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Analytical Expression of Steady State Concentration Profiles at Parallel Electrodes

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Abstract: The Theoretical model of steady-state parallel electrodes is discussed. This model is based on the product of one reactions involved in a homogeneous reaction with the reactant of the other. Homotopy Perturbation Method (HPM) is employed to solve the non-linear diffusion equation. Simple and approximate polynomial expression is derived.

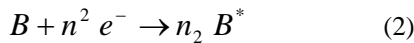
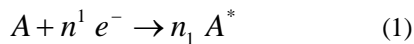
Keywords: Parallel-electrode, stoichiometry reaction, Diffusion, Non-linear equations, Homotopy perturbation method.

I. INTRODUCTION

The Process of Parallel electrodes is the product of one electrode process enters in a homogeneous reaction with stoichiometry reaction in the other parallel electrode. Stoichiometry reaction is the relationship between the relative quantities of substances taking part in a reaction or forming a compound, typically a ratio of whole integers. Kharkats and Sokirko have published paper concerning diffusion and reaction of parallel electrodes in limiting currents for the arbitrary values of the homogeneous reaction rate constant [1]. Kemula and Michalski discovered the hidden limiting currents of the second reactant current depends on the first current [2]. There have been many previous theoretical descriptions of the diffusion limiting current for the parallel electrodes in the stoichiometry reaction [3]. Feoktistov, Zhdanov and Akad were analyzed that the homogeneous reaction rate is indefinitely high. In this process the electrode reaction product interacts with the initial substrate, and hidden currents of the third kind can be observed [4]. Special case of a reaction inhibiting have been described experimentally [5]. However, to the best of our knowledge no general analytical expression of steady-state concentration profiles at parallel electrode have been reported. The purpose of this communication is to derive analytical expression of concentration by solving non-linear differential equation using Homotopy perturbation method.

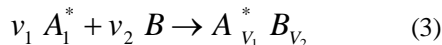
II. MATHEMATICAL FORMULATION OF ANALYSIS AND PROBLEMS

The model contain substances A and B which are reduced at the electrode. For clarity we shall suppose that B is reduced at more negative potentials:



Here n^i , $i = 1, 2$ is the number of electrons transferred in the i^{th} reaction, n are stoichiometry coefficients for electrode reactions.

If the reaction



Proceed in the diffusion layer then the terminology of [2], hidden first current of the first kind is observed in the system.

The non-linear differential equation for this model can be represented as follows [1]

$$D_{1s} \frac{d^2 c_{1^*}}{d\xi^2} - k_1 c_{1^*} c_2 = 0 \quad (4)$$

$$D_2 \frac{d^2 c_2}{d\xi^2} - k_1 c_{1^*} c_2 = 0 \quad (5)$$

Here D_{1s} and D_2 are diffusion coefficients of the corresponding substances, k_1 is the rate constant of reaction (3),

ξ is the coordinate perpendicular to the electrode surface. The boundary conditions are assumed to be specified by concentration c_2 in the bulk of solution

$c_2(L) = c^0$ and by zero concentration of substance A^* , $c_1(L) = 0$. Here L is the diffusion layer thickness, which is supposed to be approximately the same for substances A^* and B . We shall seek the solution under the condition $c_2(0) = 0$ which corresponds to achieving a limiting current in substance B .

To obtain the last boundary condition, one must find the solution of the diffusion equation for substance A , which does not participate in homogeneous reaction (3)

$$D_1 \frac{d^2 c_1}{d\xi^2} = 0 \quad (6)$$

with the boundary condition $\xi = L : c_1(L) = c_1^0$ and the condition of limiting current in substance $A : c_1(0) = 0$. Integrating (6) twice, one obtains a linear profile for $c_1 : c_1 = c_1^0 \xi / L$. Since the stoichiometry of reaction (1) shows that the fluxes of substances A and A^* near the electrode are equal and opposite in direction, the last boundary condition for c_1^* can be written in the form

$$\left[D_{1^*} \frac{d^2 c_{1^*}}{d\xi^2} \right]_{\xi \rightarrow 0} = \left[-D_1 \frac{dc_1}{d\xi} \right]_{\xi \rightarrow 0} \equiv -D_1 \frac{c_1^0}{L} \quad (7)$$

By introducing the dimensionless quantities

$$u = \frac{c_{1^*} D_{1^*}}{c^0 D_2}, \quad v = \frac{c_2}{c^0}, \quad x = \frac{\xi}{L}, \quad n = \frac{D_1 c_1^0}{D_2 c^0}, \quad k = \frac{k_1 L^2 c_0}{D_{1^*}} \quad (8)$$

where k is the dimensionless reaction rate.

Eq. (4) and Eq. (5) becomes

$$\frac{d^2 u}{dx^2} - kuv = 0 \quad (9)$$

$$\frac{d^2 v}{dx^2} - kuv = 0 \quad (10)$$

The boundary conditions may be represented as follows:

$$x = 0, \quad \frac{du}{dx} = -n; \quad v = 0 \quad (11)$$

$$x = 1, \quad u = 0; \quad v = 1 \quad (12)$$

III. ANALYTICAL SOLUTION OF THE CONCENTRATION AND CURRENT USING HPM

The advantages of analytical methods [6-8] especially HPM [8] are capable of solving both regular and strong non-linear equations. Also these methods are simple to apply and will not increase complexity. One of the most remarkable features of the HPM is that usually only a few perturbation terms are sufficient to obtain a reasonably accurate solution. Recently, many authors have applied the HPM to various problems and demonstrated the efficiency of the HPM for handling non-linear structures and solving various physics and engineering problems [9-12]. This method is a combination of homotopy in topology and classic perturbation techniques. Ji-Huan He used the HPM to solve the Lighthill equation [13], the Duffing equation [14] and the Blasius equation [15]. In this paper, the homotopy perturbation method [16-20] is applied and the obtained results show that the HPM is very effective and simple.

$$u = n - \frac{kn}{12} - \frac{53k^3 n^2}{90720} - nx + \left[\frac{kn}{6} + \frac{k^3 n^2}{864} \right] x^3 - \frac{kn}{12} x^4 - \frac{k^3 n^2}{1440} x^5 - \frac{k^3 n^2}{4320} x^6 + \frac{k^3 n^2}{6048} x^7 + \frac{k^3 n^2}{2016} x^8 - \frac{k^3 n^2}{2592} x^9 + \frac{k^3 n^2}{12960} x^{10} \quad (13)$$

$$v = \left[1 - \frac{53k^3n^2}{90720} - \frac{kn}{12} \right] x + \left[\frac{kn}{6} + \frac{k^3n^2}{864} \right] x^3 - \frac{kn}{12} x^4 - \frac{k^3n^2}{1440} x^5 - \frac{k^3n^2}{4320} x^6 + \frac{k^3n^2}{6048} x^7 + \frac{k^3n^2}{2016} x^8 - \frac{k^3n^2}{2592} x^9 + \frac{k^3n^2}{12960} x^{10} \quad (14)$$

Eq.(13) and Eq.(14) is the newanalytical expressions for the dimensionless concentrations in terms of dimensionless reaction rate.

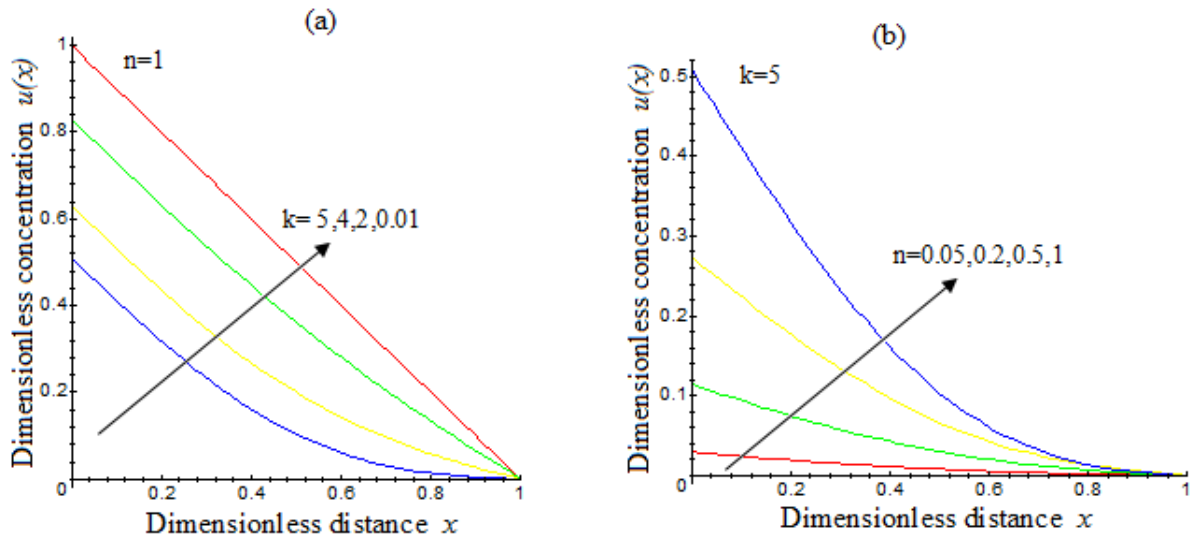


Fig.1 concentration of u versers distance in dimensionless form using Eq.(13)

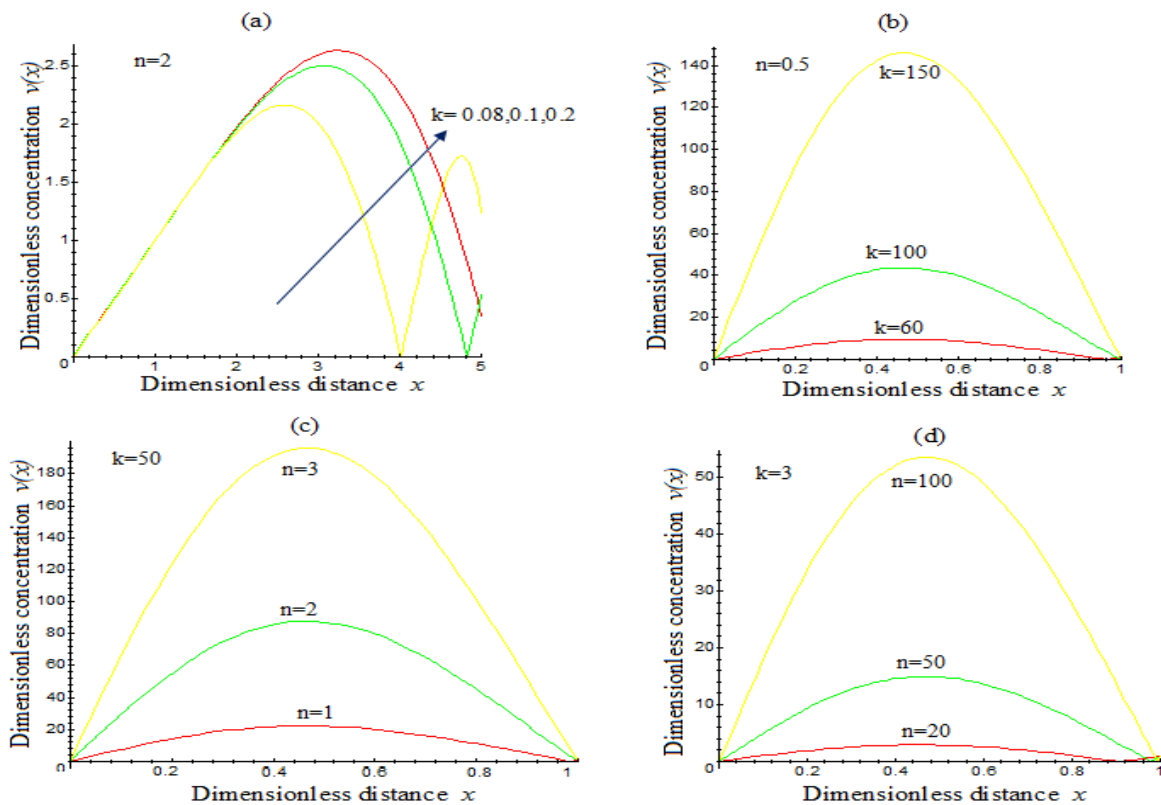


Fig.2 concentration of v versers distance in dimensionless form using Eq.(14)

IV. RESULT AND DISCUSSION

Eq. (13) and Eq. (14) are the new simple analytical expression of the dimensionless concentrations u and v . Figure 1 (a) represents the dimensionless concentration u for different values of dimensionless kinetic parameter k . Figure 1 (b) represents the dimensionless concentration u for different values of dimensionless constant n . From these figures it is inferred that, the concentration u increases when k and n increases. Figure 2 (a) and (b) represents the dimensionless concentration v for different values of dimensionless kinetic parameter k . Figure 2 (c) and (d) represents the dimensionless concentration v for different values of dimensionless constant n . From these figures it is inferred that, the concentration increases when k and n increases and attains its maximum value 1.

V. CONCLUSION

In the present paper the non-linear differential equation have been formulated and solved under steady state conditions subject to defined boundary conditions. In this work, we obtained an analytical solution for parallel electrodes. The analysis has enabled an algebraic expression for the concentrations to all possible values of dimensionless reaction rate k . The simple closed forms of analytical solutions have been proposed using HPM. The Homotopy perturbation method is extremely simple and promising to solve other non-linear equations. This method can be easily extended to find the solution of all other non-linear reaction diffusion equations in homogeneous reactions for all parallel electrodes for various complex boundary conditions.

APPENDIX A

Solution of Eq. (14) using homotopy perturbation method in this paper is derived.

$$(1 - p) \left[\frac{d^2 u}{dx^2} \right] + p \left[\frac{d^2 u}{dx^2} - kuv \right] = 0 \quad (A1)$$

$$(1 - p) \left[\frac{d^2 v}{dx^2} \right] + p \left[\frac{d^2 v}{dx^2} - kuv \right] = 0 \quad (A2)$$

The boundary conditions are

$$x = 0, \frac{du}{dx} = -n; v = 0 \quad (A3)$$

$$x = 1, u = 0; v = 1 \quad (A4)$$

The approximate solutions of Eq. (A1) is

$$u = u_0 + pu_1 + p^2 u_2 + p^3 u_3 + \dots \quad (A5)$$

$$v = v_0 + pv_1 + p^2 v_2 + p^3 v_3 + \dots \quad (A6)$$

substituting Eq. (A5) and (A6) into Eq.(A1) and (A2) comparing the coefficients of like powers of p

$$p^0 : \frac{d^2 u}{dx^2} = 0 \quad (A7)$$

$$p^0 : \frac{d^2 v}{dx^2} = 0 \quad (A8)$$

$$p^1 : \frac{d^2 u_1}{dx^2} - ku_0 v_0 = 0 \quad (A9)$$

$$p^1 : \frac{d^2 v_1}{dx^2} - ku_0 v_0 = 0 \quad (A10)$$

The boundary conditions are

$$x = 0, \frac{du_0}{dx} = -n; v_0 = 0 \quad (A11)$$

$$x = 1, u_0 = 0; v_0 = 1 \tag{A12}$$

The boundary conditions are

$$x = 0, u_1 = 0, v_1 = 0 \tag{A13}$$

$$x = 1, \frac{du_1}{dx} = 0, v_1 = 0 \tag{A14}$$

Solving the Eq. A (7) to A (10) and using the boundary conditions given in Eq. A (11) to A (14) we can obtain

$$u_0 = n(1 - x) \tag{A15}$$

$$v_0 = x \tag{A16}$$

$$u_1 = -kn \frac{x^4}{12} + kn \frac{x^3}{6} \tag{A17}$$

$$v_1 = -kn \frac{x^4}{12} + kn \frac{x^3}{6} - \frac{kn}{12} x \tag{A18}$$

According to the HPM, we can conclude that

$$u = u_0 + u_1 + \dots \tag{A19}$$

Substituting Eqs. (A15, A16, A17, A18) into Eq. (A19) we can obtain Eq. (13) and Eq.(14) in the text.

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