Analytical expression of concentrations of adsorbed CO molecules, O atoms and oxide oxygen

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ABSTRACT

A mathematical model of the oscillatory regimes of CO oxidation over plantinum-group metal catalysts are discussed. The model is based on non-stationary diffusion equation containing a non-linear term related to Michaelis-Menten kinetics of the enzymatic reaction. This paper presents the analytical and numerical solution of the system of non-linear differential equations. Here the Homotopy perturbation method (HPM) is used to find out the analytical expressions of the concentration of CO molecules, O atom and oxide oxygen respectively. A comparison of the analytical approximation and numerical simulation is also presented. A good agreement between theoretical and numerical results is observed.

Keywords: Oscillatory Dynamics;
Reaction-Diffusion; Boundary Value Problems;
Homotopy Perturbation Method

1. INTRODUCTION

Rate auto-oscillations in a heterogeneous catalytic reaction were first discussed more than two decades ago [1-3]. Some heterogeneous systems which show oscillatory behaviour on catalysts with various structures in a wide pressure range are presently known. One of the most extensively studied heterogeneous catalytic reactions exhibiting oscillatory dynamics is CO oxidation on platinum catalysts.

Various mathematical models are used in detailed analysis of the mechanism of the rate oscillations in catalytic CO oxidation. These models are based on a set of nonlinear ordinary differential equations [4-12]. Microscopic stochastic models by using the Monte Carlo method [13-18] one of the most interesting in theoretical investigation of the dynamics of fluctuating reaction systems. These stochastic models are based on detailed information concerning the elementary steps of the reaction, the structure of the catalyst surface, and the mobil-
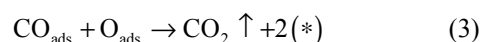
ity of species in the adsorption layer.

Therefore, the theoretical investigation and explanation of complex dynamic phenomena on a catalyst surface cannot be comprehensive. It is necessary to develop systems of consistent mathematical models describing the evolution of reaction systems on different spatial scales. This would allow the advantages of different classes of mathematical models.
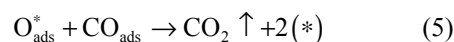
Recently Kurkina and Semendyaeva [3] described the oscillatory dynamical system which includes a Monte Carlo simulation and adsorption layer approximation. To our knowledge no analytical expressions of the concentration of CO molecules, O atom and oxide oxygen have been derived from the system. The purpose of the communication is to derive the analytical expression of $\theta_{CO}(t)$, $\theta_{O}(t)$, and $\theta_{O*}(t)$ by solving the system of non-linear differential equation using Homotopy perturbation method.

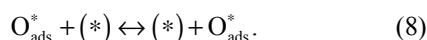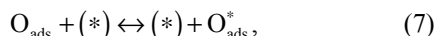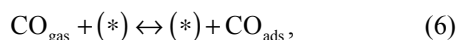## 2. MATHEMATICAL FORMULATION OF BOUNDARY VALUE PROBLEM

The oscillatory dynamics of the thickness shear model (TSM) kinetic network will be described using Lattice gas model. In this model any lattice site may be free (*) or occupied by an adsorbed carbon monoxide molecule CO_{ads}, an adsorbed oxygen atom O_{ads} or an adsorbed oxide oxygen atom O_{ads}^*. The thickness shear mode (TSM) kinetic network includes the Langmuir-Hinshelwood mechanism [3].

$$CO_{gas} + (*) \leftrightarrow CO_{ads}, \tag{1}$$

$$O_{2,gas} + 2(*) \rightarrow 2O_{ads}, \tag{2}$$

$$CO_{ads} + O_{ads} \rightarrow CO_2 \uparrow + 2(*) \tag{3}$$

and the formation and removal of surface oxide,

$$O_{ads} \rightarrow O_{ads}^*, \tag{4}$$

$$O_{ads}^* + CO_{ads} \rightarrow CO_2 \uparrow + 2(*) \tag{5}$$

Furthermore, we consider the migration of adsorbed species via a vacant-site mechanism:

$$CO_{gas} + (*) \leftrightarrow (*) + CO_{ads}, \quad (6)$$

$$O_{ads} + (*) \leftrightarrow (*) + O_{ads}^*, \quad (7)$$

$$O_{ads}^* + (*) \leftrightarrow (*) + O_{ads}^*. \quad (8)$$

Here, $(CO)_{gas}$ and $(O_2)_{gas}$ are molecules in the gas phase. Two-site process occurs on adjacent lattice sites. The rate of a two-site process is defined for a pair of sites, and the rate of a one-site process is defined for one site. The surface oxide formation step (4) is viewed as a one-site process, and step (5) is a two-site process. It is assumed that oxide oxygen retains its reactivity (see step (5)) and markedly decreases the activity of the catalyst in reactant adsorption from the gas phase.

3. STOCHASTIC AND DETERMINISTIC MODELS

The basic kinetic equations in a multidimensional system will be solved by approximate methods. In Monte Carlo stochastic modelling, state trajectories are constructed for the reaction system in the state space. Stochastic models describe the evolution of a selected lattice fragment at the atomic level. According to the above kinetic network, the variation of CO_{ads}, O_{ads} and O_{ads}^* concentrations are described by a set of following non-linear differential equations [4]:

$$\frac{d\theta_{CO}}{dt} = k_1 \left(1 - \theta_{CO} - \theta_O - \theta_{O*}\right) - k_{-1}\theta_{CO} \\ - 4k_3\theta_{CO}\theta_O - 4k_5\theta_{CO}\theta_{O*} \quad (9)$$

$$\frac{d\theta_O}{dt} = 4k_2 \left(1 - \theta_{CO} - \theta_O - \theta_{O*}\right)^2 - 4k_3\theta_{CO}\theta_O - k_4\theta_O \quad (10)$$

$$\frac{d\theta_{O*}}{dt} = k_4\theta_O - 4k_5\theta_{CO}\theta_{O*} \quad (11)$$

The initial conditions are as follows:

$$\theta_{CO}(t=0) = \theta_{CO}^o, \theta_O(t=0) = \theta_O^o, \\ \theta_{O*}(t=0) = \theta_{O*}^o \quad (12)$$

Here, $\theta_{CO}(t)$, $\theta_O(t)$, and $\theta_{O*}(t)$ are the concentrations of adsorbed CO molecules and O atoms and oxide oxygen, respectively, and $k_1, k_{-1}, k_2, \cdots, k_8$ are the rate

constants of elementary steps. The normalization conditions are as follows:

$$0 \le \theta_{CO} \le 1, 0 \le \theta_O \le 1, 0 \le \theta_{O*} \le 1, \\ \text{and } 0 \le \theta_{CO} + \theta_O + \theta_{O*} \le 1. \quad (13)$$

To simplify, we can assume that $u = \theta_{CO}$, $v = \theta_O$ and $w = \theta_{O*}$. The above **Eqs.9-11** become

$$\frac{du}{dt} = k_1 \left(1 - u - v - w\right) - k_{-1}u - 4k_3 uv - 4k_5 uw \quad (14)$$

$$\frac{dv}{dt} = 4k_2 \left(1 - u - v - w\right)^2 - 4k_3 uv - k_4 v \quad (15)$$

$$\frac{dw}{dt} = k_4 v - 4k_5 uw \quad (16)$$

Now the boundary condition (12) (or initial conditions) becomes

$$u(t=0) = u^0, v(t=0) = v^0, \text{and } w(t=0) = w^0$$

where

$$u^0 = \theta_{CO}^*, v^0 = \theta_O^*, w^0 = \theta_{O*}^0 \quad (17)$$

4. ANALYTICAL EXPRESSIONS OF CONCENTRATIONS USING HOMOTOPY PERTURBATION METHOD [HPM]

Recently, many authors have applied the HPM to various problems by demonstrating the efficiency of the HPM in handling non-linear structures and solving various physics and engineering problems [16-19]. This method is a combination in topology and classic perturbation techniques. Ji Huan He used the HPM to solve the light hill equation [20], the Duffing equation [21] and the Blasius equation [22]. The idea has been used to solve non-linear boundary value problems, integral equations and many other problems [23-27]. The HPM is unique in its applicability, accuracy and efficiency. The HPM uses the imbedding parameter p as a small parameter and only a few iterations are needed to search for an asymptotic solution. Using this method (see **Appendix A**), we can obtain the following solution to **Eqs.14-16** for the given boundary conditions (**Eq.17**).

$$u(t) = \theta_{CO}(t) = A + \left(u^0 - A\right)e^{-lt} + \frac{A\left(1 - e^{lt}\right)}{e^{lt}}\left(B + w^0 + \frac{4k_3 B}{l} + \frac{4k_5}{l}w^0 - 4\left(u_0^0 - A\right)\left(k_5 B + k_5 w\right)t \right.$$

$$\left. + \frac{\left(v^0 - B\right)\left(4k_3 + k_1\right)\left(e^{-(m-l)t} - 1\right)}{m - l} + \frac{4k_3\left(u^0 - A\right)\left(v^0 - B\right)\left(e^{-mt} - 1\right)}{m}\right) \quad (18)$$

$$v(t) = \theta_0(t) = B + t(v^0 - B)e^{-mt}$$

$$+ e^{-mt}\left[8k_2\left[(A + B + w^0)(v^0 - B)\right] - 4k_3A(v^0 - B)t + \frac{(e^{-lt} - 1)(u^0 - A)(v^0 - B)(4k_3 - 8k_2)}{l}\right.$$

$$+ \frac{(e^{-(l-m)t} - 1)\left[(4k_3B - 8k_2A)(u^0 - A) + 8k_2(1 - B - w^0)\right]}{l - m}$$

$$+ (e^{mt} - 1)\frac{\left[4k_2\left[A^2 + B^{2+} + (w^0)^2 + 2Aw^0 - 2w^0(1 - B) - 2A(1 - B) - 4k_3AB\right]\right]}{m}$$

$$\left.+ 4k_2\left[\frac{\left[(1 - e^{-(2l-m)t})\right]}{2l - m}(u^0 - A)^2 + \frac{(1 - e^{-mt})}{m}(v^0 - B)^2\right]\right] \quad (19)$$

$$w(t) = \theta_{(\theta^*)}(t)$$

$$= w^0 + (k_4B - 4k_3Aw^0)t \quad (20)$$

$$+ \frac{k_4}{m}(v^0 - B)(1 - e^{-mt}) + \frac{4k_5(u^0 - A)w^0(e^{-lt} - 1)}{l}$$

where

$$A = k_1/l, B = 4k_2/m, m = k_4 + 8k_2, l = k_1 + k_{-1} \quad (21)$$

The **Eqs.18-20** represent the new closed form of analytical expression of concentrations of CO molecules, O atom and oxide oxygen for all values of rate constant and time.

5. ANALYTICAL EXPRESSION OF CONCENTRATION FOR STEADY STATE CONDITION

For the case of steady state, the **Eqs.14-16** become

$$k_1(1 - u - v - w) - k_{-1}u - 4k_3uv - 4k_5uw = 0 \quad (22)$$

$$4k_2(1 - u - v - w)^2 - 4k_3uv - k_4v = 0 \quad (23)$$

$$k_4v - 4k_5uw = 0 \quad (24)$$

Solving the above non-linear algebraic equation by using Maple software, we can obtain the concentration of CO molecule, O atom and oxide oxygen as follows:

$$u = \theta_{CO} = 0, v = \theta_O = 0, w = \theta_{O^*} = 1. \quad (25)$$

6. NUMERICAL SOLUTION

In order to test accuracy of this method the non-linear differential **Eqs.14-16** for the boundary conditions (**Eq.17**) are solved by numerical methods. The function pdex4 in Matlab software was used to solve these equations. It is a function of solving the initial boundary value problems for non-linear differential equations. The Matlab program is also given in **Appendix B**. The numerical results are also compared with our analytical results in **Figures 1(a)-(d)**. A satisfactory agreement is noted here.

7. DISCUSSION

Figures 1(a)-(d) represent the non steady state concentration of CO molecules $u(t)$ or $\theta_{CO}(t)$, O atom $v(t)$ or $\theta_O(t)$ and oxide oxygen $w(t)$ or $\theta_{O^*}(t)$ for all values of rate constant and time. From the figure it is evident that the value of the concentration of CO molecule decrease from its initial value of concentration and reaches the steady state value zero when $t = 2$ sec for all values of rate constant. From the figures it is also inferred that the value of concentration of O atom rises initially and reaches the maximum value when $t \approx 0.5$ sec and then decreases gradually. The concentration of O atom attains the steady state value when $t = 10$ sec. From this figure it is also observed that the concentration of oxide oxygen always increases when time increases and reaches the steady state value 1 when $t = 5$ sec for all values of rate constant. From this figure it is to conclude that $0 \leq \theta_{CO} + \theta_O + \theta_{O^*} \leq 1$ for all values of time and rate constant.

8. CONCLUSION

The theory of the dynamics of catalysts CO oxidation in the frame work of the Thickness shear mode kinetic is described. Approximate analytical solutions to the system of non-linear reaction equations are presented using Homotopy perturbation method. A simple, straight forward and a new method of estimating the concentrations of CO molecules, O atom and Oxide oxygen are derived. This analytical result will be useful to know the behaviour of the reaction system. A good agreement with the numerical simulation data is also noted. The extension of
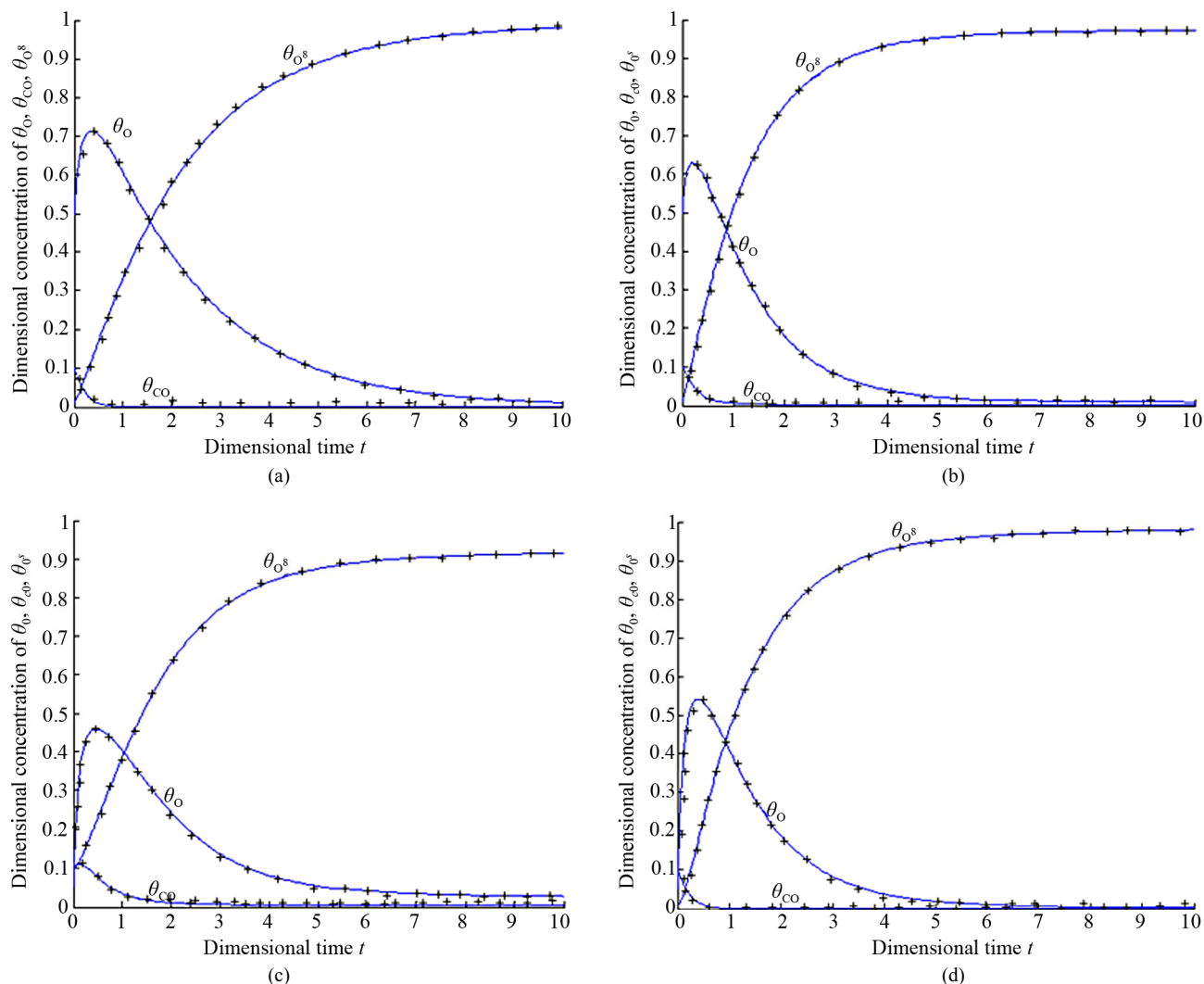
Figure 1. Dimensional concentration profile of adsorbed CO molecules θ_{CO}, O atom θ_O and oxide oxygen θ_O^* for various values of parameters and initial concentration. (a) $k_1 = 0.1$, $k_{-1} = 2$, $k_2 = 5$, $k_4 = 0.5$, $k_5 = 2$, $k_3 = 1$, $\theta_O^o = 0.1$, $\theta_{O^8}^o = 0.01$, $\theta_{CO}^0 = 0.5$; (b) $k_1 = 0.5$, $k_{-1} = 2$, $k_2 = 5$, $k_4 = 1$, $k_5 = 2$, $k_3 = 1$, $\theta_O^o = 0.1$, $\theta_{O^8}^o = 0.5$, $\theta_{CO}^0 = 0.01$; (c) $k_1 = 0.5$, $k_{-1} = 1$, $k_2 = 2$, $k_4 = 1$, $k_5 = 2$, $k_3 = 0.1$, $\theta_O^o = 0.1$, $\theta_{O^8}^o = 0.5$, $\theta_{CO}^0 = 0.01$; (d) $k_1 = 0.1$, $k_{-1} = 4$, $k_2 = 2$, $k_4 = 1$, $k_5 = 2$, $k_3 = 0.1$, $\theta_O^o = 0.1$, $\theta_{O^8}^o = 0.05$, $\theta_{CO}^0 = 0.1$.

this method with more modelling and simulation procedure to the some of the non-linear reaction diffusion mechanism in biosensor [28] seems possible.

9. ACKNOWLEDGEMENTS

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APPENDIX A

Analytical Solution of the Nonlinear Equations Using Homotopy Perturbation Method

In this appendix, we indicate how **Eqs.14**-**16** may be solved using HPM. To find the solution of **Eqs.14**-**16**, we first construct a homotopy as follows [16-19]:

$$(1-p)\left[\frac{\mathrm{d}u}{\mathrm{d}t}+\left(k_1+k_{-1}\right)u-k_1\right]$$
$$+p\left[\frac{\mathrm{d}u}{\mathrm{d}t}-k_1\left(1-u-v-w\right)+u\left(k_{-1}+4k_3v+4k_5w\right)\right]=0 \tag{A1}$$

$$(1-p)\left[\frac{\mathrm{d}v}{\mathrm{d}t}+\left(k_4+8k_2\right)v-4k_2\right]$$
$$+p\left[\frac{\mathrm{d}v}{\mathrm{d}t}-4k_2\left(1-u-v-w\right)^2+4k_3uv+k_4v\right]=0 \tag{A2}$$

$$(1-p)\frac{\mathrm{d}w}{\mathrm{d}t}+p\left[\frac{\mathrm{d}w}{\mathrm{d}t}-k_4v+4k_5uw\right]=0 \tag{A3}$$

where $p\in[0,1]$ is an embedding parameter. According to HPM, we can first use the parameter p as a "small parameter" and assume that the solution of **Eqs.14**-**16** can be written as a power series in p.

$$u=u_0+pu_1+p^2u_2+\cdots \tag{A4}$$

$$v=v_0+pv_1+p^2v_2+\cdots \tag{A5}$$

$$w=w_0+pw_1+p^2w_2+\cdots \tag{A6}$$

where u_0, v_0, and w_0 are zero-order solution (initial approximation) and u_1, v_1, w_1 are the first order approximate solution. When $p = 0$, we get zero-order solution (initial approximate solution or solution of linear terms). Setting $p = 1$, results in the approximate solution

of **Eqs.14**-**16**. Substituting **Eqs.A4**-**A6** into **Eqs.A1**-**A3** and comparing the coefficients of like powers of p we obtain the following differential equations.

$$p^0:\frac{\mathrm{d}u_0}{\mathrm{d}t}+\left(k_1+k_{-1}\right)u_0-k_1=0 \tag{A7}$$

$$p^1:\frac{\mathrm{d}u_1}{\mathrm{d}t}+\left(k_1+k_{-1}\right)u_1+k_1\left(v_0+w_0\right)$$
$$+4k_3u_0v_0+4k_5u_0w_0=0 \tag{A8}$$

$$p^0:\frac{\mathrm{d}v_0}{\mathrm{d}t}+\left(k_4+8k_2\right)v_0-4k_2=0 \tag{A9}$$

$$p^1:\frac{\mathrm{d}v_1}{\mathrm{d}t}+\left(k_4+8k_2\right)v_1$$
$$-4k_2\left(1-2v_0+\left(1-u_0-v_0-w_0\right)^2\right)+4k_3u_0v_0=0 \tag{A10}$$

and

$$p^0:\frac{\mathrm{d}w_0}{\mathrm{d}t}=0 \tag{A11}$$

$$p^1:\frac{\mathrm{d}w_1}{\mathrm{d}t}-k_4v_0+4k_5u_0w_0=0 \tag{A12}$$

The initial conditions in Equation (17) becomes

$$u_0\left(t=0\right)=u^0,v_0\left(t=0\right)=v^0,w_0\left(t=0\right)=w^0 \tag{A13}$$

$$u_i\left(t=0\right)=0,v_i\left(t=0\right)=0,w_i\left(t=0\right)=0,\text{for }i\geq1 \tag{A14}$$

Solving the equations using the initial conditions Equation (A14), we obtain the following results.

$$u_0(t)=A+\left(u^0-A\right)\mathrm{e}^{-lt} \tag{A15}$$

$$v_0(t)=B+\left(v^0-B\right)\mathrm{e}^{-mt} \tag{A16}$$

$$w_0(t)=w^0 \tag{A17}$$

$$u_1(t)=\frac{1}{\mathrm{e}^{lt}}\left[\left(1-\mathrm{e}^{lt}\right)A\left(B+w^0+\frac{4k_3B}{l}+\frac{4k_5}{l}W^0-4\left(u_0^0-A\right)\left(k_5B+k_5w\right)t\right.\right.$$
$$\left.\left.+\frac{\left(v^0-B\right)\left(4k_3+k_1\right)\left(\mathrm{e}^{-(m-l)t}-1\right)}{m-l}+\frac{4k_3\left(u^0-A\right)\left(v^0-B\right)\left(\mathrm{e}^{-mt}-1\right)}{m}\right)\right] \tag{A18}$$

$$v_1(t)=\mathrm{e}^{-mt}\left[\left(\mathrm{e}^{-(l-m)t}-1\right)\frac{\left[\left(4k_3B-8k_2A\right)\left(u^0-A\right)+8k_2\left(1-B-w^0\right)\right]}{l-m}+\frac{\left(\mathrm{e}^{-lt}-1\right)\left(u^0-A\right)\left(v^0-B\right)\left(4k_3-8k_2\right)}{l}\right.$$
$$+\left(\mathrm{e}^{mt}-1\right)\frac{\left[4k_2\left[A^2+B^{2+}+\left(w^0\right)^2+2Aw^0-2w^0\left(1-B\right)-2A\left(1-B\right)-4k_3AB\right]\right]}{m}$$
$$\left.+4k_2\left[\frac{\left[\left(1-\mathrm{e}^{-(2l-m)t}\right)\right]}{2l-m}\left(u^0-A\right)^2+\frac{\left(1-\mathrm{e}^{-mt}\right)}{m}\left(v^0-B\right)^2\right]+8k_2\left[\left(A+B+w^0\right)\left(v^0-B\right)\right]-4k_3A\left(v^0-B\right)t\right] \tag{A19}$$

$$w_1(t) = \left(k_4 B - 4k_3 A w^0\right)t + \frac{k_4}{m}\left(v^0 - B\right)\left(1 - e^{-mt}\right)$$
$$+ \frac{4k_5\left(u^0 - A\right)w^0\left(e^{-lt} - 1\right)}{l} \tag{A20}$$

According to the HPM, we can conclude that

$$u(t) = \lim_{p \to 1} u(t) = u_0 + u_1 \tag{A21}$$

$$v(t) = \lim_{p \to 1} v(t) = v_0 + v_1 \tag{A22}$$

$$w(t) = \lim_{p \to 1} w(t) = w_0 + w_1 \tag{A23}$$

where

$$A = k_1/l,\ B = 4k_2/m,\ m = k_4 + 8k_2,\ l = k_1 + k_{-1} \tag{A24}$$

After putting the **Eqs.A15**-**A20** in the **Eqs.A21**-**A24** we get the **Eqs.18**-**20** in the text.

APPENDIX B

Matlab Program to Find the Numerical Solution of Eqs.14-16

```
function main1
options = odeset ('RelTol',1e-6,'Stats','on');
%initial conditions
T=100;
Xo = [0.1; 0.5; 0.01];
tspan = [0,10];
tic
[t,X] = ode45(@TestFunction,tspan,Xo,options);
toc
figure
hold on
plot(t, X(:,1))
plot(t, X(:,2))
plot(t, X(:,3),'.')
legend('x1','x2','x3')
ylabel('x')
xlabel('t')
return
function [dx_dt]= TestFunction(t,x)
a=0.9,b=0.002,k2=0.5,k4=0.03,k5=0.2,k3=1,c=0.1,d=
0.01,O=0.5,
dx_dt(1)
=a*(1-x(1)-x(2)-x(3))-b*x(1)-4*k3*x(1)*x(2)-4*k5*x(1)
*x(3);
dx_dt(2)
=4*k2*(1-x(1)-x(2)-x(3))^2-4*k3*x(1)*x(2)-k4*x(2);
dx_dt(3)=k4*x(2)-4*k5*x(1)*x(3);
dx_dt = dx_dt';
return
```