BELOUSOV-ZHABOTINSKII OSCILLATIONS IN A BATCH REACTOR

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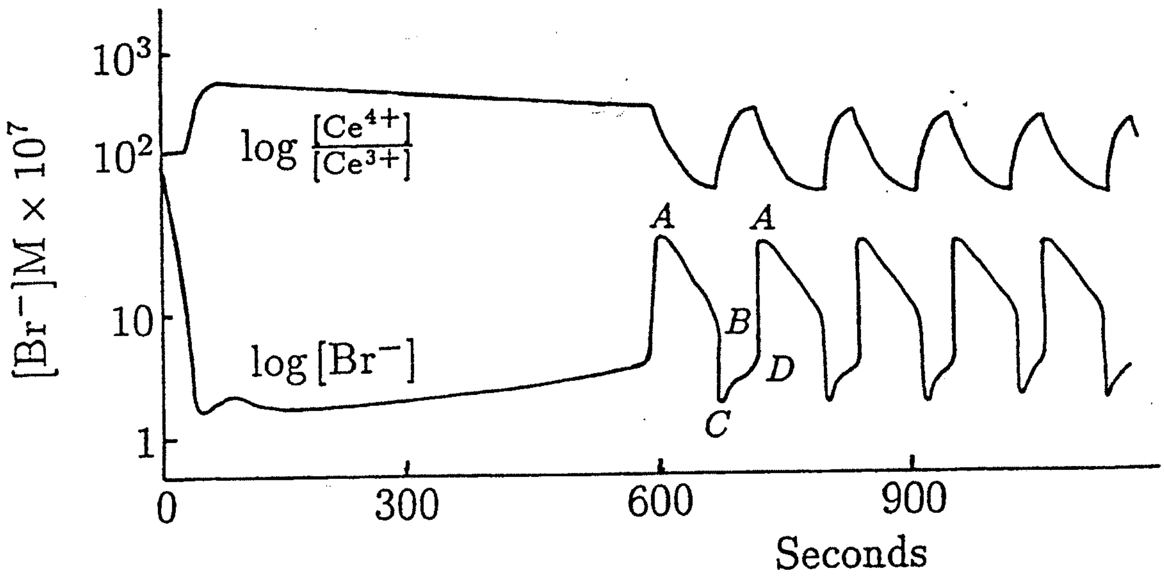
1 BZ OSCILLATIONS IN A CLOSED SYSTEM

- Malonic acid oxidation by bromate in an acid solution, catalyzed by a metal ion (Ce^{4+}).

- Long series of oscillations in the concentration of the intermediate species (with a cromatic effect).



- The main reactants are irreversibly consumed.

- Finally, the oscillations vanish and chemical equilibrium is monotonically approached.

2 MODELING BZ OSCILLATIONS

- Classical Oregonator model, where the concentration of the reactants is kept constant.

- Under the "pool chemical" approximation batch oscillations can only be simulated for a very short time.

- The consumption of the reactants during each oscillation is about 1-2% of the initial value.

- The Oregonator provides valuable information for the development of a modified model, which accounts for the consumption of the reactants.

2.1 OREGONATOR (DIMENSIONAL)

- State variables:

  $X =[HBrO_2]$ $Y =[Br^-]$ $Z =[Ce^{4+}]$

- Parameters:

  $A =[BrO_3^-]$ $B =[CH_2(COOH)_2]$ $H =[H^+]$

- Model equations:

$$
\begin{aligned}
\frac{dX}{dt} &= k_1 H^2 AY - k_2 HXY + k_3 HAX - 2k_4 X^2 \\
\frac{dY}{dt} &= -k_1 H^2 AY - k_2 HXY + hk_5 BZ \\
\frac{dZ}{dt} &= 2k_3 HAX - k_5 BZ
\end{aligned}
$$

- "Lo" values of the kinetic parameters (Tyson, 1985; Field and Försterling, 1986).

$$
\begin{aligned}
k_1 &= 2\ \mathrm{M^{-3}s^{-1}}\ , \\
k_2 &= 10^6\ \mathrm{M^{-2}s^{-1}}\ , \\
k_3 &= 10\ \mathrm{M^{-2}s^{-1}}\ , \\
k_4 &= 2000\ \mathrm{M^{-1}s^{-1}}\ , \\
k_5 &= 1\ \mathrm{M^{-1}s^{-1}}\ .
\end{aligned}
$$

2.2 OREGONATOR (DIMENSIONLESS)

- Dimensionless Oregonator:

$$\begin{aligned}
\varepsilon\frac{dx}{d\tau} &= qay - xy + ax - x^2 , \\
\delta\frac{dy}{d\tau} &= -qay - xy + fbz , \\
\frac{dz}{d\tau} &= ax - bz .
\end{aligned}$$

- $f = 2h$ $\quad\varepsilon = 0.12\quad$ $\delta = 0.0006$

- Pseudo-steady-state approximation for y

$$y = y(x,z) = \frac{fbz}{x + qa} .$$

- Two-variable reduced Oregonator:

$$\begin{aligned}
\varepsilon\frac{dx}{d\tau} &= ax - x^2 - fbz\frac{x - qa}{x + qa} , \\
\frac{dz}{d\tau} &= ax - bz .
\end{aligned}$$

to which phase-plane techniques can be applied.

2.3 ASYMPTOTIC STABILITY ANALYSIS

- In the 3-D parameter space (a, b, f).
- The only positive steady-state:

$$x_s = a x_m \qquad y_s = a y_m \qquad z_s = a^2 z_m / b$$

with:

$$x_m = z_m = \frac{(1-f-q) + [(1-f-q)^2 + 4q(1+f)]^{1/2}}{2},$$

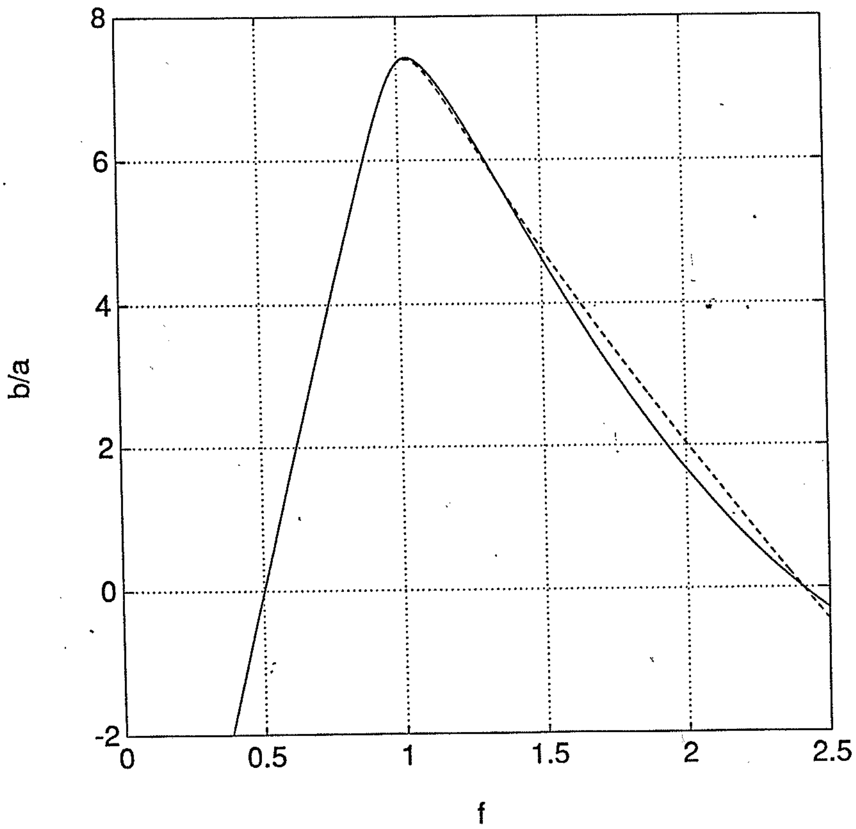
$$y_m = \frac{f x_m}{x_m + q},$$

- Hopf bifurcation set:
  - Oreg.:

$$\frac{b}{a} = \frac{-S + \sqrt{S^2 - 4RT}}{2R} = F(f)$$

  - Red. O.:

$$\frac{b}{a} = \frac{1}{\varepsilon}\left(1 - 2x_m - \frac{2qfx_m}{(x_m+q)^2}\right) = G(f)$$



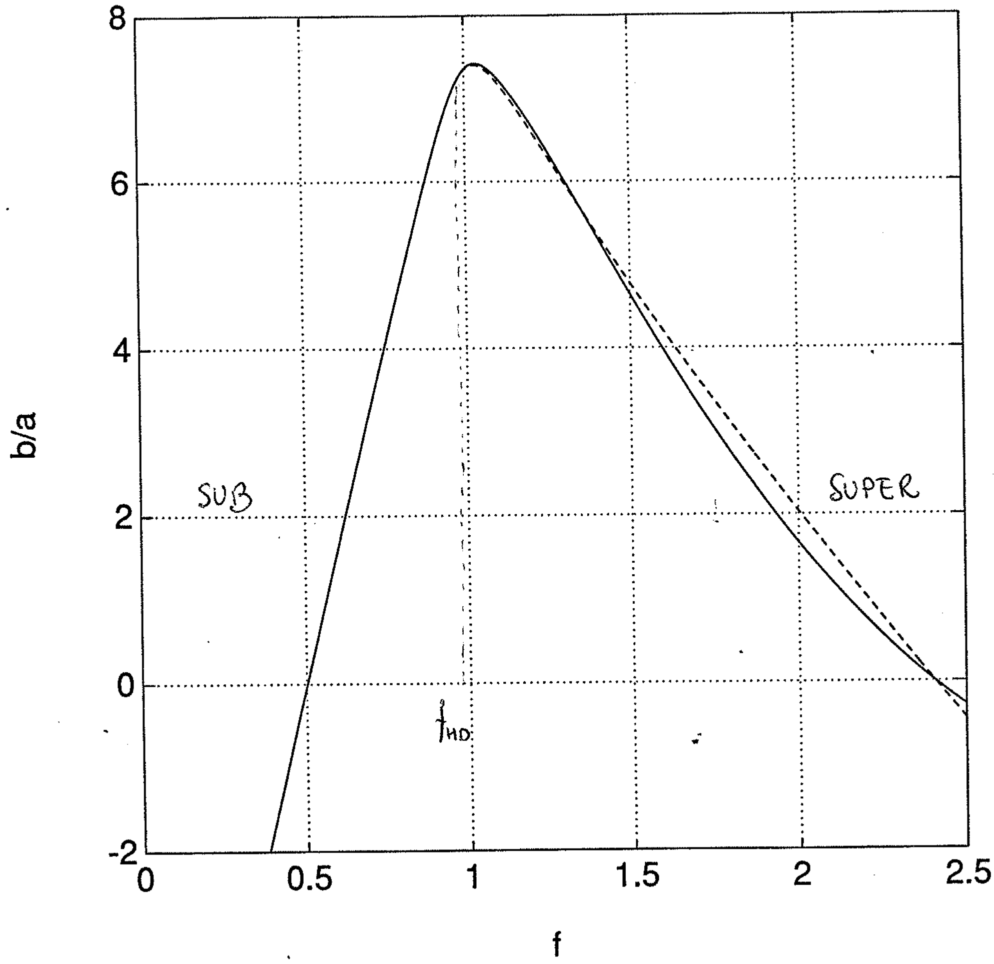
Oregonator: $f_{max} = 1.0317$

Reduced O.: $f_{max} = 1.0282$

2.4 LIMIT CYCLE STABILITY ANALYSIS

- Through normal form analysis the character of the Hopf bifurcation can be determined analitically.

- The stability of the limit cycles emerging from the bifurcation depends only on f.

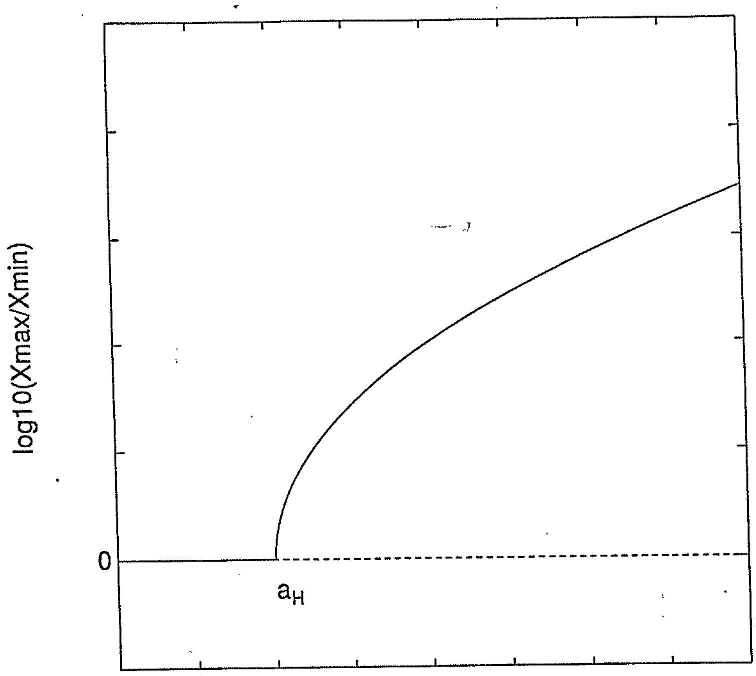


$$f_{HD} = 0.9858$$
$$(b/a)_{HD} = 7.2786$$

2.4.1 SUPERCRITICAL HOPF BIFURCATION

- Bifurcation diagram as a function of a.

- Constant values of b and f, with $f > f_{HD}$.

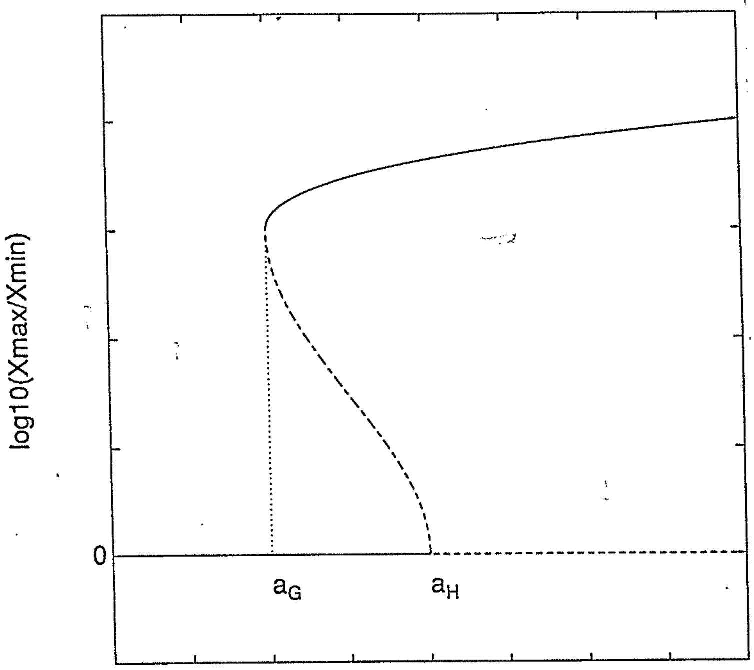


- Small amplitude stable oscillations emerging from the bifurcation point.

2.4.2 SUBCRITICAL HOPF BIFURCATION

- Bifurcation diagram as a function of a.

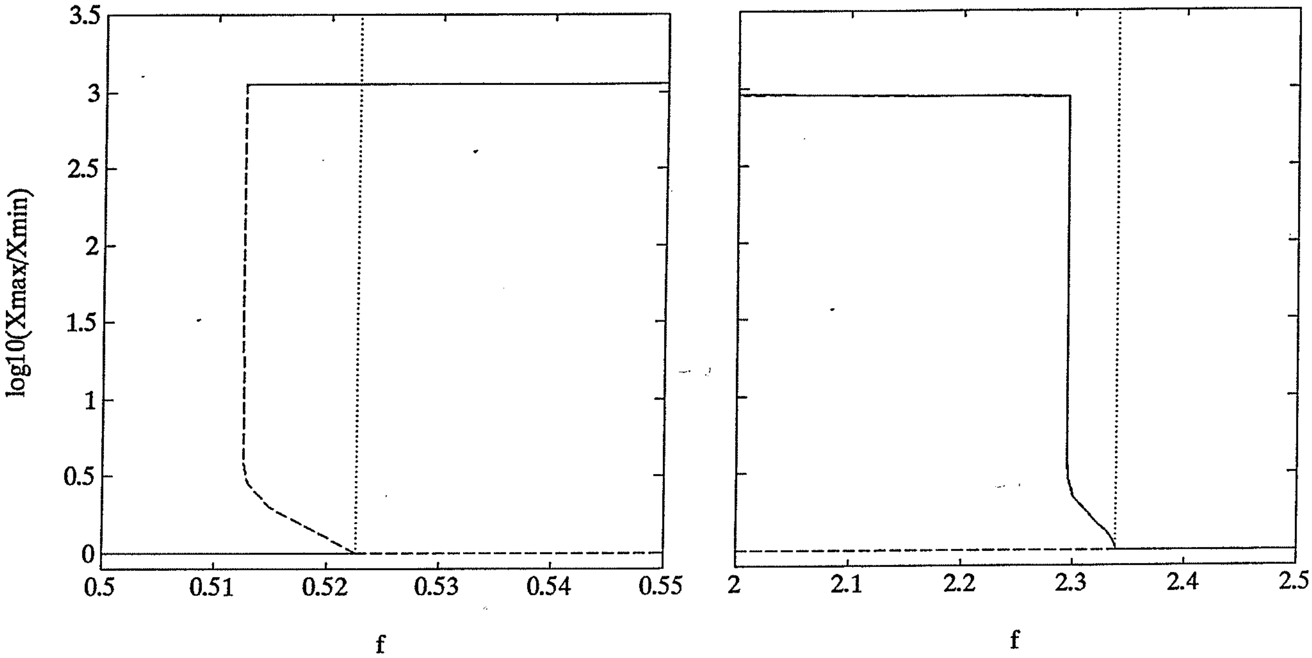
- Constant values of b and f, with $f < f_{HD}$.



- Small amplitude unstable oscillations emerging from the bifurcation point.
- Large amplitude stable relaxation oscillations.

2.4.3 BIFURCATION DIAGRAM AS A FUNCTION OF f

- Constant values of a and b, with $b/a < 7.2786$.



- Subcritical Hopf at the lower bifurcation and supercritical Hopf at the upper bifurcation.

- "Canard explosion" near the supercritical bifurcation point.

3 MODELING BATCH OSCILLATIONS

- Objective: description of the extinction of the oscillations.

- Modified Oregonator, which accounts for the consumption of the reactants.

- The consumption of bromate is well described by the inorganic subset:

$$\frac{dA}{dt} = -k_1 H^2 A Y - k_3 H A X + k_4 X^2 \, .$$

- Constant concentration of malonic acid, due to the poor description of the organic subset.

- Pseudo-steady-state approximation for y.

3.1 MODIFIED OREGONATOR

- y as a function of a, x and z:

$$y = \frac{fbz}{x + qa} \,.$$

- Model equations:

$$\left.\begin{aligned} \varepsilon\frac{dx}{d\tau} &= ax - x^2 - fbz\frac{x - qa}{x + qa} \\ \frac{dz}{d\tau} &= ax - bz \end{aligned}\right\} \text{fast subsystem}$$

$$\left.\alpha\frac{da}{d\tau} = \frac{x^2}{2} - ax - \frac{fbqaz}{x + qa}\right\} \text{slow subsystem}$$

- Time constants:

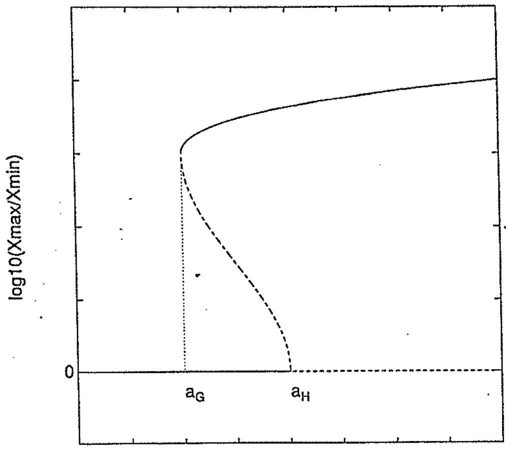
  $\varepsilon = 0.12 \qquad \alpha = 71.94$

- The fast subsystem coincides with the reduced Oregonator, but for the parameter a which slowly changes in time.

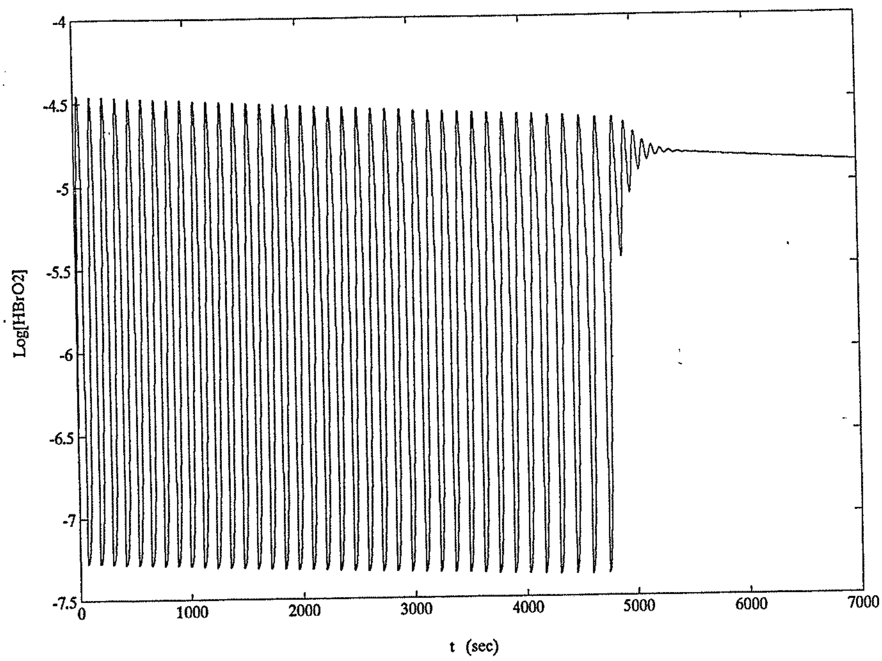
- The variation of a is driven by the slow subsystem.

3.2 SUBCRITICAL EXTINCTION OF OSCILLATIONS

- Subcritical Hopf bifurcation for the reduced Oregonator.



- Numerical integration of the modified Oregonator.



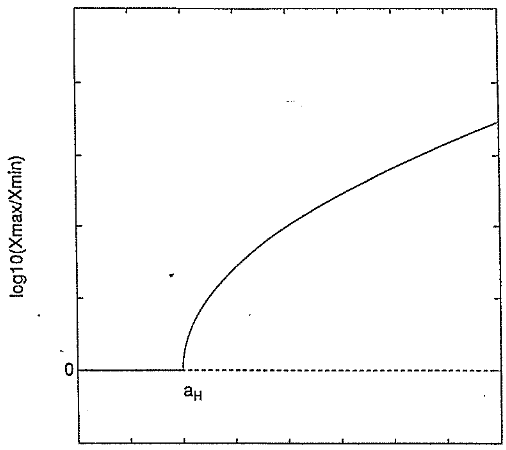
$f = 0.7$

$b = 0.1$

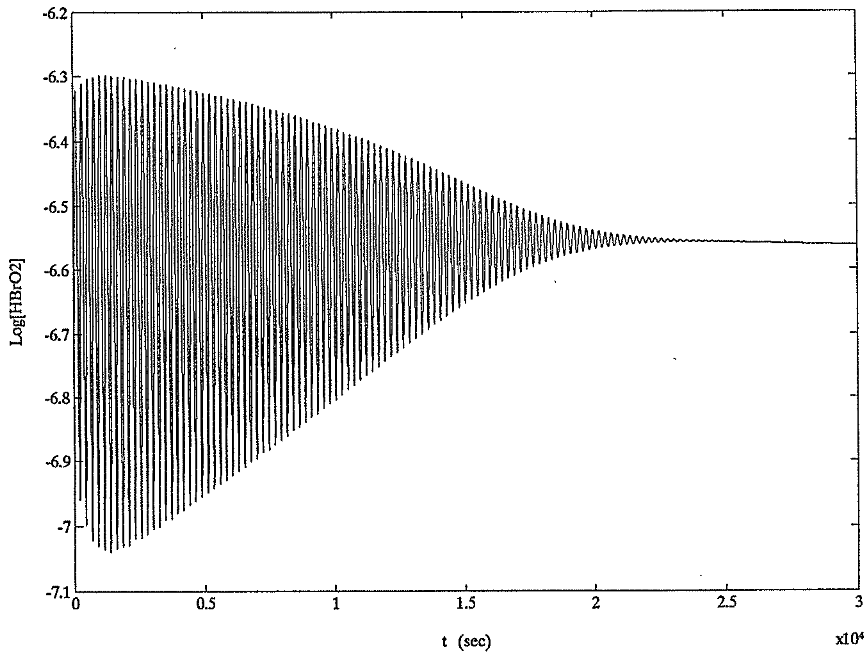
- "Persistence" of the oscillations.

3.3 SUPERCRITICAL EXTINCTION OF OSCILLATIONS

- Supercritical Hopf bifurcation for the reduced Oregonator.



- Numerical integration of the modified Oregonator.



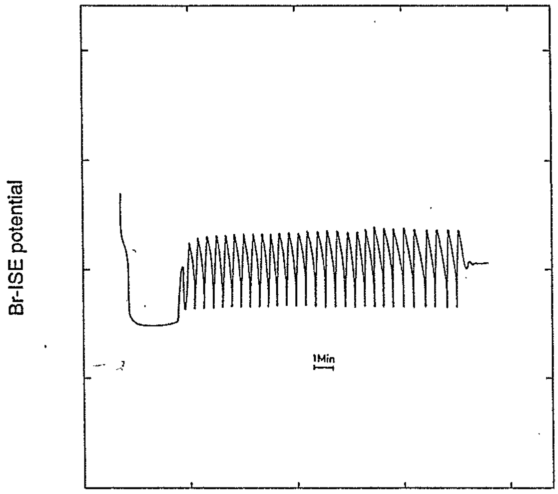
$f = 1.1$

$b = 0.07$

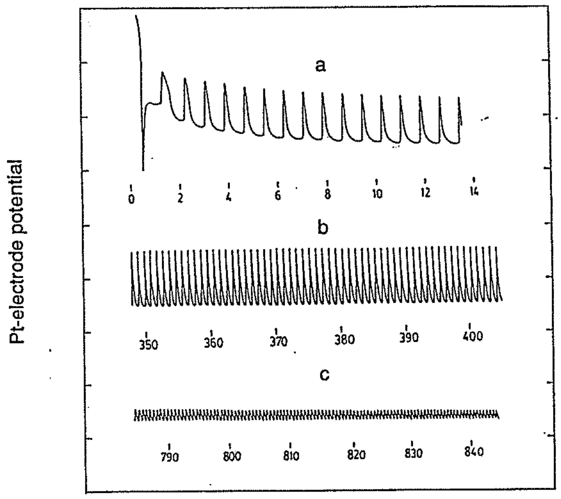
- "Persistence" of the oscillations.

3.4 COMPARISON WITH EXPERIMENTS

- Few data on batch systems.
- Qualitative agreement with experimental results reported by Ruoff and Noyes (1989).
- With O_2 (subcritical)



- No O_2 (supercritical)



- The chemical explanation refers to the chemistry of the organic subset.
- The critical parameter in the modified Oregonator model is the stoichiometric coefficient.

4 CONCLUDING REMARKS

- Hopf bifurcation set for the Oregonator in the 3-D parameter space (a, b, f).

- Hopf bifurcation subcritical or supercritical, depending only on the value of f.

- Modified Oregonator model to describe the BZ oscillations in a batch reactor.

- Two routes to the extinction of the oscillations.

- Qualitative agreement with experiments. Explanation for both experiment and model refers to the organic subset.