Chemistry 4010 Fall 2019
Test 2

Time allowed: 2 hours

Marks: 43

Handwritten notes are allowed. No printed or mechanically reproduced materials of any kind are permitted.

Software allowed: text editor, XPPAUT, MAPLE, calculator. If any other software is found to be in use during this exam, you will receive a grade of zero.

Answers are to be written in the exam booklets provided. If your answer involves the use of software, make sure to describe the calculation and to provide a reasonable sketch of any graphical results.

1. In the peroxidase-oxidase reaction, the enzyme peroxidase catalyzes the oxidation of NADH by oxygen. In a stirred tank reactor with continuous supply of reagents, the concentrations can oscillate when certain compounds are added. In particular, 2,4-dicholorophenol increases the rate of breakdown of a key intermediate in the reaction known as compound III. In a classic study of this reaction, experiments were carried out with different concentrations of 2,4-dicholorophenol added to the mixture.[1] The oxygen concentration was recorded as a function of time using an oxygen electrode. The results of these experiments are shown in figure 1. **7 marks**

   Using terminology and concepts from nonlinear dynamics, describe what happens in these experiments. This should include a description of the dynamics in each panel (i.e. the type of attractor), as well as of the changes that occur from one panel to the other.

[1] T. Geest et al., *J. Phys. Chem.* **96**, 5678 (1992).

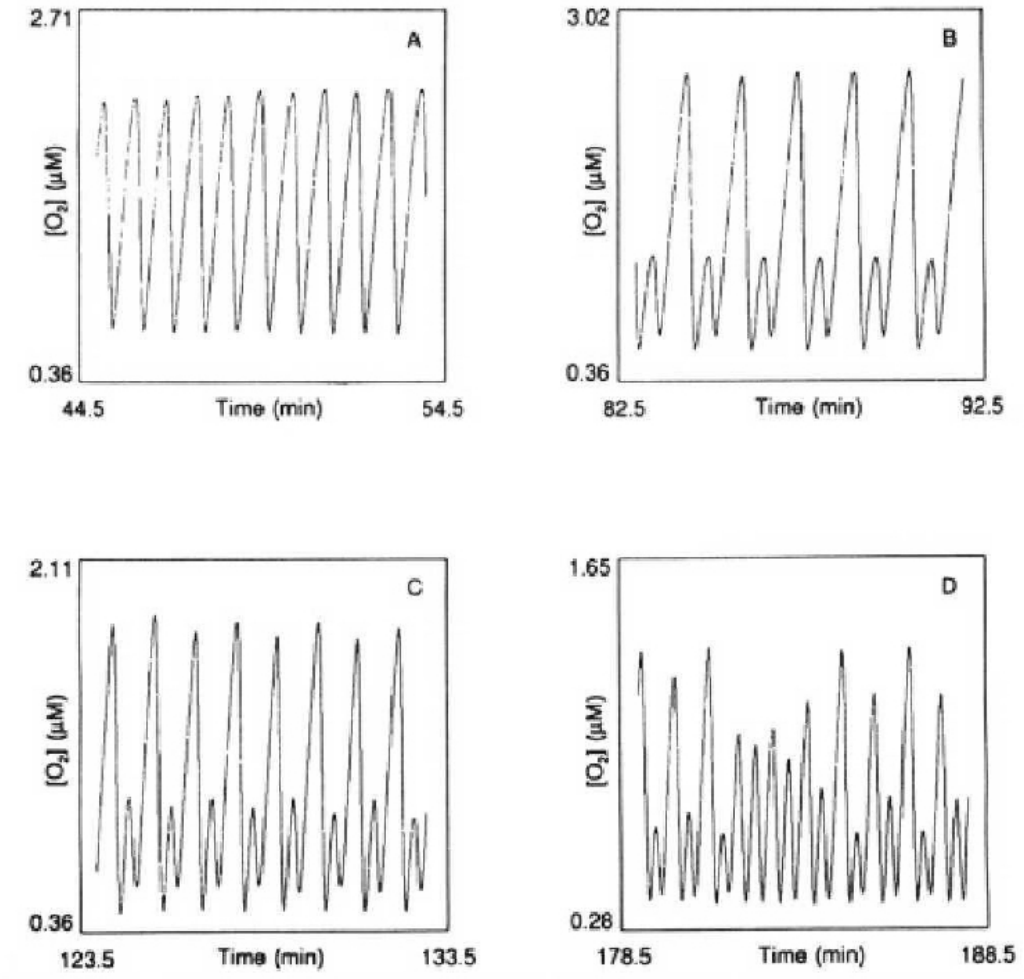

Figure 1: O_2 recordings from studies of the peroxidase-oxisase reaction at varying concentrations of 2,4-dicholorophenol: panel (A) 20 μM, (B) 25 μM, (C) 30.8 μM, and panel (D) 32.2 μM.

2. The following set of equations were first devised by Rössler to illustrate how chaotic systems could be designed. **14 marks**

$$\dot{x} = -(y + z)$$
$$\dot{y} = x + ay$$
$$\dot{z} = b + xz - cz$$

Note that this is not a chemical model, and that the variables can have both positive and negative values.

(a) In general, the equilibrium points satisfy a quadratic equation. However, there is a simple equilibrium point for the special case $a = 0$. Find the equilibrium point for this case. [3 marks]

(b) Carry out a numerical bifurcation analysis of this system using AUTO for the parameters $b = 0.2$, $c = 5.7$. Your report should include a sketch of the bifurcation diagram as well as a table of the bifurcations found (parameter value + type). You can stop once you have found three period-doubling bifurcations. [10 marks]

Hints: You can limit your bifurcation diagram to the range [0,0.3]. You will likely want to reduce `Ds`, `Dsmin` and `Dsmax` given this limited range of the parameter.

(c) Find parameter values at which chaos is observed. Report these parameter values. There is no need to sketch the attractor. [1 mark]

3. The reaction of H_2 with iodine in the gas-phase has a peculiar mechanism involving a genuine third-order step: **22 marks**

$$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,I$$

$$I + H_2 + I \xrightarrow{k_2} 2\,HI$$

(a) Write down the rate equations for this model assuming a large excess of H_2. [2 marks]

(b) Analyze the dynamics of this system using any methods that seem appropriate to you. Your objective is to eventually be able to say something about the types of attractors this system can have, and their stability. [20 marks]

Notes: Please use clear headings and/or sentences to indicate what you are attempting to do. Whatever methods you apply, you are expected to interpret the results. Just doing the math will not get you full marks. Moreover, the maximum number of marks you can obtain is 20. Even if you complete more work, there will be no bonus marks.

Scoring:

Transformation to dimensionless equations: 4 marks

Finding equilibrium point(s): 4 marks

Linear stability analysis: 6 marks

Phase-plane analysis: 10 marks

Centre-manifold analysis: 15 marks

Xppaut calculation(s): 5 marks

Other: variable, depending on difficulty and appropriateness