Chaos In Oscillating Chemical Reactions: The Peroxidase-Oxidase Reaction

Adviser Update #1

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Abstract

- In this update we recreate the results of the Karas (2007) in modeling a well studied chemical reaction, Peroxidase-Oxidase
- We use both Matlab and Maple
- We verify his results with our own

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We Model:

Chaos In Oscillating Chemical Reactions: The Peroxidase-Oxidase Reaction

Patrick Karas

Math 53: Chaos!
Professor Alex Barnett
Dartmouth College
Fall, 2007

Abstract

The peroxidase-oxidase (PO) reaction is an important example of how oscillating reactions arise in living organisms. The reaction is important mathematically because exhibits many characteristics of chaos. Of these characteristics, sensitive dependence on initial conditions illustrates how predicting the future state of the PO reaction is next to impossible. For this reason, chaotic behavior in living organisms presents many obstacles to chemists and biologists trying to predict how systems will react to perturbations. This paper explores the chaotic behaviors of the PO reaction, using a system of four differential equations as a model. The topics analyzed are timeseries data, chaotic attractors, bifurcations, tests for sensitive dependence, Lyapunov exponents, and one-dimensional time delay embedding.

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The Peroxidase-Oxidase Reaction

The peroxidase-oxidase reaction is an enzyme catalyzed redox reaction. Nicotinamide adenine dinucleotide (NADH) is oxidized and molecular oxygen acts as an electron receiver. The net reaction is

$$2\mathrm{NADH} + \mathrm{O_2} + 2\mathrm{H^+} \rightarrow 2\mathrm{NAD^+} + 2\mathrm{H_2O}$$

- O2 and NADH are continuously added
- The products are continuously removed.
- Uses a continuousflow, stirred tank reactor (CSTR)
- Exhibits oscillatory behavior and period-doubling going to chaos

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Olsen Model

$$NADH + NAD^{\bullet} \xrightarrow{k_1} 2NAD^{\bullet} \qquad B + X \xrightarrow{k_1} 2X$$

$$2NAD^{\bullet} \xrightarrow{k_2} 2CoIII \qquad 2X \xrightarrow{k_2} 2Y$$

$$O_2 + NADH + Y \xrightarrow{k_3} 3NAD^{\bullet} \qquad A + B + Y \xrightarrow{k_3} 3X$$

$$NAD^{\bullet} \xrightarrow{k_4} P \qquad X \xrightarrow{k_4} P$$

$$CoIII \xrightarrow{k_5} Q \qquad Y \xrightarrow{k_5} Q$$

$$NAD_0^{\bullet} \xrightarrow{k_6} NAD^{\bullet} \qquad X_0 \xrightarrow{k_6} X$$

$$O_{2,0} \xrightarrow{k_7} O_2 \qquad A_0 \xrightarrow{k_7} A$$

$$NADH_0 \xrightarrow{k_8} NADH \qquad B_0 \xrightarrow{k_8} B$$

oxyferrous peroxidase

(compound III)

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Results

Mechanism I:

$$\mathrm{B} + \mathrm{X} \rightarrow 2\mathrm{X}$$

$$2\mathrm{X} \rightarrow 2\mathrm{Y}$$

$$\mathrm{B} + \mathrm{X} \rightarrow 2\mathrm{Y}$$

- Net reaction of the autocatalytic production of X from B and X, and production of 2Y from 2X
- Dominates when [X] is high, but uses up X to create Y

Mechanism II:

$$\mathrm{A} + \mathrm{B} + \mathrm{Y} \rightarrow 3\mathrm{X}$$

- Termolecular reaction of A, B, and Y to form X
- Dominates when [Y] is high, but uses Y to create X

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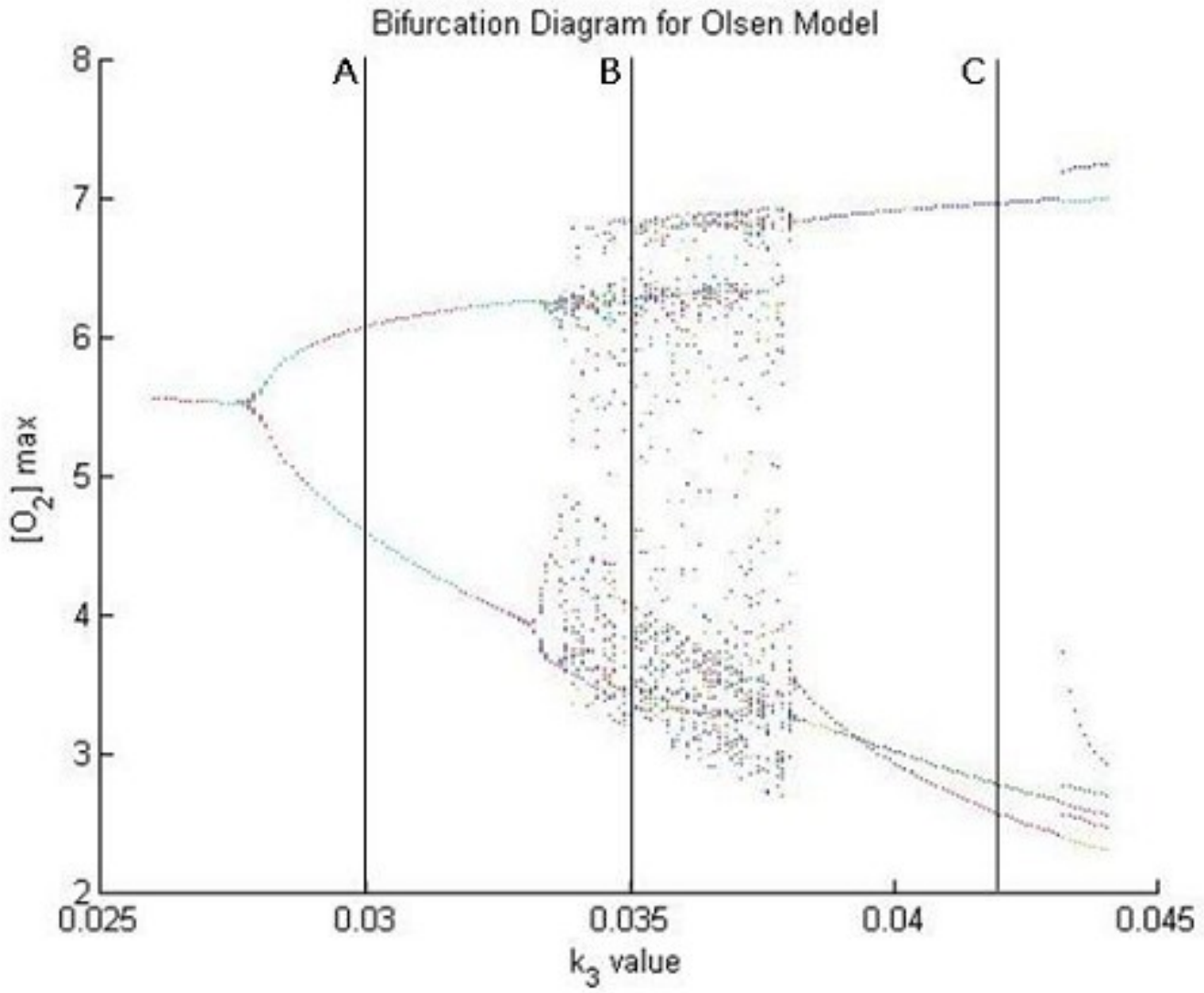
Paras Results - Bifurcation



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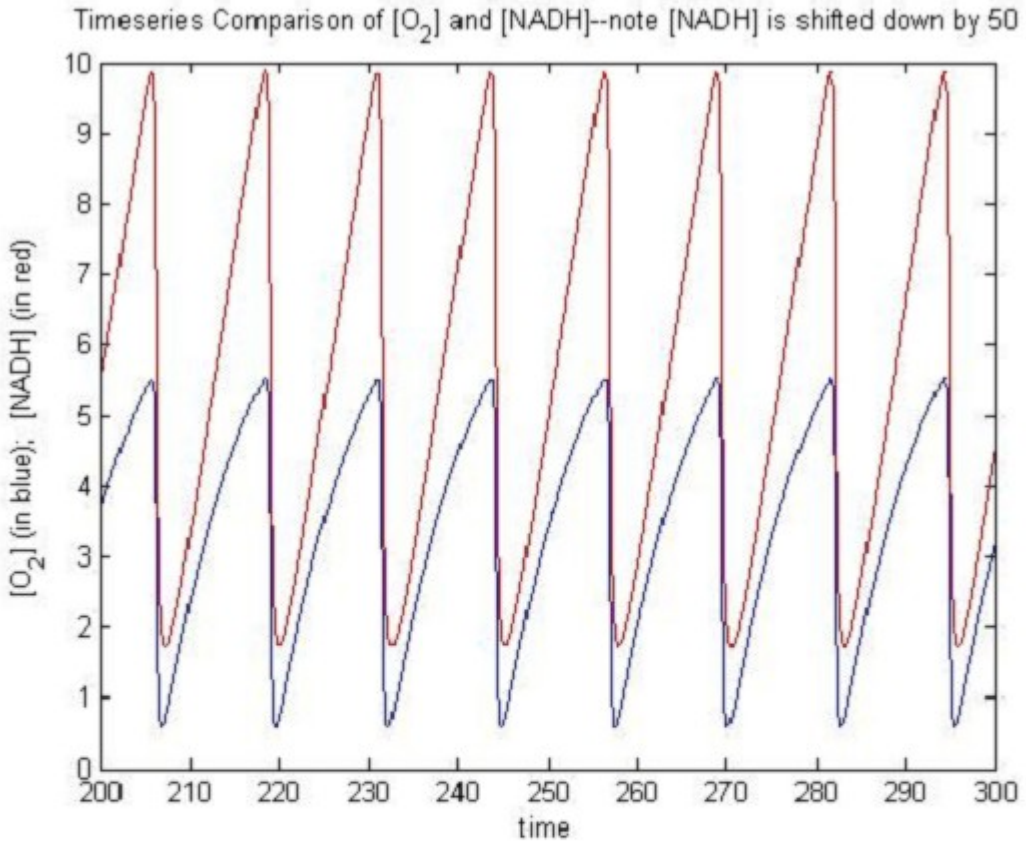
Karas Results



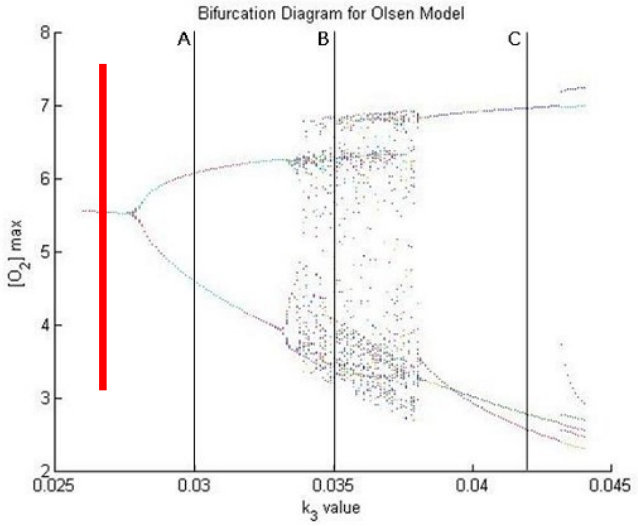


Figure 1: Timeseries plot of $[O_2]$ and [NADH] to illustrate the correlation of the concentrations between the two species. Here mechanism I and mechanism II are constantly battling to be the dominant reaction mechanism, resulting in oscillating concentrations of $[O_2]$ and [NADH].

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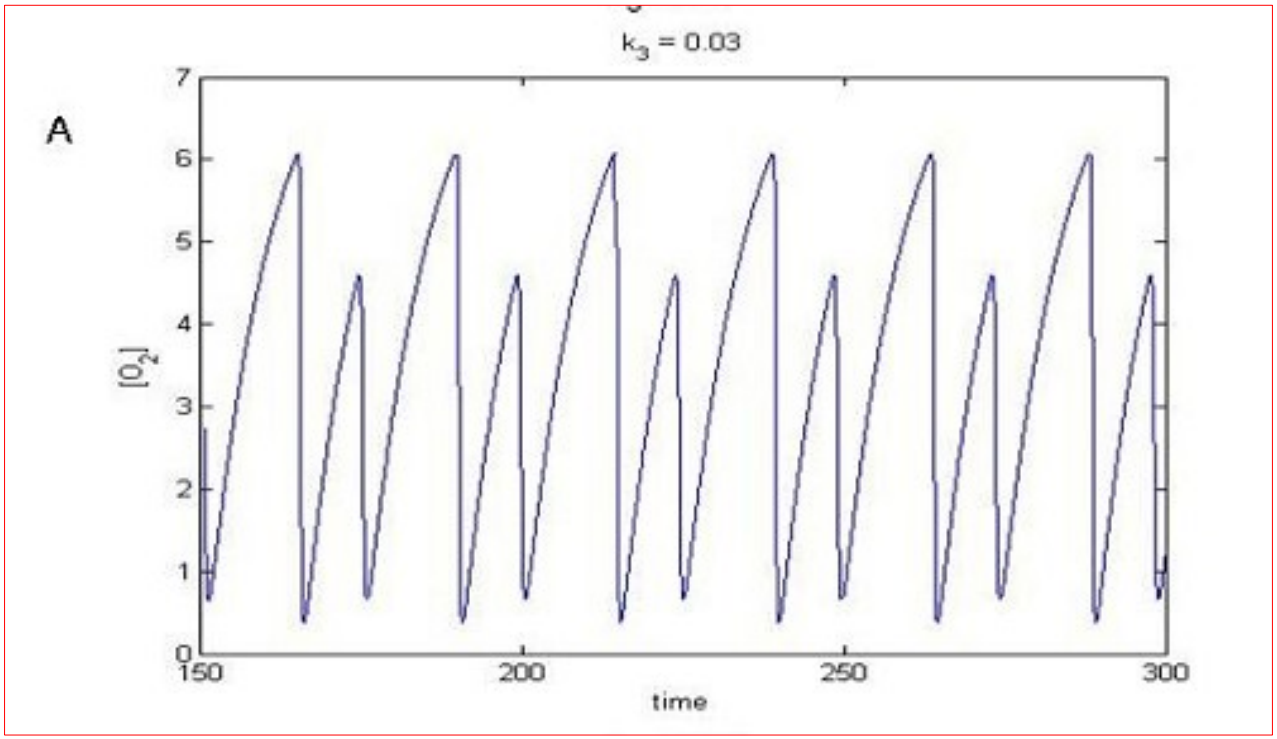
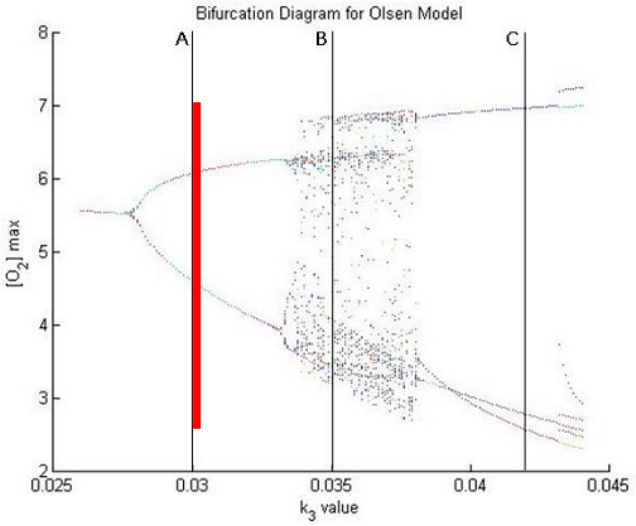
Karas Results





there are two alternating peaks, corresponding to the two points above k3= 0.03 on the bifurcation diagram

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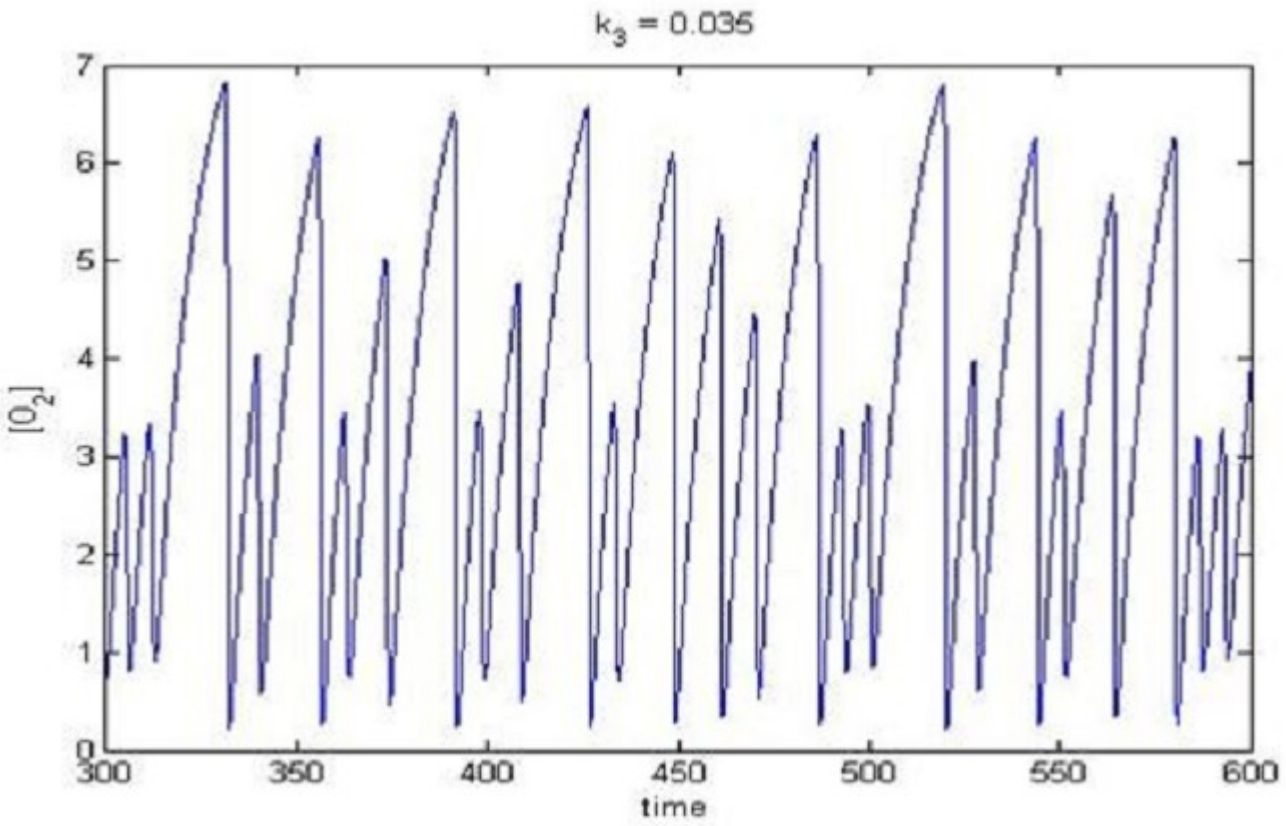
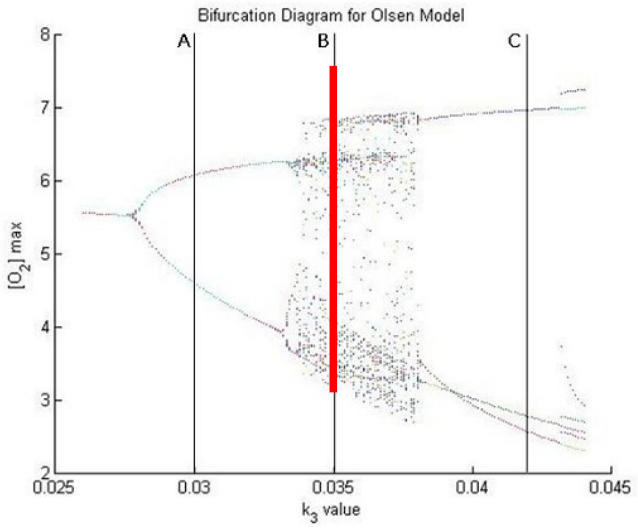
Karas Results





there is no easily discernable pattern to the peaks in the time-series data, corresponding to the chaotic region in the bifurcation diagram at k3= 0.035

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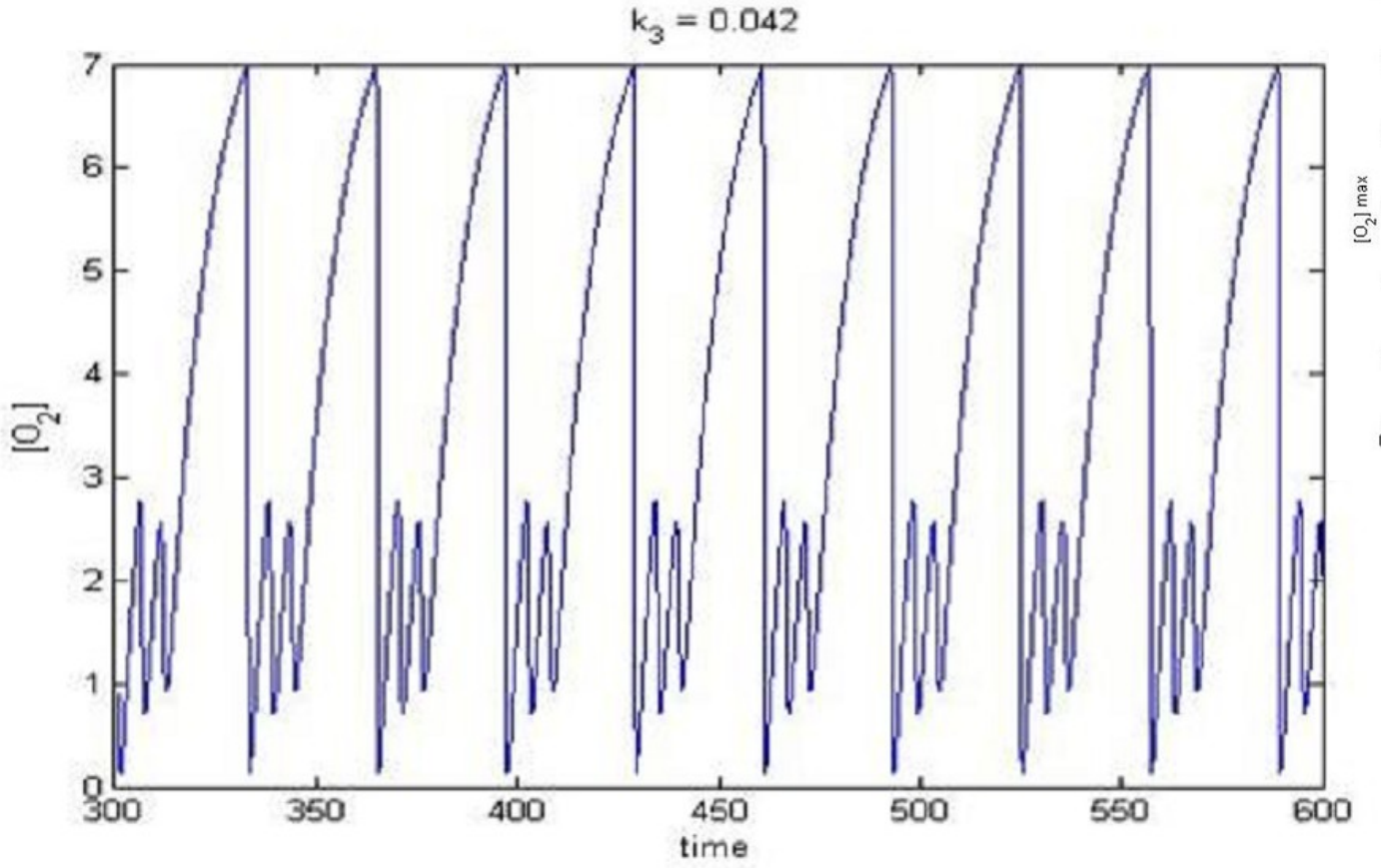
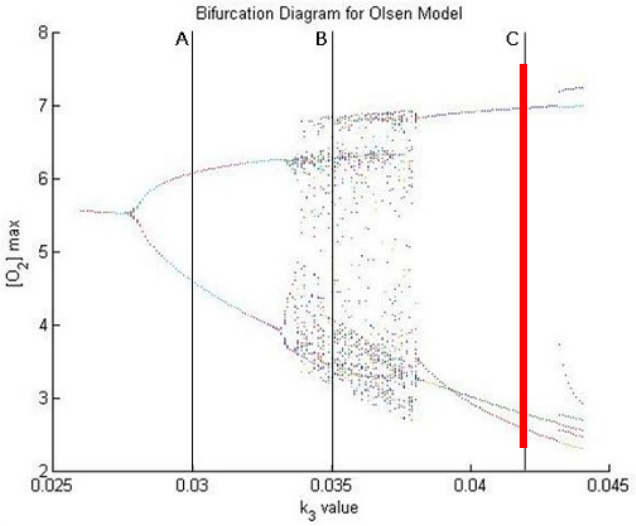
Karas Results





there are three alternating peaks

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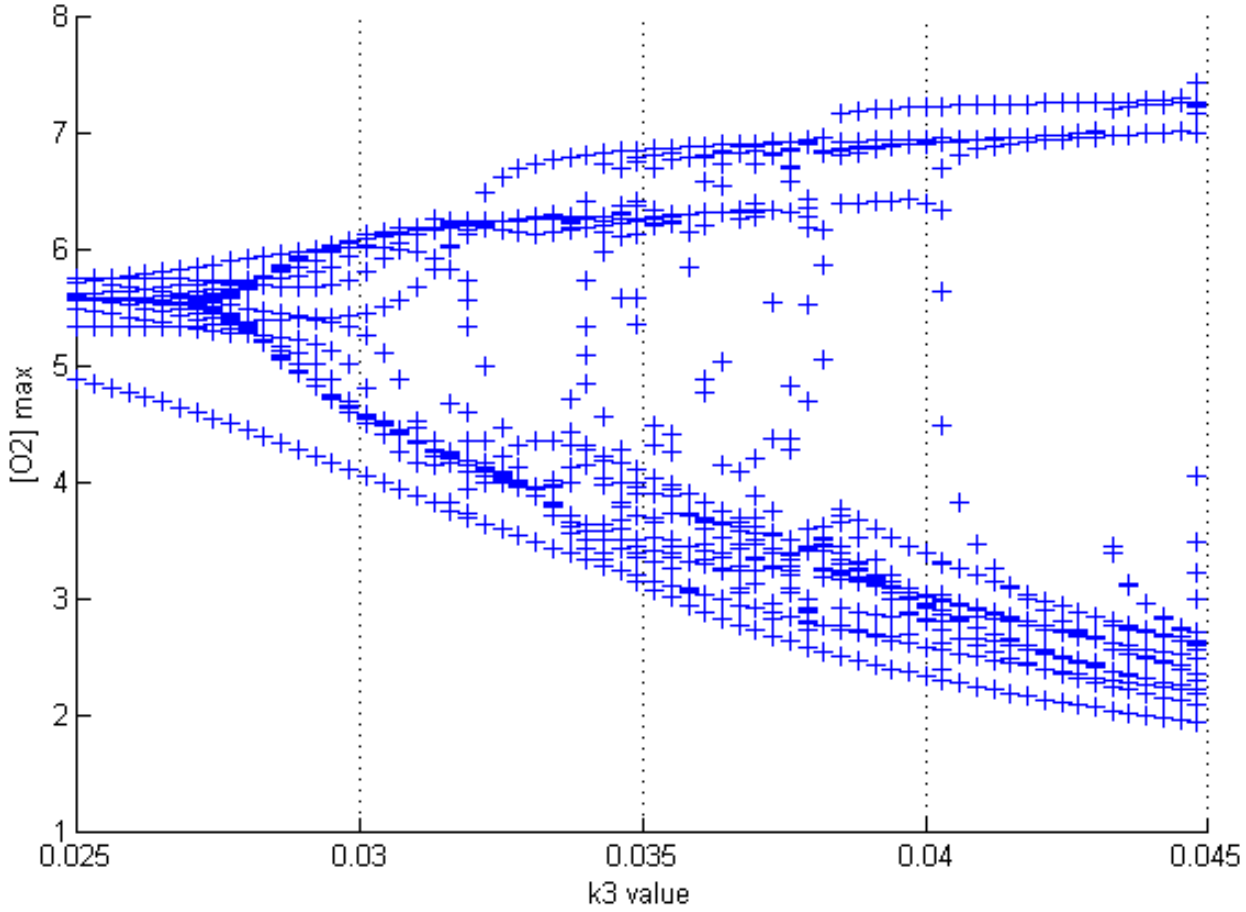
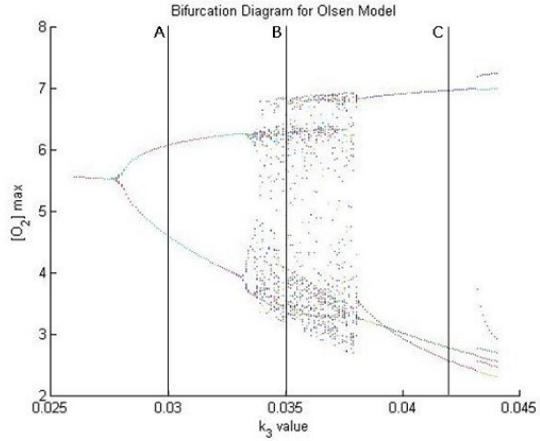
Canseco Results





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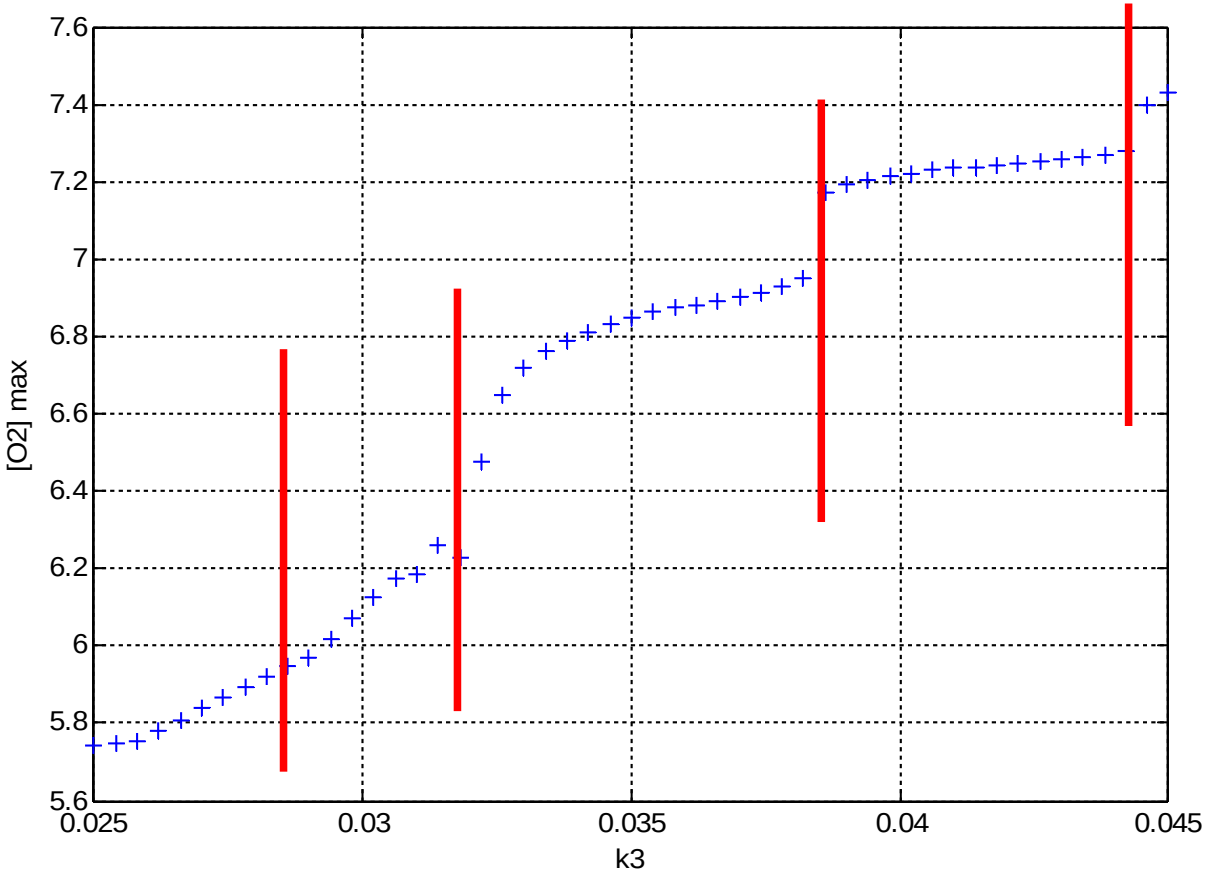
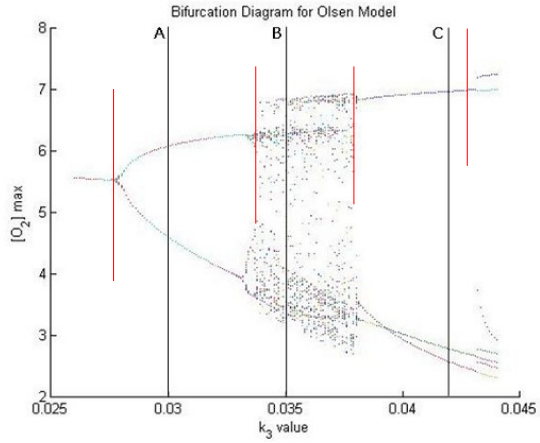
Bifurcation diagram envelope





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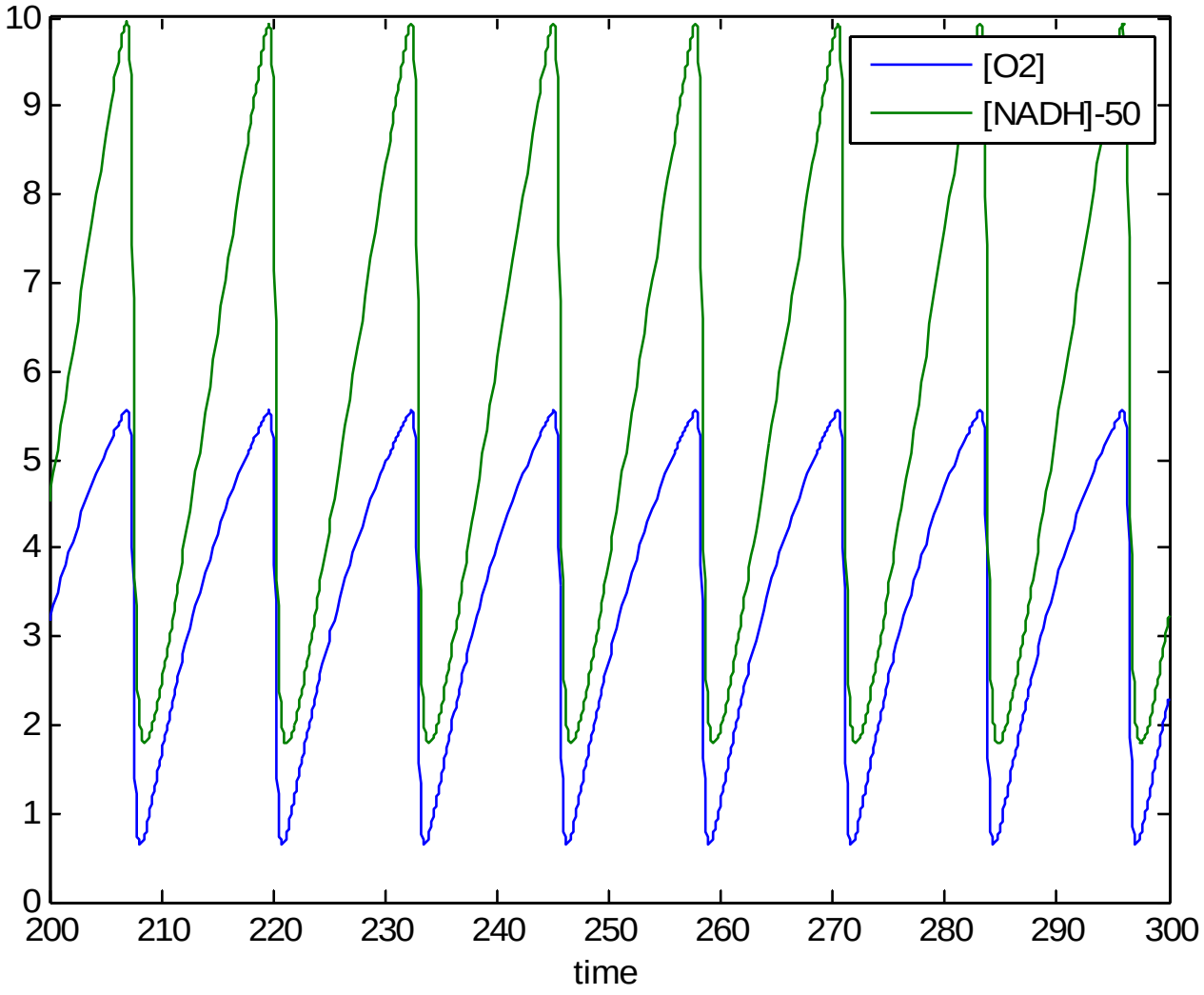
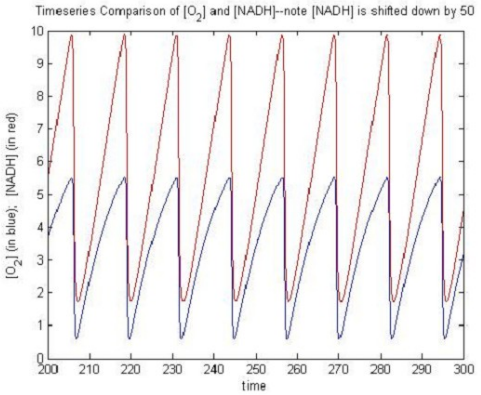
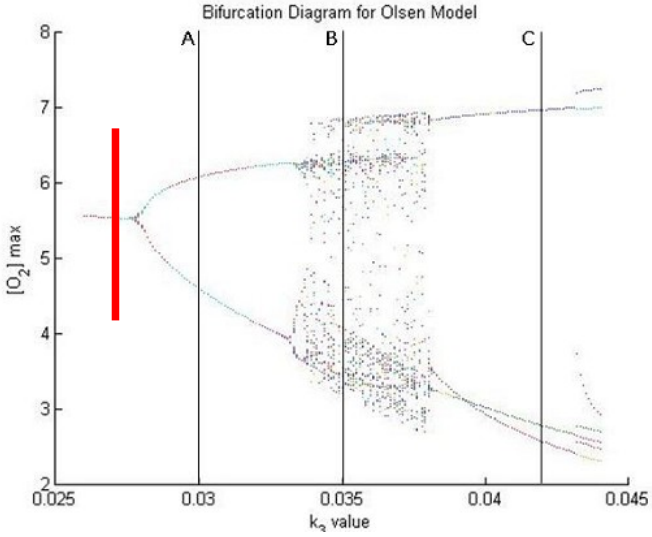
Canseco Results







Taken at k3 = 0.026

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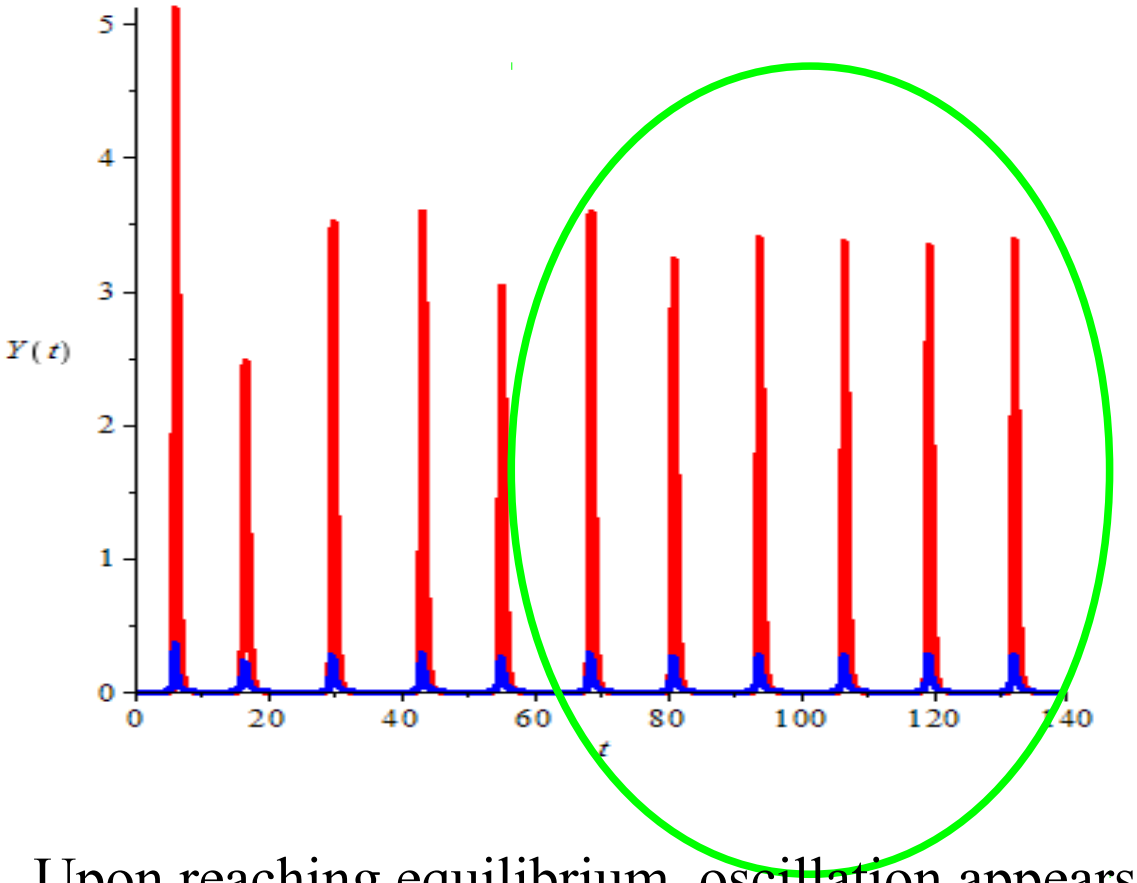
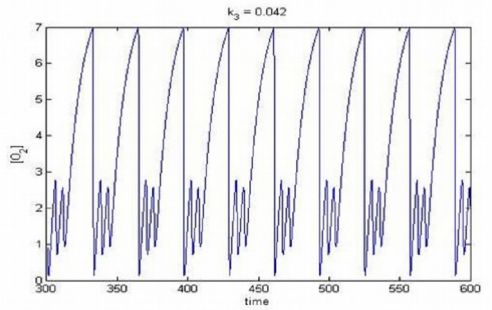
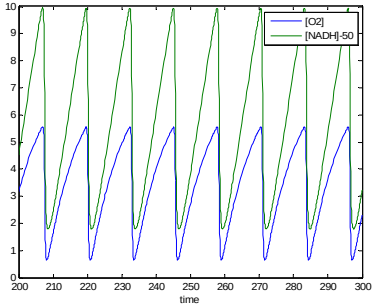
Maple Results Confirmation







Upon reaching equilibrium, oscillation appears

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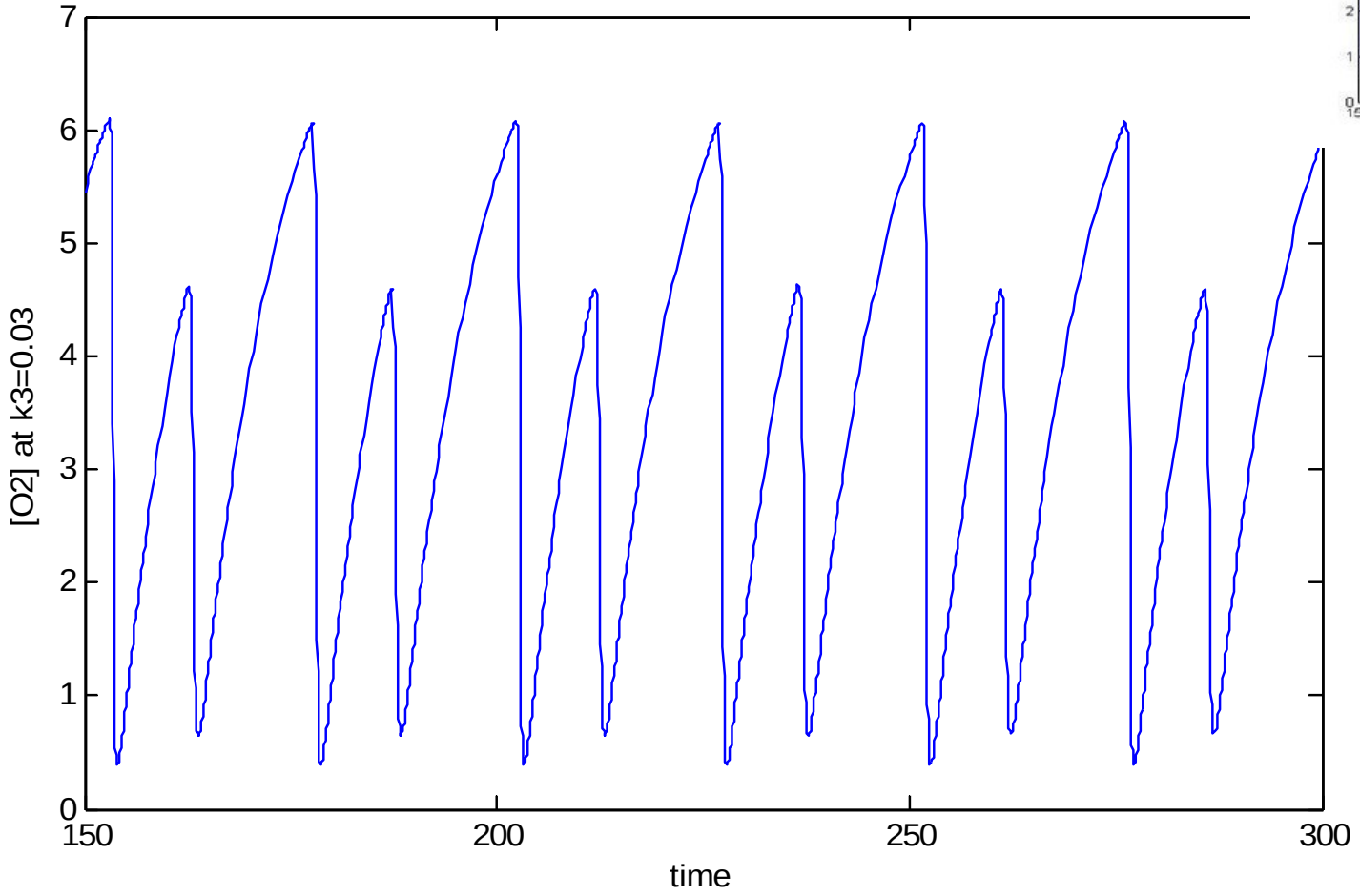
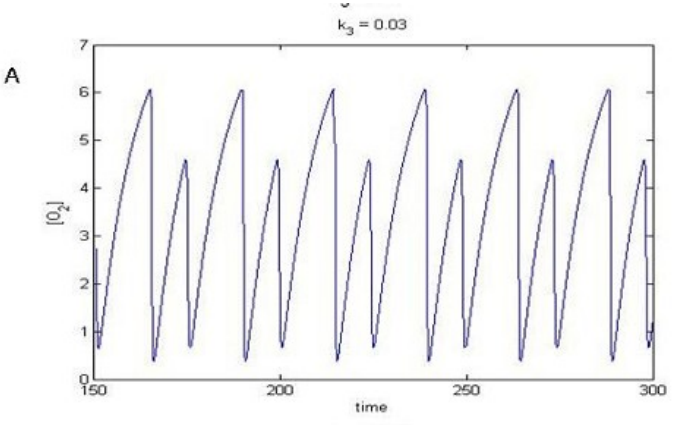
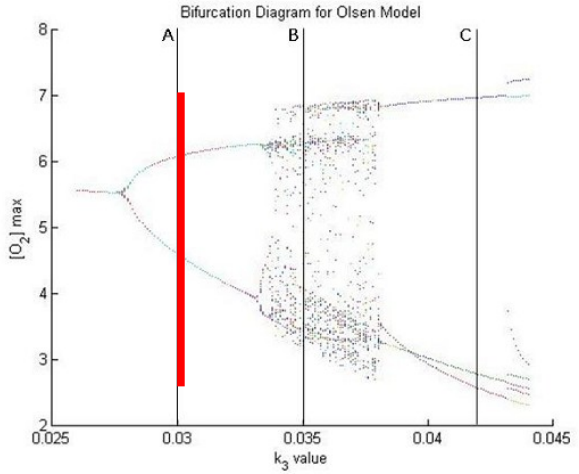
Canseco Results







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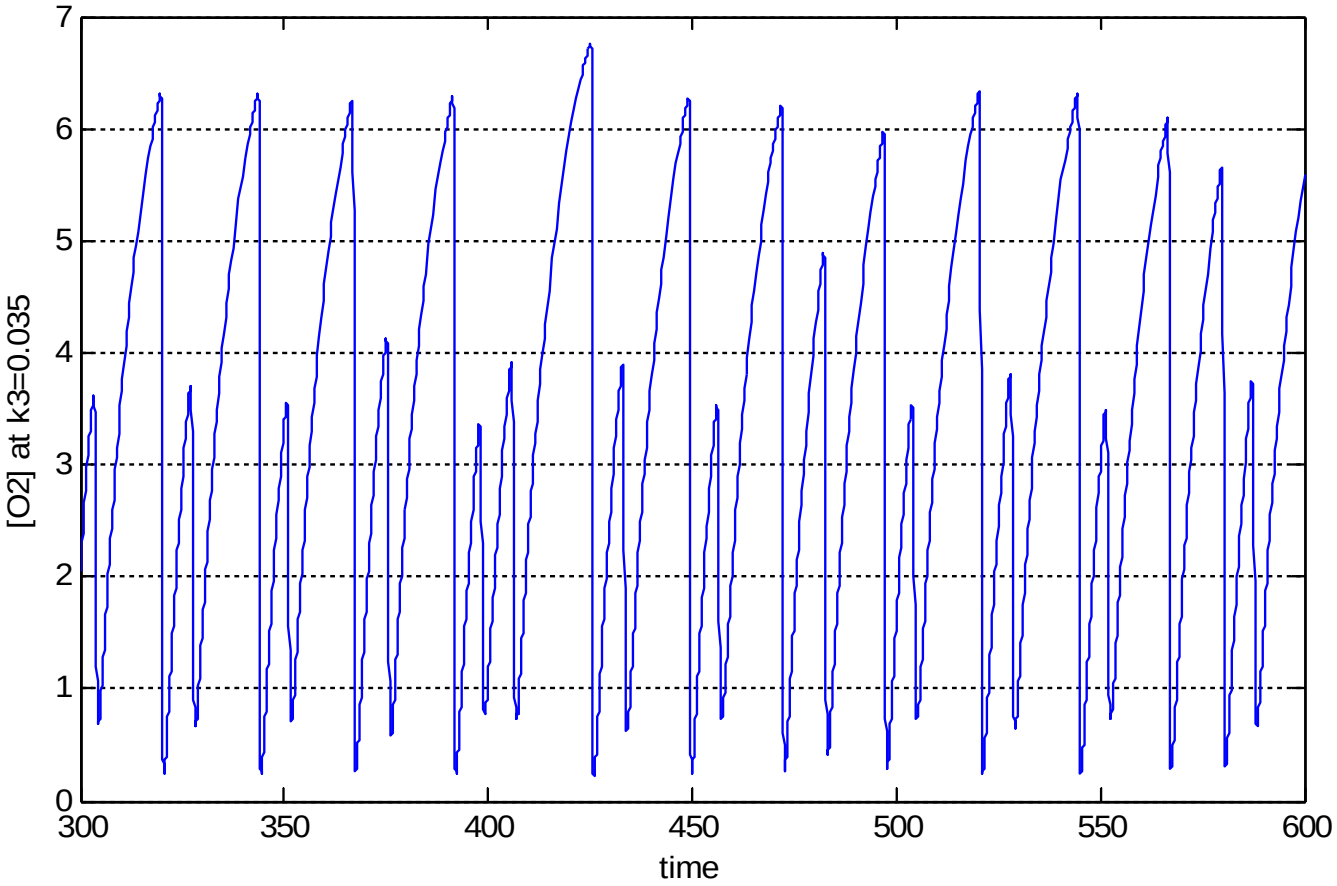
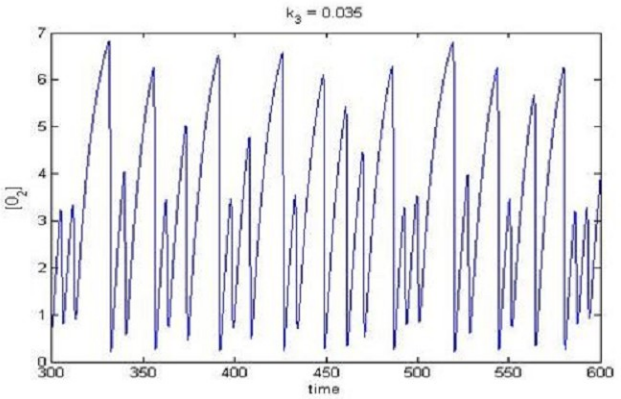
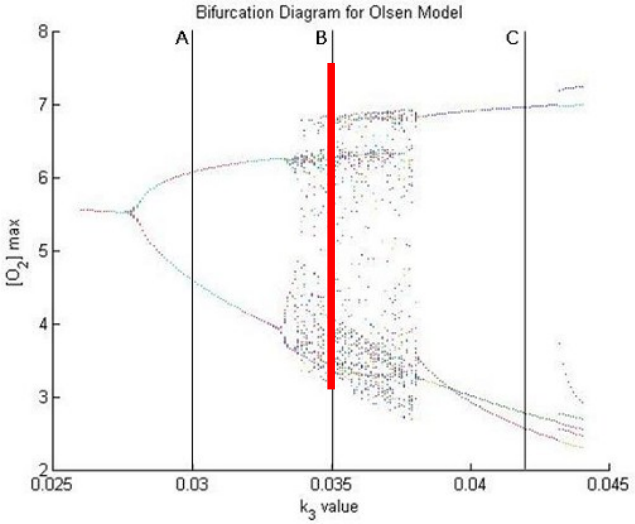
Chaotic region







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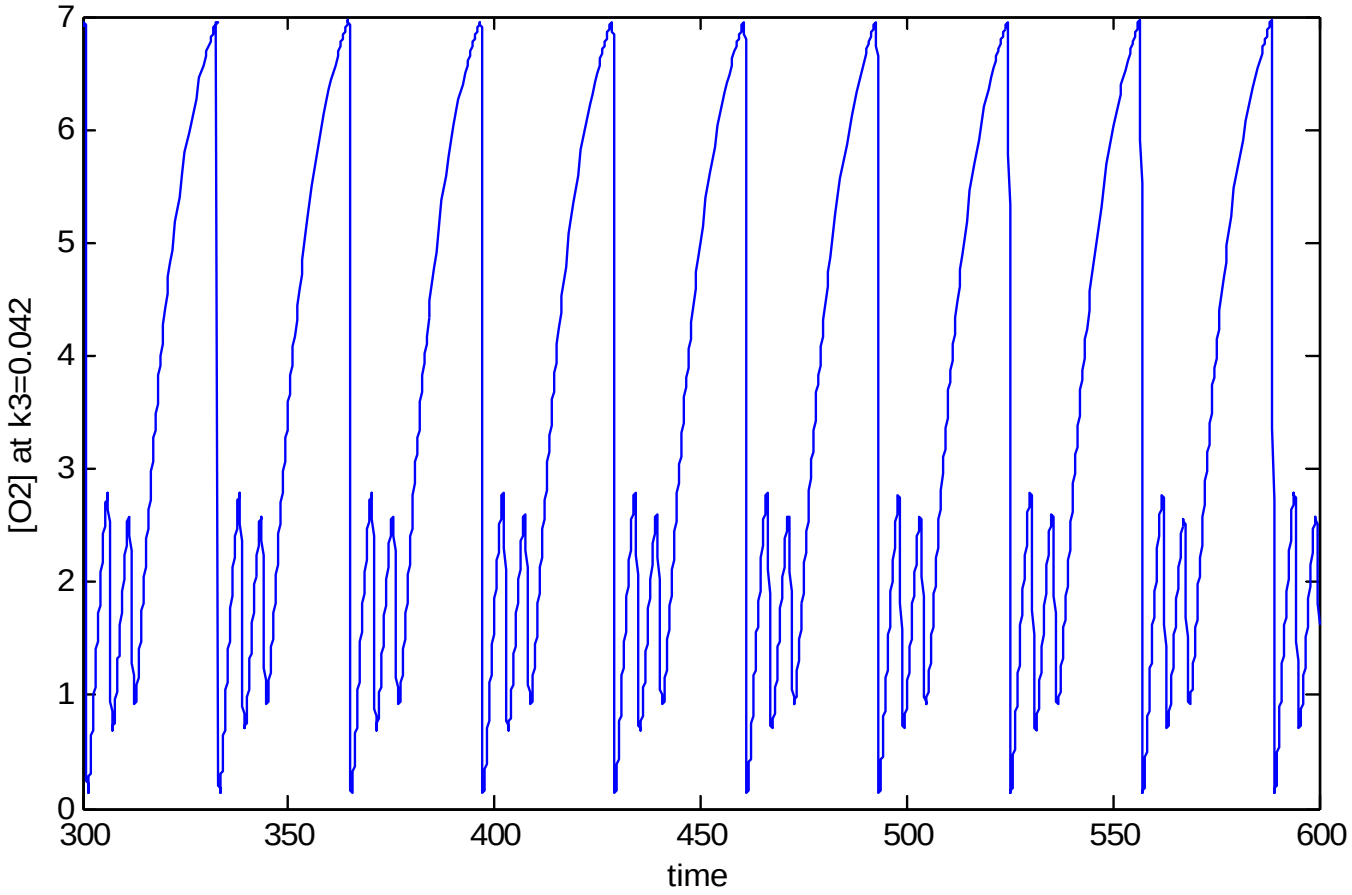
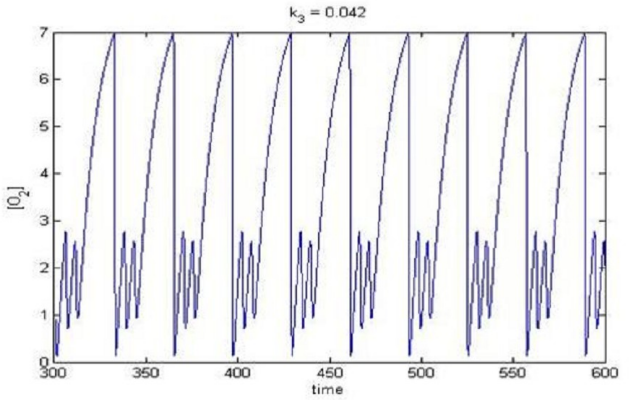
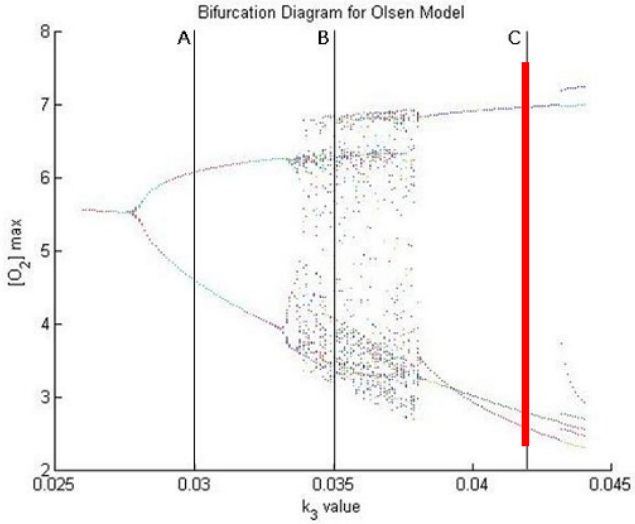
Canseco Results

Higher peak hasn't doubled yet







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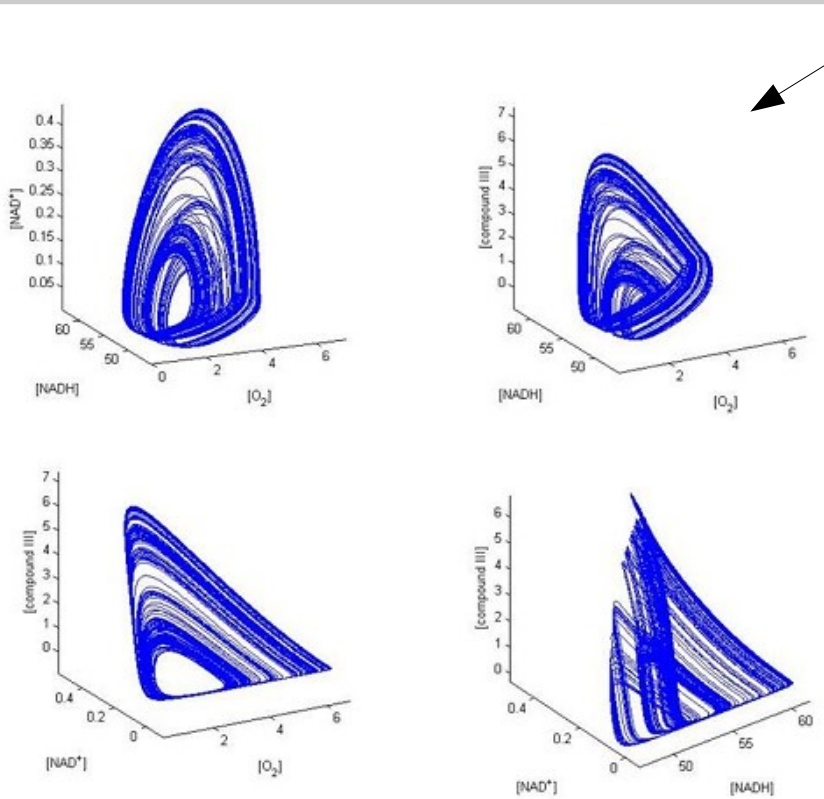
Results: Karas, Canseco



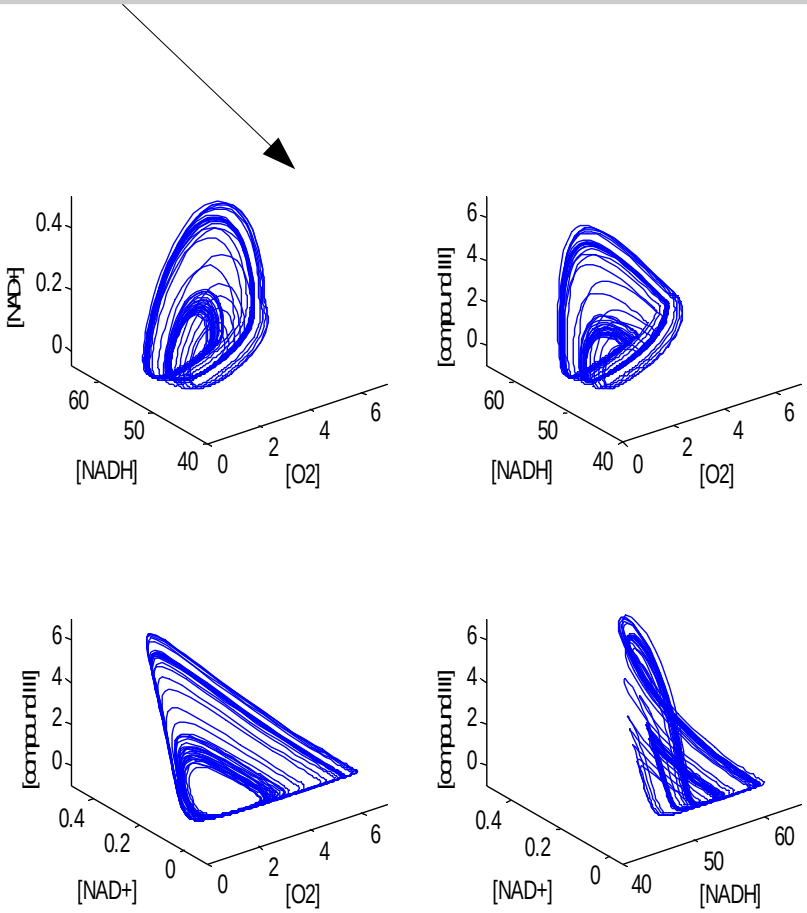


Figure 2: Projections of the four dimensional phase space ([O_2], [NADH], [$NAD^{\cdot}$], [Co III]) of a chaotic attractor for the PO reaction with $k_1 = 0.35$, and $k_3 = 0.035$.

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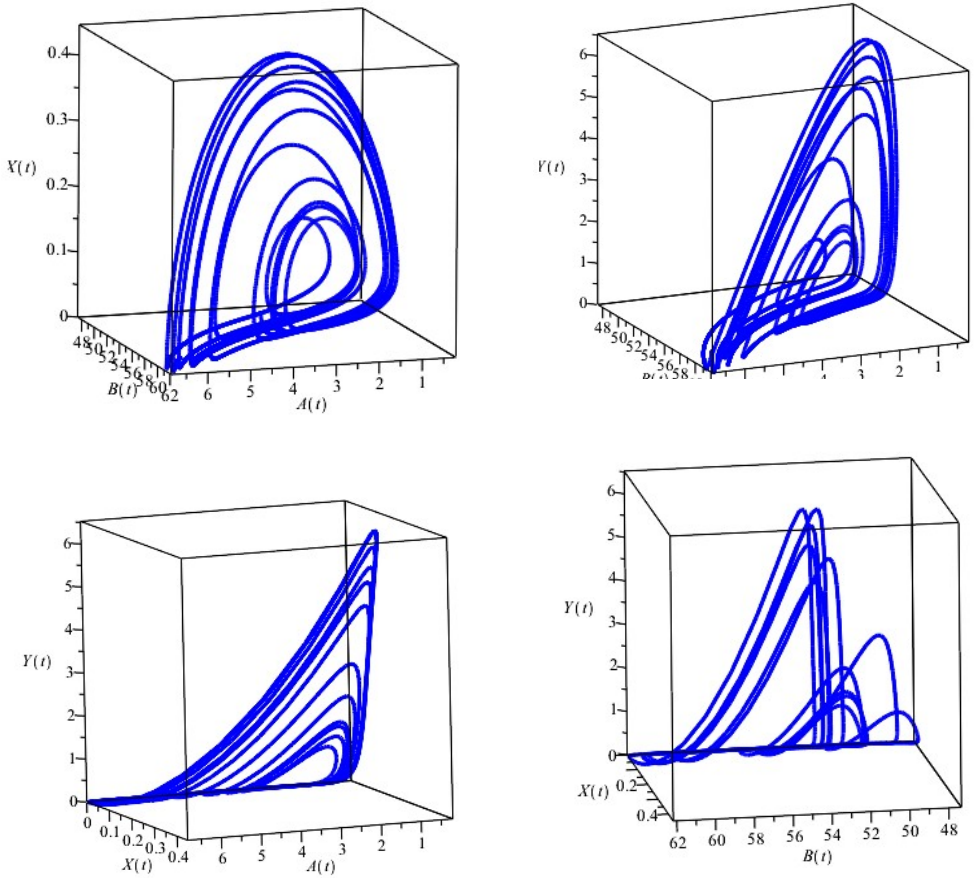
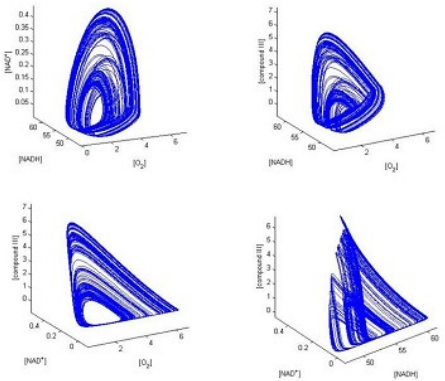
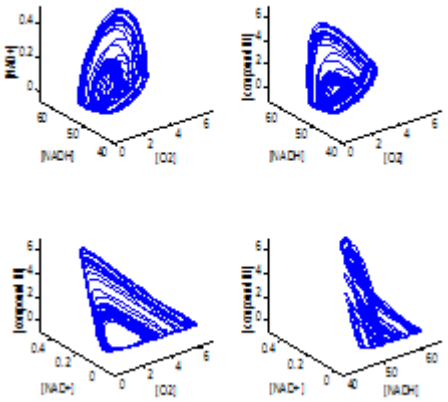
Maple Results Confirmation





Karas - Matlab



Canseco - Matlab

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Bifurcation Results for k1 - Karas

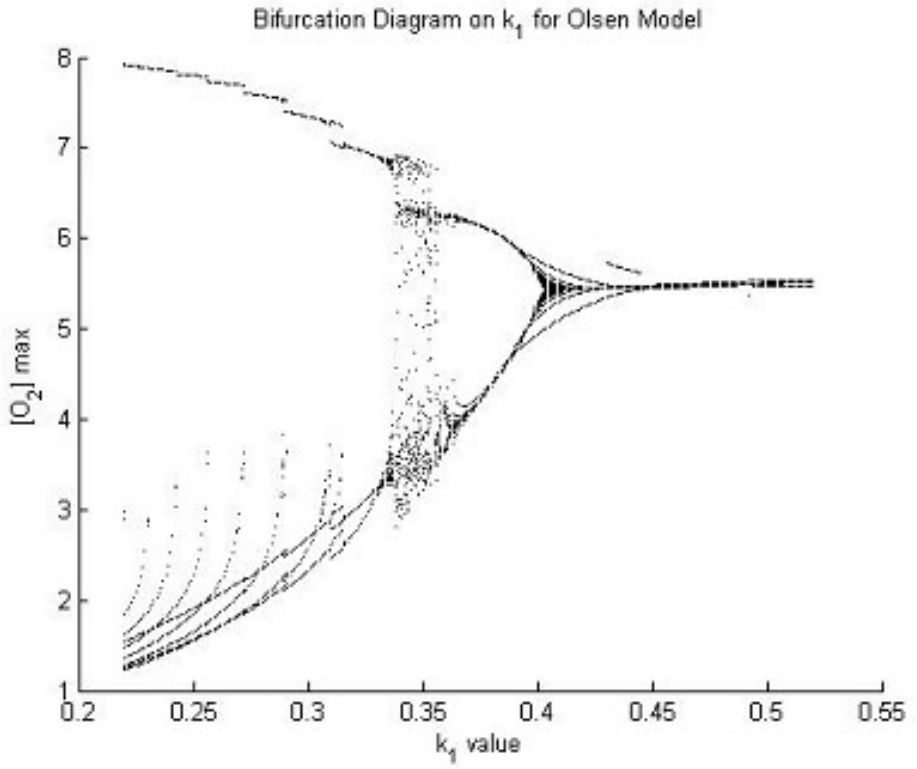

Figure 3: Bifurcation diagram of $[O_2]_{max}$ on k_1 (here $k_3 = 0.035$). Decreasing k_1 leads to period-doubling and chaos. Decreasing k_1 past the chaotic range once again yields periodic oscillations in $[O]_2$. Bifurcations on k_1 all have a similar structure no matter what value of k_3 is used. However, the values of k_1 that show chaotic behavior change depending on k_3.

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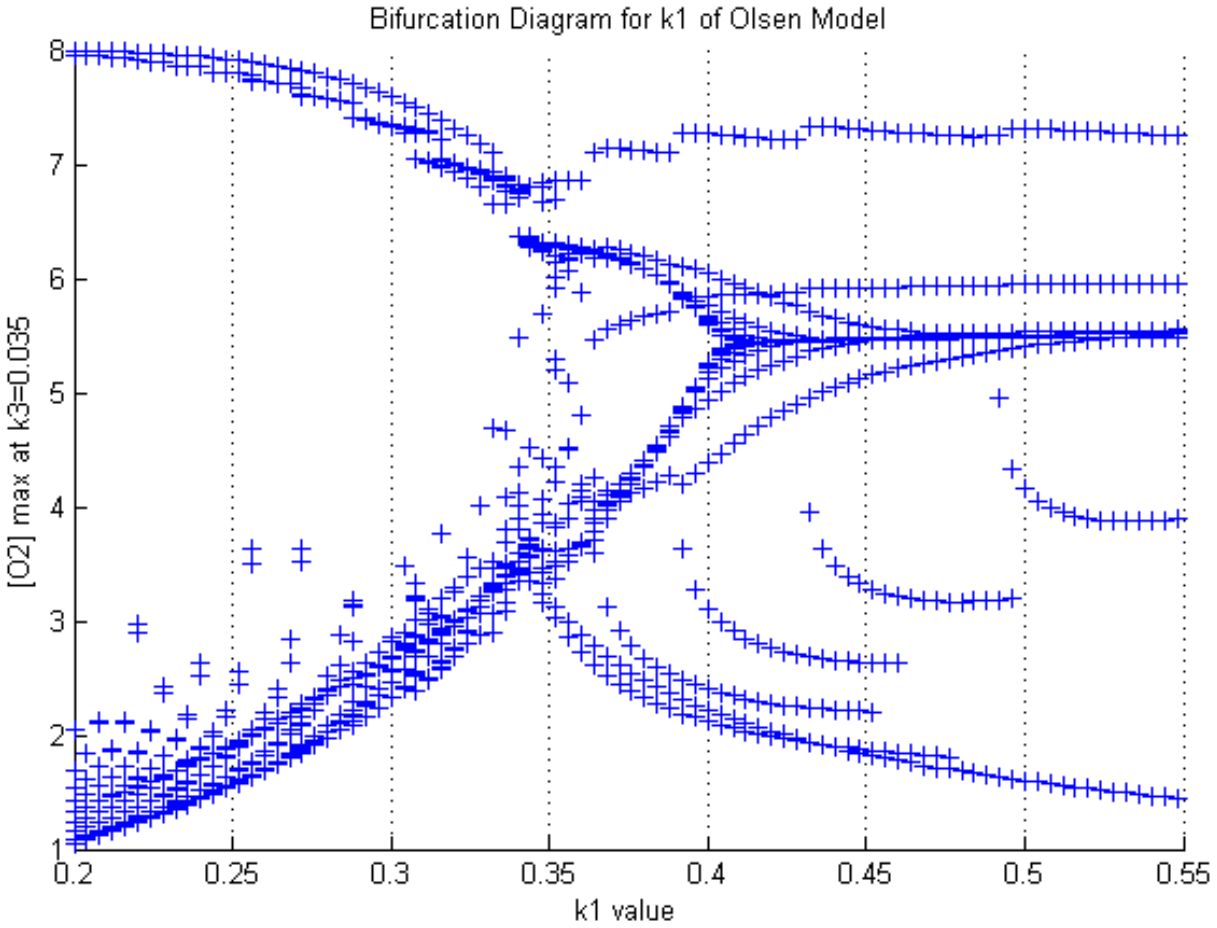
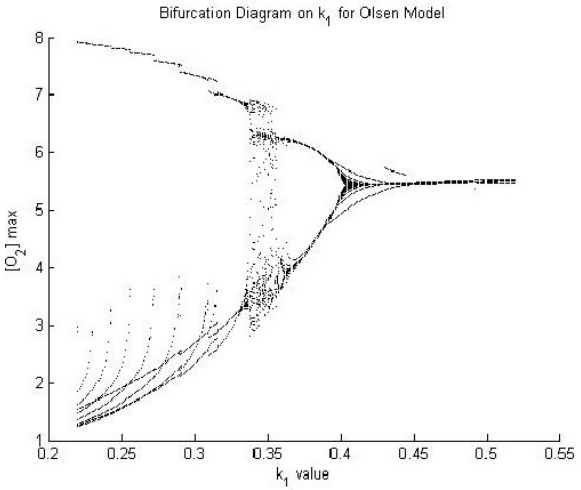
Bifurcation Results for k1 - Canseco





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Conclusions

- We have reimplemented the results of Karas (2007) on chaotic behavior of the Peroxidase-Oxidase reaction (PO).
- This gives us confidence in the results, which we shall use in the creation of the agent-based model of PO.
- The exploration done gained us the ff:
  - Better understanding of how chemical reactions are modeled
  - Our own Matlab code for looking at bifurcations in chemical reaction dynamics
  - Deeper knowledge in the advantages and limitations of Maple and Matlab for modeling chemical kinetics in non-elementary reactions

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