   Both λ_1 and λ_2 are real and negative

Critically Damped

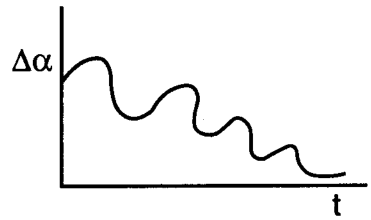


$$\lambda_{1,2} = -a \pm \underbrace{\sqrt{a^2 - 4b}}_{\substack{\text{Less than a} \\ \therefore \text{ both roots} \\ \text{negative}}}$$

2. $\mathrm{Tr}(\mathbf{F}) < 0\,,\ \mathrm{Det}\,(\mathbf{F}) > 0\,,\ [\mathrm{Tr}^2(\mathbf{F}) - 4\,\mathrm{Det}(\mathbf{F})] < 0$

$\lambda_{1,2} = -a \pm i\omega$

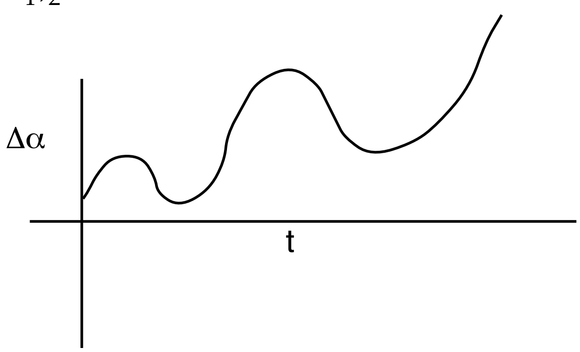
Damped oscillations



3. $\mathrm{Tr}(\mathbf{F}) > 0\,,\ \mathrm{Det}\,(\mathbf{F}) > 0\,,\ [\mathrm{Tr}^2(\mathbf{F}) - 4\,\mathrm{Det}(\mathbf{F})] < 0$

Unstable oscillations

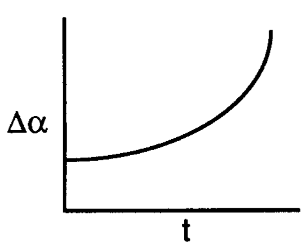
$\lambda_{1,2} = a \pm i\omega$



4. $\mathrm{Tr}(\mathbf{F}) > 0\,,\ \mathrm{Det}\,(\mathbf{F}) > 0\,,\ [\mathrm{Tr}^2(\mathbf{F}) - 4\,\mathrm{Det}(\mathbf{F})] > 0$

$$\lambda_{1,2} = +a \pm \underbrace{\sqrt{a^2 - 4b}}_{\text{Less than a}}$$

Both roots positive + and real



unstable

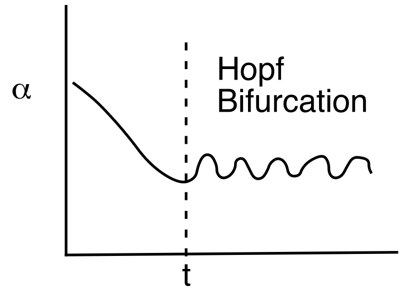
5. $\mathrm{Tr}(\mathbf{F}) = 0\,,\ \mathrm{Det}\,(\mathbf{F}) > 0\,,$

$$\lambda_{1,2} = \frac{0 \pm \sqrt{0 - 4\mathrm{Det(F)}}}{2} = \pm i\sqrt{\mathrm{Det(F)}} \quad , \ \omega = \left(\mathrm{Det}(\mathbf{F})\right)^{1/2}$$

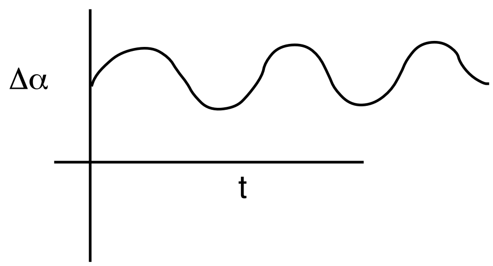
$$\lambda_{1,2} = \pm i\omega \quad , \ \omega = \left(\mathrm{Det}(\mathbf{F})\right)^{1/2}$$

Hopt Bifurcation

The real part of λ_1, λ_2 is zero



An exchange of stability from a stable critical point to a limit cycle, a bifurcation of this type, from an equilibrium to a periodic solution is called a Hopf bifurcation.
Oscillatory



(41) $$\alpha_{SS} = \frac{\mu}{\left(\mu^2 + \kappa_u\right)}$$

(42) $$\beta_{SS} = \mu$$

$$f(\alpha,\beta) = \mu - \alpha\beta^2 - \kappa_u\alpha$$

$$g(\alpha,\beta) = \alpha\beta^2 + \kappa_u\alpha - \beta$$

(43) $$\left.\frac{\partial f}{\partial \alpha}\right)_{SS} = -\left(\beta_{SS}^2 + \kappa_u\right) = -\left(\mu^2 + \kappa_u\right)$$

(44) $$\left.\frac{\partial f}{\partial \beta}\right)_{SS} = -2\alpha_{SS}\beta_{SS} = -\frac{2\mu^2}{\left(\mu^2 + \kappa_u\right)}$$

(45) $$\left.\frac{\partial g}{\partial \alpha}\right)_{SS} = \beta_{SS}^2 + \kappa_u = \mu^2 + \kappa_u$$

(46) $$\left.\frac{\partial g}{\partial \beta}\right)_{SS} = 2\alpha_{SS}\beta_{SS} - 1 = \left(\mu^2 - \kappa_u\right)\Big/\left(\mu^2 + \kappa_u\right)$$

$$\mathrm{Tr}(\mathbf{F}) = \left.\frac{\partial f}{\partial \alpha}\right)_{ss} + \left.\frac{\partial g}{\partial \beta}\right)_{ss} = -\left(\mu^2 + \kappa_u\right) + \frac{\mu^2 - \kappa_u}{\mu^2 + \kappa_u}$$

$$= -\frac{\left[\mu^4 - \left(1 - 2\kappa_u\right) + \kappa_u\left(1 + \kappa_u\right)\right]}{\mu^2 + \kappa_u}$$

(5) $$\boxed{\mathrm{Tr}(\mathbf{F}) = -\frac{\left[\mu^4 - \left(1 - 2\kappa_u\right)\mu^2 + \kappa_u\left(1 + \kappa_u\right)\right]}{\mu^2 + \kappa_u}}$$

Det

$$\frac{\partial f}{\partial \alpha} = -\beta^2 - \kappa_u, \quad \text{and} \quad \frac{\partial f}{\partial \beta} = -2\alpha\beta$$

$$\frac{\partial g}{\partial \alpha} = -\beta^2 + \kappa_u, \quad \text{and} \quad \frac{\partial g}{\partial \beta} = 2\alpha\beta - 1$$

$$\left(\frac{\partial f}{\partial \alpha}\right)\left(\frac{\partial g}{\partial \beta}\right) = \left(-\beta^2 - \kappa_u\right)\left(2\alpha\beta - 1\right)$$

$$= -2\alpha\beta^2 + \beta^2 - 2\alpha\beta\kappa_u + \kappa_u$$

$$\left(\frac{\partial f}{\partial \beta}\right)\left(\frac{\partial g}{\partial \alpha}\right) = \left(-2\alpha\beta\right)\left(\beta^2 + \kappa_u\right)$$

$$= -2\alpha\beta^3 - 2\alpha\beta\kappa_u$$

$$\mathrm{Det}\ (\mathrm{F}) = \left(\frac{\partial f}{\partial \alpha}\right)\left(\frac{\partial g}{\partial \beta}\right) - \left(\frac{\partial f}{\partial \beta}\right)\left(\frac{\partial g}{\partial \alpha}\right) = -\cancel{2\alpha}\beta^3 + \beta^2 - \cancel{2\alpha\beta}\kappa_u + \kappa_u + \cancel{2\alpha}\beta^3 + 2\cancel{\alpha\beta}\kappa_u$$

$$= \beta^2 + \kappa_u$$

$\mathrm{Det}\ (\mathrm{F}) = \mu^2 + \kappa_u$ / QED

$$\boxed{\mathrm{Det}\ [\mathbf{F}] = \mu^2 + \kappa_u}$$

If $\mathrm{Tr}(\mathbf{F}) = 0$ then

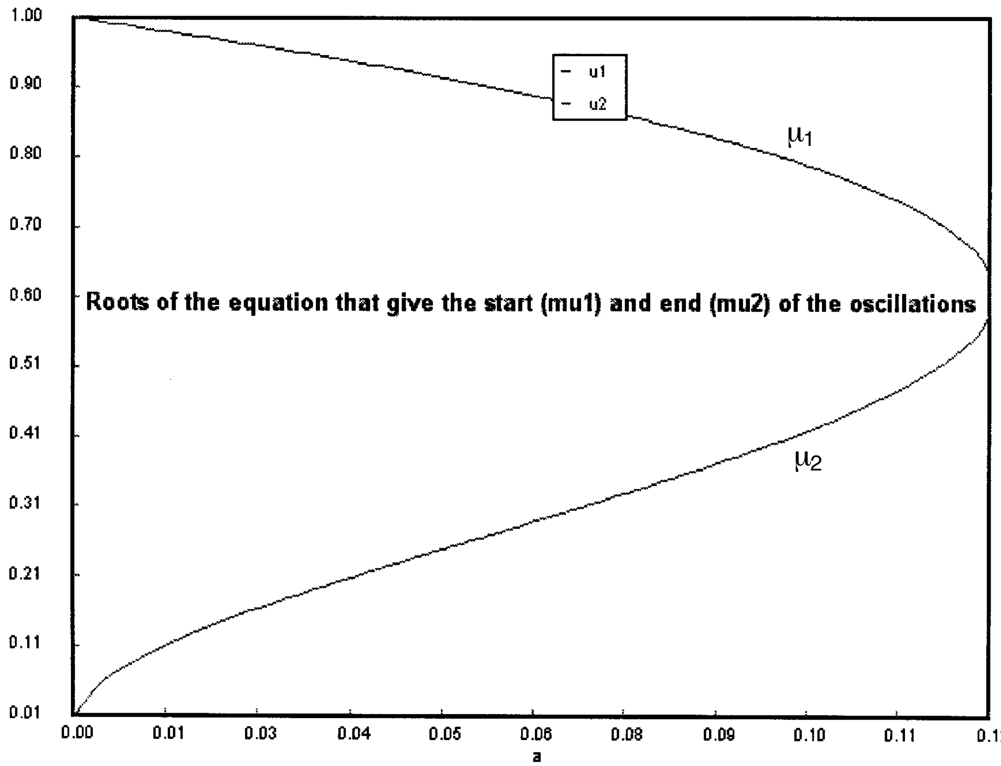
$$\mu^4 - \left(1 - 2\kappa_u\right) + \kappa_u\left(1 + \kappa_u\right) = 0$$

$$\mu_{1,2}^2 = \frac{\left(1 - 2\kappa_u\right) \pm \sqrt{\left(1 - 2\kappa_u\right)^2 - 4\kappa_u\left(1 + \kappa_u\right)}}{2}$$

(48) $$\mu_{1,2}^* = \left[\frac{\left(1 - 2\kappa_u\right) \pm \sqrt{1 - 8\kappa_u}}{2}\right]^{1/2}$$

where $\mu_{1,2}$ are the roots of the equation with μ_1^* taking the + sign

The figure below shows how the roots vary with κ_u.



κappa

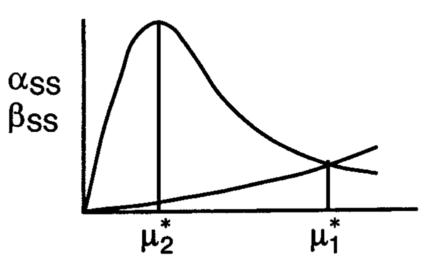
$$\mu^*_{1,2} = \mu_o \exp\left[-\varepsilon\tau^*_{1,2}\right]$$

we see that we start at τ=0 and μ=μ_o and that μ decreases with τ (time). The oscillations start at when μ reaches μ_1^*. The corresponding dimensionless time is

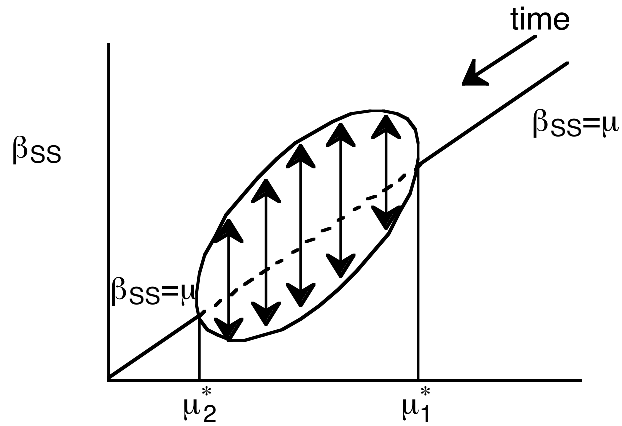
$$\tau_1^* = \frac{1}{\varepsilon}\ \ln\ \frac{\mu_o}{\mu_1^*}$$

The oscillations end when μ reaches μ_2^*.

$$\tau_2^* = \frac{1}{\varepsilon}\ \ln\ \frac{\mu_o}{\mu_2^*}$$



$$\lambda_{1,2} = 0 \pm \frac{\sqrt{-4\mathrm{Det}(\mathbf{F})}}{2} = 2i\,\frac{\sqrt{\mathrm{Det}(\mathbf{F})}}{2} = i\sqrt{\mu^2 + \kappa_u} = i\omega$$



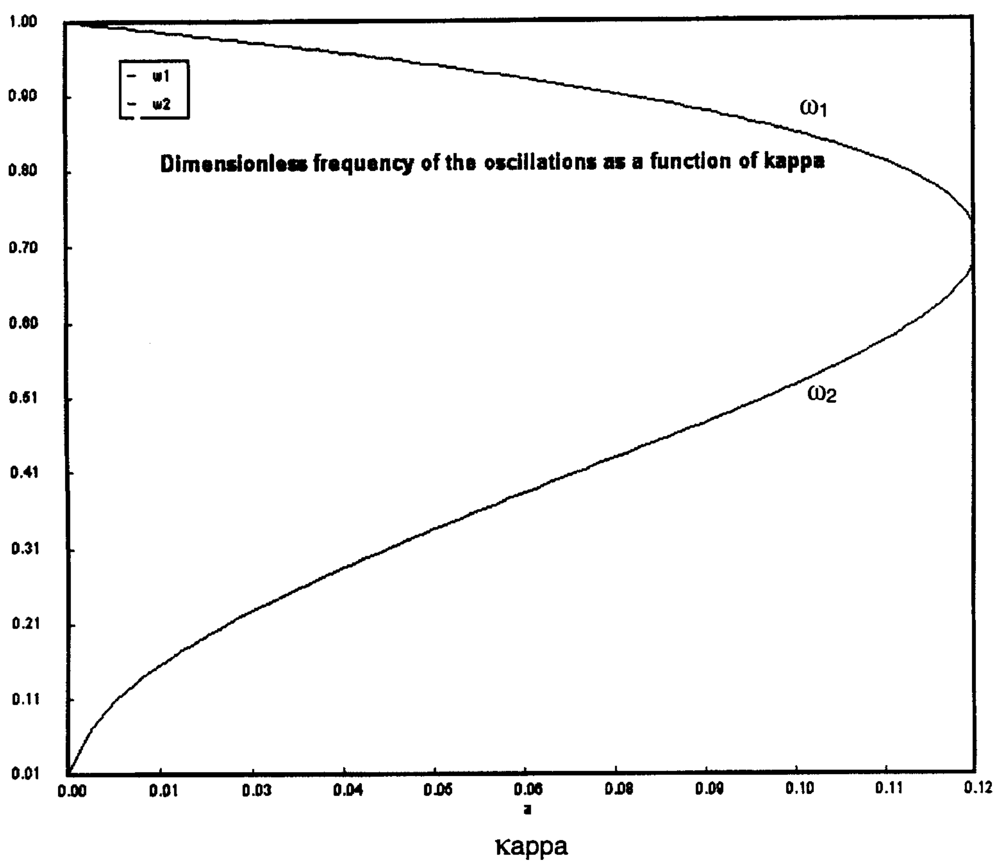
$$\Delta\alpha = K_1 e^{i\omega\tau} + K_2 e^{-i\omega\tau}$$

$$\Delta\beta = K_3 e^{i\omega\tau} + K_4 e^{+i\omega\tau}$$

The dimensionless frequency of oscillation is

$$\omega = \left[\mathrm{Det}(\mathbf{F})\right]^{1/2} = \left[\mu^2 + \kappa_u\right]^{1/2}$$

The figure below show the frequencies of oscillation near the start (ω_1) and end (ω_2) of the oscillations as a function of κ_u.



The dimensionless period of the oscillation

$$\tau_p = \frac{2\pi}{\omega}$$

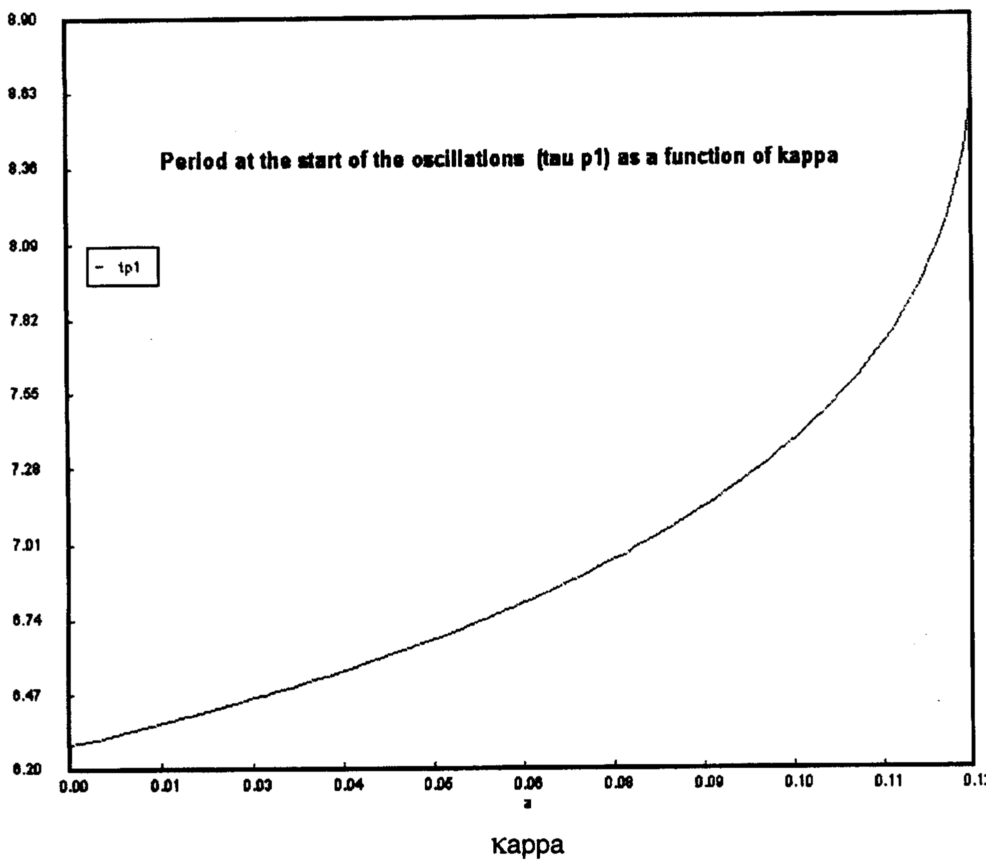
At the start of the oscillations

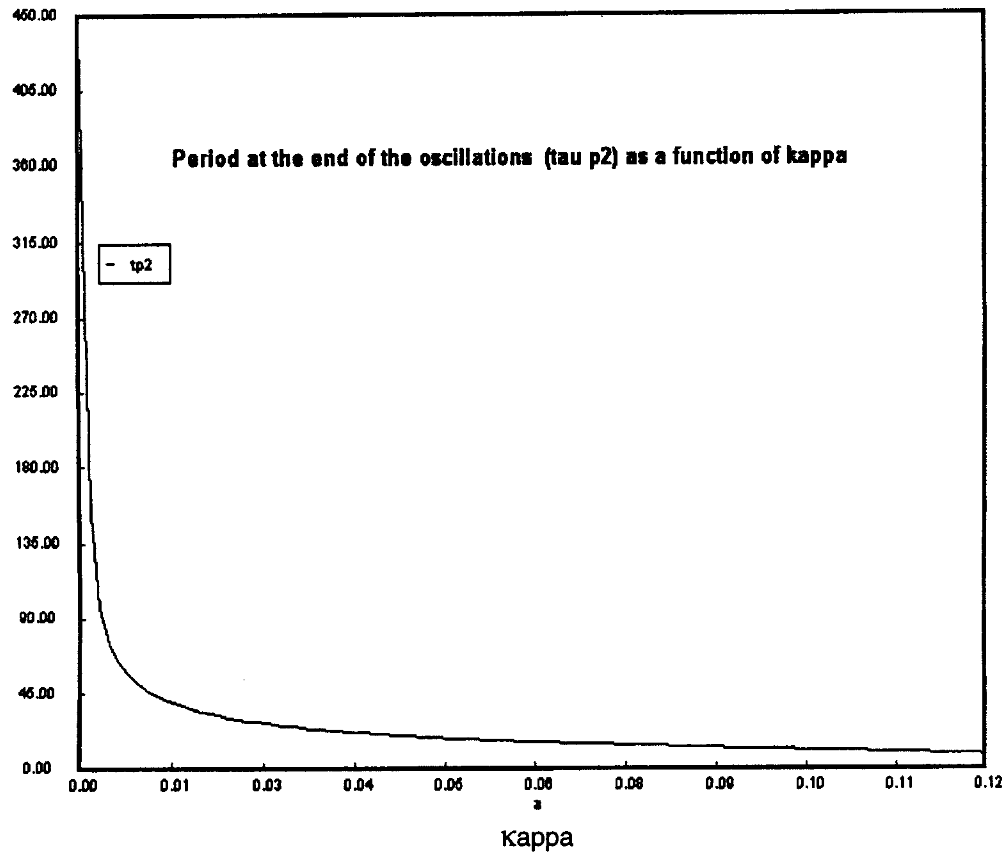
$$\boxed{\tau_{p_1} = \frac{2\pi}{\omega_1^*} = \frac{2\pi}{\left(\mu_1^{*2} + \kappa_u\right)^{1/2}}}$$

Near the end of the oscillation

$$\boxed{\tau_{p_2} = \frac{2\pi}{\omega_2^*} = \frac{2\pi}{\left(\mu_2^{*2} + \kappa_u\right)^{1/2}}}$$

The figures below shows the dimensionless periods of oscillation, τ_{p_1} and τ_{p_2} as a function of κ_u.





The geometric mean period of oscillation

$$\tau_{p_m} = \sqrt{\tau_{p_1}\tau_{p_2}}$$

The time of the oscillation is

$$\tau_2 - \tau_1 = \frac{1}{\varepsilon}\ \ln \frac{\mu_o}{\mu_2^*} - \frac{1}{\varepsilon}\ \ln \frac{\mu_o}{\mu_1}$$

$$\boxed{\Delta\tau = \frac{1}{\varepsilon}\ \ln \frac{\mu_1^*}{\mu_2^*}}$$

The number of oscillations

$$N_{OSC} = \frac{\Delta\tau}{\tau_{pm}} = \frac{1}{\varepsilon\tau_{pm}} \ln \frac{\mu_1^*}{\mu_2^*}$$

At the start of the oscillations the period is

$$\boxed{\tau_p\left(\mu_1^*\right) = \frac{2\pi}{\left[\left(\mu_1^*\right)^2 + \kappa_u\right]^{1/2}}} \tag{57}$$

At the end of the oscillations the period is

(58) $$\tau_p\left(\mu_2^*\right) = \frac{2\pi}{\left[\left(\mu_2^*\right)^2 + \kappa_u\right]^{1/2}}$$

The geometric mean of the period of the oscillations is

(59) $$\tau_{pm} = \left[\tau_p\left(\mu_1^*\right)\tau_p\left(\mu_2^*\right)\right]^{1/2}$$

For small values of κ_u equation (48) can be expanded to

$$\mu_1^* = 1 - \frac{3}{2}\kappa_u \ldots \approx 1$$

$$\mu_2^* = \kappa_u^{1/2}\left(1 + 2\kappa_u\right) + \ldots \approx \kappa_u^{1/2}$$

$$\tau_{pm} = \left[\left(\frac{2\pi}{1}\right)\frac{2\pi}{\left[\left[\underbrace{\left(\kappa_u^{1/2}\right)^2 + \kappa_u}_{2\kappa_u}\right]^{1/2}\right]^{1/2}}\right]^{1/2}$$

(60) $$\tau_{pm} = \frac{2\pi}{\left(2\kappa_u\right)^{1/4}}$$

The number of oscillations is

(61) $$N_{CS} = \frac{\tau_2^* - \tau_1^*}{\tau_{pm}} \cong \varepsilon^{-1}\left(2\kappa_u\right)^{1/4} \ln\left(\kappa_u^{-1}\right)/4\pi$$

Numerical Values

1) Parameters

$$k_0 = 10^{-3} \text{ s}^{-1}$$

$$k_u = 10^{-2} \text{ s}^{-1}$$

$$k_1 = 25 \times 10^8 \text{ dm}^6/\text{mol} \cdot \text{s}$$

$$k_2 = 1 \text{ s}^{-1}$$

$$\pi_0 = \left(\frac{k_1}{k_2}\right)^{1/2} C_{P_0} = \left(\frac{25 \times 10^8}{1}\right)^{1/2} 0.1 = 5000,\ \varepsilon = \frac{k_0}{k_2} = 10^{-3},\ \kappa_u = \frac{k_u}{k_2} = 10^{-2},\ \mu_0 = \varepsilon\pi_0 = 5$$

2) Variables

$$\mu_1 = \left[\frac{1}{2}\left[(1-2\kappa_u) + (1-8\kappa_u)^{1/2}\right]\right]^{1/2}$$

$$\mu_1^* = \left[\frac{1}{2}\left[(1-.02) + (1-.08)^{1/2}\right]\right]^{1/2}$$

$$\boxed{\mu_1^* = 0.9847}$$

The oscillations begin at τ_1 (t_1)

$$\tau_1^* = \frac{1}{\varepsilon}\ln\left(\frac{\mu_o}{\mu_1^*}\right)$$

$$\tau_1^* = \frac{1}{10^{-3}}\ln\left(\frac{5}{.9847}\right)$$

$$\tau_1^* = 1625$$

$$t_1 = \tau_1/k_2 = \frac{1625}{1\ s^{-1}}$$

$$t_1 = 1625\ \text{s}$$

$$\mu_2^* = \left[\frac{1}{2}\left[(1-2\kappa_u) - (1-8\kappa_u)^{1/2}\right]\right]^{1/2}$$

$$= \left[\frac{1}{2}\left[(1-2(.01)) - (1-.08)^{1/2}\right]\right]^{1/2}$$

$$\boxed{\mu_2^* = 0.1021}$$

$$\tau_2^* = \frac{1}{10^{-3}}\ln\left(\frac{5}{.1021}\right)$$

$$\tau_2^* = 3891$$

$$t_2 = 3891\ \text{s}$$

The oscillations end at $t_2 = \frac{1}{\varepsilon}\ln\frac{\mu_0}{\mu_2}$

The oscillation starts at approximately 1625s and ends at approximately 3891s. The frequency of oscillation at the start is

$$\omega_1 = \left[\left(\mu_1^*\right)^2 + \kappa_u\right]^{1/2} = \left[(.9847)^2 + .01\right]^{1/2} = 0.98$$

The period of the oscillation at the start is

$$\tau_p\left(\mu_1^*\right) = \frac{2\pi}{\left[\left(\mu_1^*\right)^2 + \kappa_u\right]^{1/2}} = \frac{2\pi}{\left[(.9847)^2 + .01\right]^{1/2}}$$

$$\tau_{p_1} = 6.35$$

$$t_{p_1} = \tau_{p_1}/k_2$$

$$t_{p_1} = 6.35 \text{ s}$$

The period of oscillation near the end is

$$\tau_p\left(\mu_2^*\right) = \frac{2\pi}{\left[(.1021)^2 + .01\right]^{1/2}}$$

$$\tau_{p_2} = 44$$

$$t_{p_2} = 44 \text{ s}$$

The geometric mean period t_{pm} is

$$\bar{\tau}_{pm} = \sqrt{\tau_{p_1}\tau_{p_2}} = 16.71$$

$$\bar{t}_{pm} = 16.71 \text{ s}$$

Average number of oscillations

$$N_{osc} = \frac{\tau_2^* - \tau_1^*}{\bar{\tau}_{pm}} = \frac{3891 - 1625}{16.71}$$

$$N_{osc} = 136$$

Dimensionless mean frequency = $\omega_m = \dfrac{2\pi}{\tau_{pm}}$,

$$\nu_m = \frac{2\pi}{t_{pm}} = \frac{2\pi}{\tau_{pm}/k_2} = \frac{2\pi}{\tau_{pm}} = \frac{2\pi}{16.7 \text{ s}} = 0.038 \text{ s}^{-1} = \underline{22 \text{ min}^{-1}}$$

$$\nu_m = 22 \text{ cycles/minute}$$

Dimensional Variables

Let's now put everything in terms of concentrations

(48) $$\mu_{1,2}^* = \left[\frac{1}{2}\left[(1-2\kappa_u) \pm (1-8\kappa_u)^{1/2}\right]\right]^{1/2}$$

For $k_0 = 10^{-3} \text{ s}^{-1}$, $k_u = 10^{-2} \text{ s}^{-1}$, $k_1 = 25 \times 10^8 \text{ dm}^6/\text{mol}\cdot\text{s}$, and $k_2 = 1 \text{ s}^{-1}$

(49) $$\pi = \left(\frac{k_1}{k_2}\right)^{1/2} C_P$$

$$\kappa_u = \frac{k_u}{k_2} = 10^{-2} \quad , \quad \varepsilon = \frac{k_0}{k_2} = 10^{-3}$$

$$\pi_0 = \left(\frac{k_1}{k_2}\right)^{1/2} C_{P_0} = \left(\frac{25 \times 10^8}{1}\right)^{1/2} (0.1) = 5000$$

$$\mu_0 = \varepsilon\pi_0 = 5$$

$$\boxed{\frac{\pi}{\pi_0} = \frac{C_P}{C_{P_0}} = \frac{\mu}{\mu_0}}$$

$$C_P = \frac{C_{P_0}}{\mu_0}\ \mu \ , \quad \mu_0 = \varepsilon\pi_0 = \frac{k_0}{k_2^{3/2}} k_1^{1/2} C_{P_0}$$

(50) $$\boxed{C_P = \frac{k_2^{3/2}}{k_0 k_1^{1/2}}\ \mu = \left(\frac{k_2^3}{k_0^2 k_1}\right)^{1/2} \mu}$$

(51) $$C^*_{P,1,2} = \left(\frac{k_2^3}{2k_0^2 k_1}\right)^{1/2} \left[\left(1 - 2\,k_u/k_2\right) \pm \left(1 - 8\,k_u/k_2\right)^{1/2}\right]^{1/2}$$
$$= \left[\frac{k_2^2}{2k_0 k_1}\right]^{1/2} \left[\left(k_2 - 2k_u\right) \pm \left(k_2^2 - 8k_u k_2\right)^{1/2}\right]^{1/2}$$

(52) $$\boxed{C^*_{P,1,2} = \left[\frac{k_2^2}{2k_0 k_1}\right]^{1/2} \left[\left(k_2 - 2k_u\right) \pm \left(k_2\left(k_2 - 8k_u\right)\right)^{1/2}\right]^{1/2}}$$

(53) $$C^*_{P,1} = C_{P_0}\ e^{-k_0 t_1^*}$$

The oscillation starts at

(54) $$t_1^* = k_0^{-1} \ln\left(\frac{C_{P_0}}{C^*_{P_1}}\right) \qquad \boxed{\tau_1^* = \varepsilon^{-1} \ln\left(\frac{\mu_0}{\mu_1^*}\right)}$$

The oscillations end at

(55) $$t_2^* = k_0^{-1} \ln\left(\frac{C_{P_0}}{C^*_{P_2}}\right) \qquad \boxed{\tau_2^* = \varepsilon^{-1} \ln\left(\frac{\mu_0}{\mu_2^*}\right)}$$

The duration of the oscillations is

(56) $$\boxed{t_2^* - t_1^* = k_0^{-1} \ln\left(\frac{C^*_{P_1}}{C^*_{P_2}}\right)} \qquad \boxed{\tau_2 - \tau_1 = \varepsilon^{-1} \ln\left(\frac{\mu_1^*}{\mu_2^*}\right)}$$

The frequency of the oscillation is

$$\omega_0 = \left(\det(\mathbf{F})\right)^{1/2} = \left[\mu^2 + \kappa_u\right]^{1/2}$$

Equations:	Initial value
d(P)/d(t)=-ko*P	0.1
d(A)/d(t)=ko*P-ku*A-k1*A*B^2	0
d(B)/d(t)=k1*A*B^2+ku*A-k2*B	0
d(C)/d(t)=k2*B	0

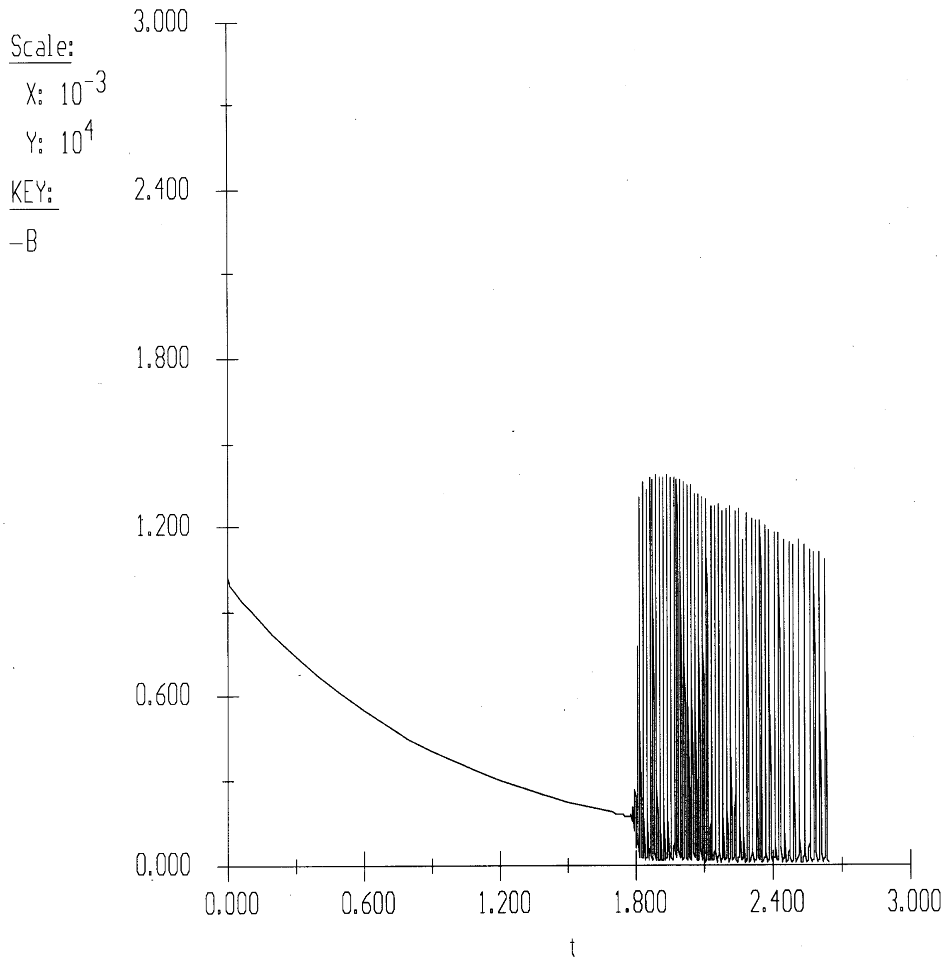
ko=.001

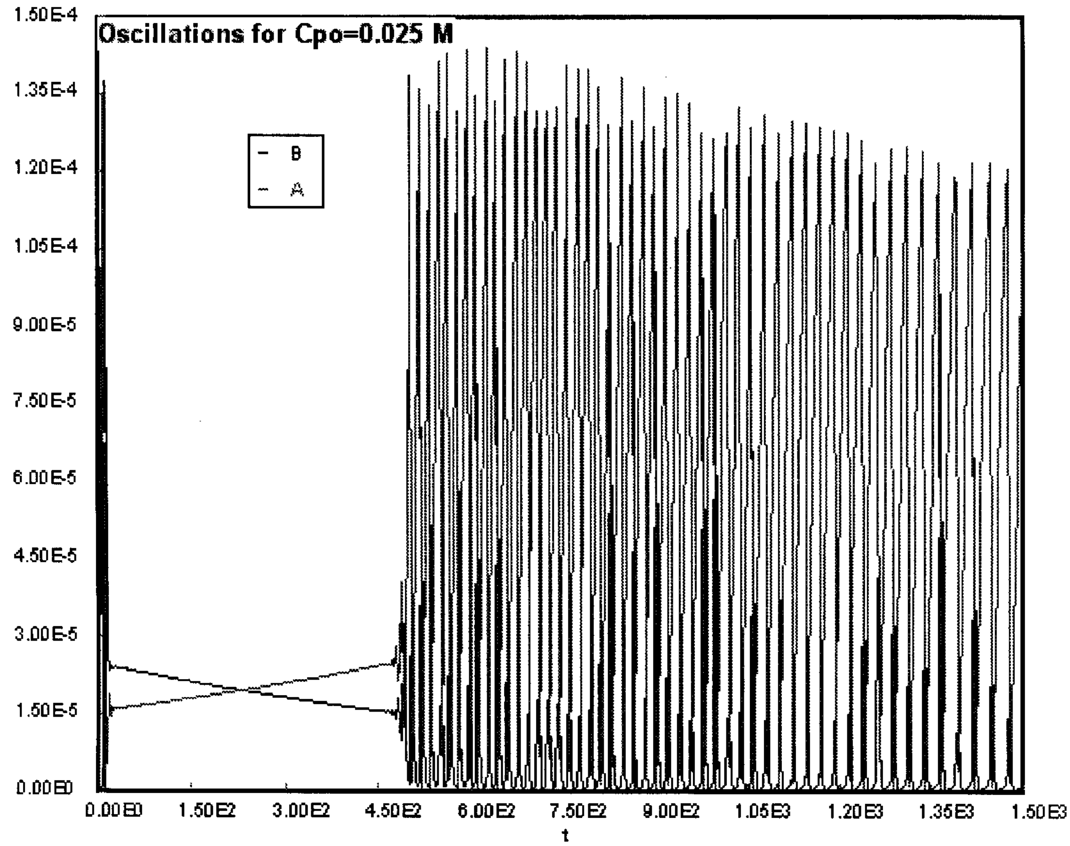
ku=.01

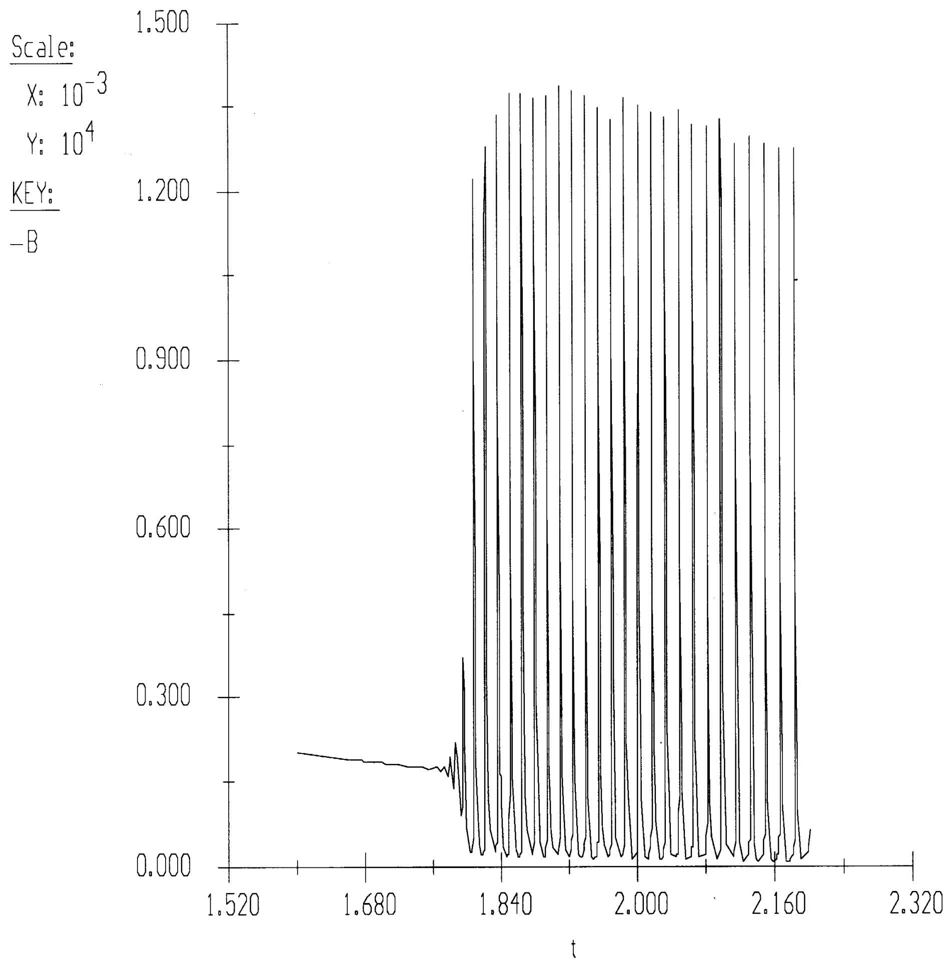
k1=2.5*10^9

k2=1

$t_0 = 0, \quad t_f = 1840$




Oscillations for Cpo=0.025 M
B
A
1.50E-4
1.35E-4
1.20E-4
1.05E-4
9.00E-5
7.50E-5
6.00E-5
4.50E-5
3.00E-5
1.50E-5
0.00E0
0.00E0
1.50E2
3.00E2
4.50E2
6.00E2
7.50E2
9.00E2
1.05E3
1.20E3
1.35E3
1.50E3
t



Scale:
X: 10^{-3}
Y: 10^{4}
KEY:
–B
1.500
1.200
0.900
0.600
0.300
0.000
1.520
1.680
1.840
2.000
2.160
2.320
t