

Perturbation Solution of the Jackson's Dusty Gas Model Equations for Ternary Gaseous Systems

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ABSTRACT

A perturbation technique was used to obtain an approximate closed-form solution for the mass balance equations when the dusty gas model (DGM) is used to calculate total molar fluxes of components of ternary gaseous systems. This technique employed the straight-forward expansion method to the second-order approximation. Steady-state, isobaric, isothermal and no reaction conditions were assumed. The obtained solution is a set of equations expressed to calculate mole fractions as functions of dimensionless length, boundary conditions, properties of the gases and parameters of transport mechanisms (i.e., Knudsen diffusivity and effective binary diffusivity). Three different systems represent field and experimental conditions were used to test the applicability of perturbation solution. Findings indicate that the obtained solution provides an effective tool to calculate mole fractions and total molar fluxes of components of ternary gaseous systems.

KEYWORDS: Dusty Gas Model, Perturbation, Gas Transport Mechanisms, Diffusive Transport, Porous Media, VOC, Groundwater Contamination.

INTRODUCTION

Many significant environmental problems require quantification of diffusive transport mechanisms in the gaseous phase. Examples of such problems include: the use of natural unsaturated zones as landfills and disposal sites for hazardous wastes, groundwater contamination by volatile organic compounds (VOCs), subsurface remediation and the health effects of Radon and its decay products.

Three models have been commonly used to model

diffusive transport in natural porous media. These include: Fick's first law of diffusion, the Stefan-Maxwell equations and the Dusty Gas Model (DGM). Many studies investigated the applicability of Fick's first law of diffusion to model vapor diffusion and highlighted the importance of flux mechanisms other than molecular diffusion flux to adequately model the diffusive transport in a porous medium. Thorestenson and Pollock (1989a, b) used the Stefan-Maxwell equations and the DGM to assess the limitations of Fick's first law through a theoretical investigation of the relative importance of different transport mechanisms in binary and multi-component gaseous systems. Baehr and Bruell (1990) analyzed results of hydrocarbon vapor transports column experiments and calculated the tortuosity factors

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necessary to fit these experimental data when using Fick's law and the Stefan-Maxwell equations. Abriola et al. (1990) numerically investigated the importance of different gas transport mechanisms in non-steady-state binary systems. Voudrias and Li (1992) experimentally investigated the importance of Knudsen diffusion in an unsaturated soil sample containing benzene vapor. Abu-El-Sha'r and Abriola (1997) experimentally evaluated the relative importance of different gaseous transport mechanisms in natural porous media systems.

Findings of the above studies indicated that a multicomponent treatment incorporating different gas transport mechanisms should be undertaken to obtain better modeling of gas transport in natural porous media. This is of special importance when modeling systems where Knudsen diffusion contributes significantly to the total diffusion (e.g., clay). In such systems, Fick's diffusion and the Stefan-Maxwell equations may be inadequate to model diffusive gaseous transport. Therefore, analysis of natural environmental problems requires consideration of ternary systems (systems consisting of a gaseous contaminant and air which is usually modeled as a mixture of oxygen and nitrogen).

The use of the DGM to solve for concentrations and molar fluxes of species of gaseous systems when the number of components of three or more exists is limited by the availability of a closed-form solution to the DGM. To our knowledge, there is no analytical solution in the literature to the mass balance equations when the DGM is used to calculate concentrations or total molar fluxes of gaseous species in a porous medium. Numerical solutions however are limited and have their own limitations. The objectives of this paper are: (1) to obtain an approximate closed-form solution to the DGM equations when incorporated in mass balance equations for ternary systems using perturbation methods. The following conditions are also assumed: steady-state, isothermal, no chemical or biological reactions occur in the system and surface diffusion is neglected, (2) to apply the obtained approximate closed-form solution to different natural porous media systems.

BACKGROUND

Gas Transport Mechanisms through Porous Media

Gas transport through a porous medium occurs via four different mechanisms: (1) surface flow or diffusion; (2) viscous flow; (3) Knudsen flow; (4) ordinary diffusion (i.e., molecular and non-equimolar fluxes). A brief discussion of these mechanisms is given below and a detailed discussion can be found in Cunningham and Williams (1980), Mason and Malinauskas (1983) and Abu-El-Sha'r (1993).

Surface flux occurs when gas molecules are adsorbed on specific sites at the surface of the particles of the porous media. Due to the continuous movement (vibrations) of the adsorbed molecules, each molecule transfers by hopping to other adsorption sites a number of times before it returns to the gaseous phase. Surface diffusion is usually modeled by employing Fick's Law of diffusion where the concentration gradients refer to the surface concentration gradients and all the complexities of the porous medium geometry, surface structure and adsorption equilibrium are lumped into the surface diffusion coefficient. The Fickian model is useful only at low surface coverage (Mason and Malinauskas, 1983). In this paper, the number of molecules adsorbed to the soil surface adsorption sites is assumed equal to the number of molecules leaving the adsorption sites (steady-state conditions). Thus, net surface flux will not effect the total gaseous flux and is neglected.

Viscous flux occurs when a pressure gradient is applied on the system. The damping effects due to the high rate of interaction (i.e., collisions) among gas molecules compared to the interaction between gas molecules and the boundaries of the system cause a constant viscous flux. On the other hand, when there is more interaction between gas molecules and system boundaries than the interaction among gas molecules, Knudsen flux dominates. In a multicomponent gaseous system, there is a concentration gradient for each component and thus a net Knudsen flux of each component as well. The net Knudsen flux of gas i can be calculated as (Cunningham and Williams, 1980):

$$N_i^K = -D_i^K \frac{dc_i}{dz} \quad (1)$$

where N_i^K is the Knudsen molar flux of component i , c_i is molar concentration of component i and D_i^K is the Knudsen diffusivity, given as:

$$D_i^K = Q_p \left(\frac{RT}{M_i} \right)^{1/2} \quad (2)$$

where Q_p is the obstruction factor for Knudsen diffusivity, T is the temperature, R is the ideal gas constant and M_i is the molecular weight of gas i . For a porous media with a single pore size, D_i^K is given by (Geankoplis, 1972):

$$D_i^K = 9.7 \times 10^3 \bar{r} \sqrt{\frac{T}{M_i}} \quad (3)$$

where \bar{r} is the average pore radius.

Ordinary diffusion of gases in a porous medium is a combination of two different flux mechanisms: diffusive (molecular) flux and viscous (nonequimolar) flux. The total molar diffusive flux of component i is given by (Cunningham and Williams, 1980):

$$N_i^T = N_i^D + X_i N^v \quad (4)$$

where N_i^T is the total diffusive flux of component i , N_i^D is molar diffusive flux of component i , X_i is the mole fraction of component i and N_i^v is the molar viscous flux of component and can be given as:

$$N^v = -\frac{P}{RT} \frac{k}{\mu} \nabla P \quad (5)$$

where k is the intrinsic permeability, μ is the dynamic viscosity and ∇P is the pressure gradient.

Gas Transport Models

As mentioned previously, Fick's first law of diffusion, Stefan-Maxwell equations and the Dusty Gas Model (DGM) have been used to study gas transport through

porous media. Fick's law has been reported in the literature of hydrology and soil physics to model molecular diffusion. It originated based on solute studies as an empirical equation and then extended for prediction of gaseous diffusion through porous media (Kirham and Powers, 1972; Abu-El-Sha'r, 1993).

Fick's law for one-dimensional and steady-state conditions is written in molar form as (Jaynes and Rogowski, 1983):

$$(N_i^D)_F = -D_{ij} c \frac{dX_i}{dz} \quad (6)$$

where $(N_i^D)_F$ is Fick's first law diffusive molar flux of component i , D_{ij} is the binary diffusivity of components i and j and c is the total molar concentration. D_{ij} can be calculated as (Perry and Green, 1997):

$$D_{ij} = \frac{10^{-3} T^{1.75} \left[\frac{(M_i + M_j)}{M_i M_j} \right]^{1/2}}{P \left[(\sum V_i)^{1/3} + (\sum V_j)^{1/3} \right]^2} \quad (7)$$

here T is the temperature (Kelvin), P is the pressure (Kpa), and $\sum V$ is the sum of atomic diffusion volumes. For gaseous transport through porous media, D_{ij} is replaced by the effective diffusive coefficient D_{ij}^e , which is given by:

$$D_{ij}^e = Q_m D_{ij} \quad (8)$$

where Q_m is an obstruction factor, which is a function of porosity and tortuosity of the porous medium. One suggested correlation for Q_m is given by (Cunningham and Williams, 1980):

$$Q_m = T_p / 3 \quad (9)$$

where T_p is the porosity of the porous media.

Stefan-Maxwell equations are usually used in chemical engineering to study multicomponent gas diffusion. The general form of Stefan-Maxwell equations can be given as:

$$\sum_{j=1, j \neq i}^n \frac{X_i N_j^D - X_j N_i^D}{D_{ij}^e} = \frac{1}{RT} \nabla P_i \quad (10)$$

where n is the number of gaseous component in the system. Note that Equation (10) represents $n-1$ independent equations, since

$$\sum_{i=1}^n X_i = 1.0 \quad (11)$$

The form of Stefan-Maxwell equations given in Equation (10) can be written in a form similar to Fick's law, where diffusion coefficients are function of the composition of gaseous components and properties of the porous media. It is to be noted that both Fick's law of diffusion and Stefan-Maxwell equations do not incorporate Knudsen diffusion, therefore, both models may be inadequate to model systems where Knudsen diffusion is significant.

Although the DGM can be used to model multicomponent gaseous transport through porous media, it has been rarely used in natural systems

$$\sum_{j=1, j \neq i}^n \frac{X_i N_j^D - X_j N_i^D}{D_{ij}^e} - \frac{N_i^D}{D_i^K} = \frac{1}{RT} \nabla P_i + n' \sum_{j=1}^n X_i X_j \alpha_{ij} \nabla \ln T \quad (12)$$

where n' is the gas and particle density, α_{ij} is the generalized thermal diffusivity and the remaining parameters are previously defined. The summation term on the left hand side of Equation (12) is the momentum lost through molecule-molecule collisions with component other than i (but not the particle), the second term is the momentum lost by component i through molecule-particle collisions, the first term on the right hand side is the component pressure gradient of component i and the second term is the thermal gradient which may be neglected for isothermal systems.

Analysis of Gaseous Systems

The analysis of a particular gaseous system requires solution of mass balance equations for system components based on given boundary and initial conditions. The mass balance equations on a molar basis, assuming uniform void fraction in time, can be written in

applications (Alzyadi, 1975; Thorstenson and Pollock, 1989a, b; Abriola et al., 1992; Voudrias and Li, 1992). In addition, few measurements have been made to estimate the different transport parameters and coefficients incorporated in the model (Allawi and Gunn, 1987; Abu-El-Sha'r and Abriola, 1997). The DGM incorporates the different transport mechanisms (i.e., molecular diffusion, non-equimolar flux, Knudsen diffusion, surface diffusion and viscous flux) in a rigorous way based on the kinetic theory treatment. The DGM treats the porous medium as a collection of suspended large dust particles. The dust particles (i.e., solid matrix) are considered as one component of the gaseous mixture, uniformly distributed, and much larger and heavier than the gas molecules (Jackson, 1977; Cunningham and Williams, 1980; Mason and Malinauskas, 1983).

The constitutive equations of the DGM in molar form are given by:

a general form as:

$$\nabla \cdot N_i^T + \varepsilon \frac{\partial c_i}{\partial t} + R_{vi} = 0 \quad (13)$$

where N_i^T is the total molar flux of component i which can be calculated using either Fick's law, Stefan-Maxwell equations, or DGM; ε is the void fraction of the porous medium; c_i is the number of moles per unit void volume; R_{vi} is the reaction rate of species i per unit volume of porous media.

In this paper, the following conditions were assumed: isothermal, steady-state, isobaric, no chemical or biological reactions occur in the system and surface diffusion is insignificant. Therefore, Equation (13) is reduced to:

$$\nabla \cdot N_i^T = 0 \quad (14)$$

For ternary gas system, the total molar fluxes for the different gas components may be explicitly written using the DGM equation as (Feng and Stewart, 1973):

$$[N_z] = -[c] \frac{r^2}{8\mu} \frac{dp}{dz} - [F(r)]^{-1} \left[\frac{dc}{dz} \right] - [D_s(r)] \left[\frac{dc}{dz} \right] \quad (15)$$

where $[N_z]$ and $[c]$ are n -element column vectors consisting of elements N_{iz} and c_i , respectively; r is the radius of pore; μ is the gas dynamic viscosity; $[D_s(r)]$ is an $n \times n$ diagonal matrix of surface diffusivities, $D_{is}(r)$; $[F(r)]$ is the $n \times n$ matrix formed as:

$$F_{ij}(r) = -\frac{X_i}{D_{ij}}, (i \neq j) \quad (16-a)$$

$$F_{ij}(r) = \frac{1}{D_i^k(r)} + \sum_{h=1, h \neq i}^n \frac{X_h}{D_{ih}} \quad (16-b)$$

For steady-state, isobaric conditions, Equation 15 may be written as:

$$[N_z] = -[F(r)]^{-1} \left[\frac{dc}{dz} \right] \quad (17)$$

Perturbation

Perturbation theory is a collection of methods for systematic analysis of the global behavior of solutions to the differential equations. The general procedure of perturbation theory is to identify a parameter (small or large), usually denoted by ϵ , then the solution is represented by the first few terms of an asymptotic expansion, usually not more than two terms. The expansion may be carried out in terms of ϵ which appears naturally in the equations, or may be artificially and temporarily introduced into a difficult problem

having no small parameter. Then $\epsilon=1$ is set, if necessary, to recover the original problem. This artificial conversion to a perturbation problem may be the only way to solve the problem. However, it is preferable to introduce ϵ in such away that the zero-order solution (i.e., the leading terms in the perturbation series) is obtainable as a closed-form analytic expression. Such expansion is called parameter perturbation. Alternatively, the expansion may be carried out in terms of a coordinate (either small or large). These are called coordinate perturbation. The idea of perturbation theory is to decompose a tough problem into an infinite number of relatively easy ones. Hence, perturbation theory is most useful when the first few terms reveal the important features of the solution and the remaining ones give small corrections (Bender and Orszag, 1999; Nayfeh, 2000).

Details of Solution of the DGM

Molar fluxes of species along a given direction (i.e., the z direction) in a multicomponent gaseous system are given by Equation (15). For steady-state diffusive mass transport, it is commonly assumed that viscous flow and surface diffusion are insignificant (Farmer et al., 1980; Karimi et al., 1987; Baeher and Bruell, 1990; Voudrious and Li, 1992). Therefore, the first and third terms of the right hand side of Equation (15) may be neglected. Using Equations (15) and (16) and the relations: $P_i=X_i P$ and $C_i = P_i/RT$, the molar fluxes of a three-component gaseous system can be given as (i.e., Equation 17):

$$\begin{bmatrix} N_1 \\ N_2 \\ N_3 \end{bmatrix} = - \begin{bmatrix} \frac{1}{D_1^k} + \frac{X_2}{D_{12}} + \frac{X_3}{D_{13}} & -\frac{X_1}{D_{12}} & -\frac{X_1}{D_{13}} \\ -\frac{X_2}{D_{21}} & \frac{1}{D_2^k} + \frac{X_1}{D_{21}} + \frac{X_3}{D_{23}} & -\frac{X_2}{D_{23}} \\ -\frac{X_3}{D_{31}} & -\frac{X_3}{D_{32}} & \frac{1}{D_3^k} + \frac{X_1}{D_{31}} + \frac{X_2}{D_{32}} \end{bmatrix}^{-1} \begin{bmatrix} \frac{P}{RT} \dot{X}_1 \\ \frac{P}{RT} \dot{X}_2 \\ \frac{P}{RT} \dot{X}_3 \end{bmatrix} \quad (18)$$

Dots in the above equation represent the derivative with respect to z . For formulation convenience, let:

$$A = \frac{1}{D_1^k}; B = \frac{1}{D_2^k}; E = \frac{1}{D_3^k}; H = \frac{1}{D_{12}}; G = \frac{1}{D_{13}}; Q = \frac{1}{D_{23}}$$

where gaseous components 1, 2 and 3 are chosen so that $M_1 < M_2 < M_3$ (M_i is the molecular weight of component i).

$$\nabla \cdot N_1^T = 0$$

$$\begin{aligned} & \alpha_1 \dot{X}_2^2 + \alpha_2 X_2 \dot{X}_2^2 + \alpha_3 X_2^2 \dot{X}_2^2 + \alpha_4 X_3 \dot{X}_2^2 + \alpha_5 X_2 X_3 \dot{X}_2^2 + \alpha_6 X_3^2 \dot{X}_2^2 + \alpha_7 \dot{X}_2 \dot{X}_3 + \\ & \alpha_8 X_2 \dot{X}_2 \dot{X}_3 + \alpha_9 X_2^2 \dot{X}_2 \dot{X}_3 + \alpha_{10} X_3 \dot{X}_2 \dot{X}_3 + \alpha_{11} X_2 X_3 \dot{X}_2 \dot{X}_3 + \alpha_{12} X_3^2 \dot{X}_2 \dot{X}_3 + \\ & \alpha_{13} \dot{X}_3^2 + \alpha_{14} X_2 \dot{X}_3^2 + \alpha_{15} X_2^2 \dot{X}_3^2 + \alpha_{16} X_3 \dot{X}_3^2 + \alpha_{17} X_2 X_3 \dot{X}_3^2 + \alpha_{18} X_3^2 \dot{X}_3^2 + \alpha_{19} \ddot{X}_2 + \\ & \alpha_{20} X_2 \ddot{X}_2 + \alpha_{21} X_2^2 \ddot{X}_2 + \alpha_{22} X_2^3 \ddot{X}_2 + \alpha_{23} X_3 \ddot{X}_2 + \alpha_{24} X_2 X_3 \ddot{X}_3 + \alpha_{25} X_2^2 X_3 \ddot{X}_2 + \\ & \alpha_{26} X_3^2 \ddot{X}_2 + \alpha_{27} X_2 X_3^2 \ddot{X}_2 + \alpha_{28} X_3^3 \ddot{X}_2 + \alpha_{29} \ddot{X}_3 + \alpha_{30} X_2 \ddot{X}_3 + \alpha_{31} X_2^2 \ddot{X}_3 + \alpha_{32} X_2^3 \ddot{X}_3 + \\ & \alpha_{33} X_3 \ddot{X}_3 + \alpha_{34} X_2 X_3 \ddot{X}_3 + \alpha_{35} X_2^2 X_3 \ddot{X}_3 + \alpha_{36} X_3^2 \ddot{X}_3 + \alpha_{37} X_2 X_3^2 \ddot{X}_3 + \alpha_{38} X_3^3 \ddot{X}_3 = 0 \end{aligned} \tag{19}$$

$$\nabla \cdot N_2^T = 0$$

$$\begin{aligned} & \alpha_{39} \dot{X}_2^2 + \alpha_{40} X_2 \dot{X}_2^2 + \alpha_{41} X_2^2 \dot{X}_2^2 + \alpha_{42} X_3 \dot{X}_2^2 + \alpha_{43} X_2 X_3 \dot{X}_2^2 + \alpha_{44} X_3^2 \dot{X}_2^2 + \alpha_{45} \dot{X}_2 \dot{X}_3 + \\ & \alpha_{46} X_2 \dot{X}_2 \dot{X}_3 + \alpha_{47} X_2^2 \dot{X}_2 \dot{X}_3 + \alpha_{48} X_3 \dot{X}_2 \dot{X}_3 + \alpha_{49} X_2 X_3 \dot{X}_2 \dot{X}_3 + \alpha_{50} X_3^2 \dot{X}_2 \dot{X}_3 + \\ & \alpha_{51} \dot{X}_3^2 + \alpha_{52} X_2 \dot{X}_3^2 + \alpha_{53} X_2^2 \dot{X}_3^2 + \alpha_{54} X_3 \dot{X}_3^2 + \alpha_{55} \ddot{X}_2 + \alpha_{56} X_2 \ddot{X}_2 + \alpha_{57} X_2^2 \ddot{X}_2 + \alpha_{58} X_3 \ddot{X}_2 + \\ & \alpha_{59} X_2 X_3 \ddot{X}_2 + \alpha_{60} X_2^2 X_3 \ddot{X}_2 + \alpha_{61} X_3^2 \ddot{X}_2 + \alpha_{62} X_2 X_3^2 \ddot{X}_2 + \alpha_{63} X_3^3 \ddot{X}_2 + \\ & \alpha_{64} X_2 \ddot{X}_3 + \alpha_{65} X_2^2 \ddot{X}_3 + \alpha_{66} X_2^3 \ddot{X}_3 + \alpha_{67} X_2 X_3 \ddot{X}_3 + \alpha_{68} X_2^2 X_3 \ddot{X}_3 + \alpha_{69} X_2 X_3^2 \ddot{X}_3 = 0 \end{aligned} \tag{20}$$

$$\nabla.N_3^T = 0$$

$$\begin{aligned} & \alpha_{70} X_3 \dot{X}_2^2 + \alpha_{71} X_2 X_3 \dot{X}_2^2 + \alpha_{72} X_3^2 \dot{X}_2^2 + \alpha_{73} \dot{X}_2 \dot{X}_3 + \alpha_{74} X_2 \dot{X}_2 \dot{X}_3 + \alpha_{75} X_2^2 \dot{X}_2 \dot{X}_3 + \\ & \alpha_{76} X_3 \dot{X}_2 \dot{X}_3 + \alpha_{77} X_2 X_3 \dot{X}_2 \dot{X}_3 + \alpha_{78} X_3^2 \dot{X}_2 \dot{X}_3 + \alpha_{79} \dot{X}_3^2 + \alpha_{80} X_2 \dot{X}_3^2 + \alpha_{81} X_2^2 \dot{X}_3^2 + \\ & \alpha_{82} X_3 \dot{X}_3^2 + \alpha_{83} X_2 X_3 \dot{X}_3^2 + \alpha_{84} X_3^2 \dot{X}_3^2 + \alpha_{85} X_3 \ddot{X}_3 + \alpha_{86} X_2 X_3 \ddot{X}_2 + \alpha_{87} X_2^2 X_3 \ddot{X}_2 + \\ & \alpha_{88} X_3^2 \ddot{X}_2 + \alpha_{89} X_2 X_3^2 \ddot{X}_2 + \alpha_{90} X_3^3 \ddot{X}_2 + \alpha_{91} \ddot{X}_3 + \alpha_{92} X_2 \ddot{X}_3 + \alpha_{93} X_2^2 \ddot{X}_3 + \alpha_{94} X_2^3 \ddot{X}_2 + \\ & \alpha_{95} X_3 \ddot{X}_3 + \alpha_{96} X_2 X_3 \ddot{X}_3 + \alpha_{97} X_2^2 X_3 \ddot{X}_3 + \alpha_{98} X_3^2 \ddot{X}_3 + \alpha_{99} X_2 X_3^2 \ddot{X}_3 + \alpha_{100} X_3^3 \ddot{X}_3 = 0 \end{aligned} \quad (21)$$

where α_i is a coefficient function of D_i^K and D_{ij} , values of α_i are given in the Appendix. Note from Equation (11), for an n -component gaseous system, that there are $n-1$ independent total molar flux equations. Therefore, one equation out of Equations (19), (20) and (21) is redundant. Equations (20) and (21) were chosen to solve for the concentrations of the components. As mentioned earlier, the fundamental idea behind perturbation is to turn a difficult problem to a simple one; this can be achieved by identifying terms in Equations (20) and (21) that contribute insignificantly to the equations. The less significant terms are then

removed from the equations to reduce the non-linearity of the equations. The relative importance of the terms in Equations (20) and (21) was examined by calculating the coefficients of the equations (i.e., α_i) for different ternary gaseous representing typical subsurface contaminates and having widely different molecular weights. Details of the procedure adapted in this study to obtain first-order approximate solutions of the molar fractions are presented in Appendix A. Results are shown below:

The first-order approximate solution of X_2 as:

$$X_2 = \frac{I}{k_{11}} \left(\frac{(Z + \psi_2)(k_1 + k_{11})}{\psi_1} \right)^{k_{11}/(k_1 + k_{11})} - \frac{k_{10}}{k_{11}} + \frac{\alpha_{80}}{\alpha_{95}} (m_7 Z^2 + m_8 Z^3 + m_9 Z^4) \quad (22)$$

The first-order approximate solution of X_3 can be found using the same procedure used to solve for X_2 . X_3 is given as:

$$X_3 = \left(\frac{(Z + \psi_4)(k_{23} + I)}{\psi_3} \right)^{I/(k_{23} + I)} - k_{28} + \frac{\alpha_{80}}{\alpha_{95}} (m_{16} Z^2 + m_{17} Z^3 + m_{18} Z^4) \quad (23)$$

For ternary gaseous system, Equation (11) is used to solve for X_1 :

$$\sum_{i=1}^n X_i = 1.0 \quad (24)$$

where:

$$k_1 = \alpha_{39} / \alpha_{95} \tag{25}$$

$$k_{10} = \alpha_{54} / \alpha_{95} \tag{26}$$

$$k_{11} = \alpha_{55} / \alpha_{95} \tag{27}$$

$$k_{23} = \alpha_{79} / \alpha_{95} \tag{28}$$

$$k_{28} = \alpha_{91} / \alpha_{95} \tag{29}$$

$$m_7 = \left\{ \frac{k_{76}}{2k_{82}^2} \right\} \tag{30}$$

$$m_8 = \left\{ \frac{-k_{76}k_{81}}{3k_{82}^3} - \frac{k_1k_{76}}{3c_2k_{82}^3} \right\} \tag{31}$$

$$m_9 = \left(\frac{k_{81}^2k_{76}}{3k_{82}^4} + \frac{k_1k_{76}k_{81}}{3c_2k_{82}^4} + \frac{k_1^2k_{76}}{6c_2^2k_{82}^4} - \frac{k_{76}k_{81}}{12k_{82}^4} + \frac{k_1k_1k_{76}}{12c_2^2k_{82}^4} \right) \tag{32}$$

$$m_{16} = \left(\frac{k_{97}}{2k_{82}^4} \right) \tag{33}$$

$$m_{17} = \left(\frac{-k_{83}k_{97}}{3k_{84}^3} - \frac{k_{23}k_{97}}{3c_6k_{84}^3} \right) \tag{34}$$

$$m_{18} = \left(\frac{k_{83}^2k_{97}}{3k_{84}^4} + \frac{k_{23}k_{97}k_{83}}{3c_6k_{84}^4} + \frac{k_{23}^2k_{97}}{6c_6^2k_{84}^4} - \frac{k_{97}k_{83}^2}{12k_{84}^4} + \frac{k_{97}k_{23}}{24c_6^2k_{84}^4} \right) \tag{35}$$

$$k_{34} = \alpha_{58} / \alpha_{80} \tag{36}$$

$$k_{44} = \alpha_{59} / \alpha_{80} \tag{37}$$

$$k_{45} = \alpha_{61} / \alpha_{80} \tag{38}$$

$$k_{46} = \alpha_{62} / \alpha_{80} \tag{39}$$

$$k_{47} = \alpha_{63} / \alpha_{80} \tag{40}$$

$$k_{59} = \alpha_{92} / \alpha_{80} \tag{41}$$

$$k_{60} = \alpha_{96} / \alpha_{80} \tag{42}$$

$$k_{61} = \alpha_{98} / \alpha_{80} \tag{43}$$

$$k_{62} = \alpha_{99} / \alpha_{80} \tag{44}$$

$$k_{63} = \alpha_{100} / \alpha_{80} \tag{45}$$

$$k_{76} = \left(\frac{k_{43}k_{28}k_1}{c_2^2} + \frac{k_{10}k_{44}k_1k_{28}}{k_{11}c_2^2} + \frac{k_{28}^2k_{45}k_1}{c_2^2} - \frac{k_{10}k_{46}k_1k_{28}^2}{k_{11}c_6^2} - \frac{k_{47}k_{28}^3k_1}{c_2^2} \right) \tag{46}$$

$$k_{81} = \left(\frac{k_1 + k_{11}}{c_2} \right) \tag{47}$$

$$k_{82} = \frac{c_3}{c_2} (k_1 + k_{11}) \tag{48}$$

$$k_{83} = \frac{(k_{23} + 1)}{c_6} \tag{49}$$

$$k_{84} = \frac{c_7}{c_6}(k_{23} + 1) \tag{50}$$

$$k_{97} = \left(\frac{k_{10}k_{59}k_{23}}{k_{11}c_6^2} - \frac{k_{10}k_{60}k_{23}k_{28}}{k_{11}c_6^2} + \frac{k_{28}^3k_{63}k_{23}}{c_6^2} - \frac{k_{23}k_{61}k_{28}^2}{c_6^2} + \frac{k_{10}k_{62}k_{28}^2k_{23}}{k_{11}c_6^2} \right) \tag{51}$$

$$\alpha_{39} = (-a^2c^2d + abc^2d - 2a^2c ds + 2abc ds - a^2 ds^2 + ab ds^2) \tag{52}$$

$$\alpha_{54} = (-a^2c^2b - a^2c^2d - 2a^2bc s + 2a^2cd s - a^2bs^2 + a^2 ds^2) \tag{53}$$

$$\alpha_{55} = (a^2c^2d - abc^2d - 2a^2bck - 2a^2cdk + 2a^2bc s + 4a^2cd s - 2abc ds - 2a^2bks - 2a^2dks + 2a^2bs^2 + 3a^2ds^2 - ab ds^2) \tag{54}$$

$$\alpha_{58} = (a^2c^2d - a^2c^2k + 2a^2bc - 2abc^2s + 4a^2cd s - 2ac^2ds - 2a^2cks + 2a^2bs^2 - 2abc s^2 + 3a^2ds^2 + 2ac ds^2 - a^2ks^2) \tag{55}$$

$$\alpha_{59} = (2a^2cdk - ac^2dk - a^2ck^2 - 4a^2cd s + 2abc ds + 2ac^2ds - bc^2ds + 2a^2bks - 3abc ks + 4a^2dks - 3ac dks - a^2k^2s - 2a^2bs^2 + 2abc s^2 - 6a^2ds^2 + 2ab ds^2 + 4ac ds^2 - bc ds^2 + 2a^2ks^2 - ab ks^2) \tag{56}$$

$$\alpha_{61} = (-2a^2cd s + 2ac^2ds - 2a^2cks - 2ac^2ks - a^2cks^2 + 2abc s^2 - bc^2s^2 - 3a^2ds^2 + 4ac ds^2 - c^2ds^2 + 2a^2ks^2 - 2ac ks^2) \tag{57}$$

$$\alpha_{62} = (-2a^2dks + 3ac dks - c^2dks + a^2k^2s - ack^2s + 3a^2ds^2 - ab ds^2 - 4ac ds^2 + bc ds^2 + c^2ds^2 - 2a^2ks^2 + ab ks^2 + 2ac ks^2 - bc ks^2) \tag{58}$$

$$\alpha_{63} = (a^2ds^2 - 2ac ds^2 + c^2ds^2 - a^2ks^2 + 2ac ks^2 - c^2ks^2) \tag{59}$$

$$\alpha_{79} = (-a^2b^2s + ab^2cs - 2a^2bds + 2ab ds - a^2d^2s + ac d^2s) \tag{60}$$

$$\alpha_{80} = (abcdk + -acd^2k - a^2bk^2 - 2a^2bds - 2ab^2ds - 2abc ds + b^2cds + 2a^2d^2s - 2abd^2s - 2acd^2s + bcd^2s + ab^2ks + ab dks) \tag{61}$$

$$\alpha_{91} = (-a^2b^2c - 2a^2bcd - a^2cd^2 - a^2b^2s - 2a^2bds - a^2d^2s) \tag{62}$$

$$\alpha_{92} = (2a^2bcd - 2ab^2cd + 2a^2cd^2 - 2abcd^2 - a^2b^2k - 2a^2bdk - a^2d^2k + a^2b^2s + 4a^2bds - 2ab^2ds + 3a^2d^2s - 2abd^2s) \tag{63}$$

$$\alpha_{95} = (2a^2bcd + 2a^2cd^2 - 2a^2bck - 2a^2cdk + a^2b^2s - ab^2cs + 4a^2bds - 2abc ds + 3a^2d^2s - ac d^2s - 2a^2bks - 2a^2dks) \tag{64}$$

$$\alpha_{96} = (-2a^2cd^2 + 2abcd^2 + 2a^2bdk + 2a^2cdk - 3abcdk + 2a^2d^2k - ac d^2k - a^2bk^2 - a^2dk^2 - a^2bds + 2ab^2ds + 2abc ds - b^2cds - 6a^2d^2s + 4abd^2s + 2acd^2s - bcd^2s + 2a^2bks - ab^2ks + 4a^2dks - 3abdks) \tag{65}$$

$$\alpha_{98} = (-a^2cd^2 + 2a^2cdk - a^2ck^2 - 2a^2bds + 2abc ds - 3a^2d^2s + 2acd^2s + 2a^2bks - 2abc ks + 4a^2dks - 2ac dks - a^2k^2s) \tag{66}$$

$$\alpha_{99} = (-a^2d^2k + ac d^2k + a^2dk^2 + ac d^2k + 3a^2d^2s - 2abd^2s - 2acd^2s + bcd^2s - 4a^2dks + 3abdks + 2ac dks - bcdks + a^2k^2s - abk^2s) \tag{67}$$

$$\alpha_{100} = (a^2d^2s - ac d^2s - 2a^2dks + 2ac dks + a^2k^2s + ack^2s) \tag{68}$$

$$\begin{aligned} a &= \frac{1}{D_{1k}} \\ b &= \frac{1}{D_{2k}} \\ c &= \frac{1}{D_{3k}} \\ d &= \frac{1}{D_{12}} \\ s &= \frac{1}{D_{13}} \\ k &= \frac{1}{D_{23}} \end{aligned} \tag{69}$$

Here, $a < b < c$ (i.e. $M_1 < M_2 < M_3$)

where, M_i is the molecular volume weight of i . Note that Z in Equations (22) and (23) is a dimensionless parameter: $Z = l/L$, where l is a distance along the diffusion path at which the concentrations to be calculated (measured from the boundary) and L is the total length of diffusion path.

Although the solution requires the evaluation of the terms given in equations (22 – 69), it is a relatively simple approach when compared to the reported numerical solutions (Remick and Geankoplis, 1970). If a spread sheet is prepared to evaluate these terms, the solution can be obtained in a fast and effective manner for different boundary conditions.

Solution Verification

To verify the perturbation solution of the DGM, concentration profiles of components of a ternary gaseous system were calculated using Equations (22) and (23) and compared to concentrations obtained by an independent numerical solution of a set of equations that describe the transition region between Knudsen and molecular diffusion. While the numerical solution obtained by Remick and Geankoplis (1970) did not utilize the DGM equations, it provides a base for verification because it

incorporates the same transport mechanisms assumed in this paper to solve for the DGM. The ternary gaseous system used consisted of components that have widely different molecular weights and exhibit no surface diffusion. Physical properties of the components of the system and boundary concentrations are given in Table (1). Note that D_{ij} and D_i^K are chosen to be approximately of the same order of magnitude to provide equal contribution from Knudsen and molecular mechanisms. Figure (1) shows the concentrations of X_A , X_B and X_C plotted vs. Z ($Z = l/L$) at $P=100$ atm obtained by perturbation and numerical solutions. There is a good agreement between the two solutions. However, in the case of the numerical solution, concentration lines of X_A and X_B are curved in opposite direction. Remick and Geankoplis (1970) reported that this behavior was observed at high pressures, concentration lines tend to be more linear as pressure decreases.

Application Examples

Equations (22), (23) and (11) can be used to calculate mole fractions of ternary gaseous systems components. In addition, the total molar fluxes can be calculated explicitly for each component by incorporating the mole fractions using the following equations (Jackson, 1977):

$$(N_1^T)_{DGM} = \frac{-\Delta_{12}\Delta_{23}\Delta_{31}}{X_1\Delta_{23} + X_2\Delta_{31} + X_3\Delta_{12}} \left\{ \frac{\frac{A_1}{\Delta_{23}} \left(\frac{X_2}{D_2^K} + \frac{X_3}{D_3^K} \right) - X_1 \left(\frac{A_2}{D_2^K \Delta_{31}} + \frac{A_3}{D_3^K \Delta_{12}} \right)}{\frac{X_1}{D_1^K} + \frac{X_2}{D_2^K} + \frac{X_3}{D_3^K}} \right\} \tag{70}$$

$$(N_2^T)_{DGM} = \frac{-\Delta_{12}\Delta_{23}\Delta_{31}}{X_1\Delta_{23} + X_2\Delta_{31} + X_3\Delta_{12}} \left\{ \frac{\frac{A_2}{\Delta_{13}} \left(\frac{X_1}{D_1^K} + \frac{X_3}{D_3^K} \right) - X_2 \left(\frac{A_1}{D_1^K \Delta_{23}} + \frac{A_3}{D_3^K \Delta_{12}} \right)}{\frac{X_1}{D_1^K} + \frac{X_2}{D_2^K} + \frac{X_3}{D_3^K}} \right\} \tag{71}$$

$$(N_3^T)_{DGM} = \frac{-\Delta_{12}\Delta_{23}\Delta_{31}}{X_1\Delta_{23} + X_2\Delta_{31} + X_3\Delta_{12}} \left\{ \frac{\frac{A_3}{\Delta_{21}} \left(\frac{X_1}{D_1^K} + \frac{X_2}{D_2^K} \right) - X_3 \left(\frac{A_1}{D_1^K \Delta_{23}} + \frac{A_2}{D_2^K \Delta_{31}} \right)}{\frac{X_1}{D_1^K} + \frac{X_2}{D_2^K} + \frac{X_3}{D_3^K}} \right\} \tag{72}$$

$$A_i = \frac{P}{RT} \nabla X_i \tag{73}$$

$$\frac{I}{\Delta_{ij}} = \frac{I}{D_{ij}} + \frac{I}{D_i^k D_j^k \sum_{i=1}^n X_i / D_i^k} \quad (74)$$

To test the validity of Equations (22-24), the Equations are applied to scenarios including both experimental and field applications as follows:

- (1) The first example represents a field application where the scenario and the data are borrowed from Thorstenson and Pollock (1989a). This example represents a typical subsurface contamination problem in which a contaminant is generated at a continuous rate at a specific depth below the ground surface. One-dimensional transport is assumed (i.e., transport in the vertical direction). The system is treated as a ternary system where Methane (CH₄), the major contaminant in this example, is considered as one component and the major constituents of air (i.e., N₂ and O₂) are considered as two distinct components. System properties and boundary conditions are given in Table (2); note that Knudsen diffusion is neglected in this example. Of particular interest in such scenario is to calculate concentrations (i.e., mole fraction) as a function of depth for the different components in the system. Figure (2) shows mole fractions of the components of the system as obtained from the perturbation solution.
- (2) The second example used is an experimental diffusion system used by Karimi et al., (1987) to investigate vapor phase diffusion of C₆H₆ in soil. The experiment was designed to accommodate diffusion cell contained soil sample extracted from cover of a landfill used for disposal of industrial wastes. A source of C₆H₆ was placed beneath the cell to mimic the landfill by allowing diffusion through the soil sample. At the top of the soil sample, an N₂ source was placed to sweep away C₆H₆. Properties and boundary conditions of the system are shown in Table (3). The objective of this example is to calculate the concentration of C₆H₆ at different points of the landfill cover. Mole fractions of the components of the system as calculated by Equations

- (60), (61) and (11) are shown in Figure (3).
- (3) The third example used is an experimental system used by Abu-El-Sha'r (1993) to evaluate the relative importance of different transport mechanisms in gaseous systems. The system considered herein is an open system where CH₄ was injected at one side of a soil sample placed in a diffusion cell and air (i.e., N₂ and O₂) was injected at the other side. System properties and boundary conditions are given in Table (4). The objective of this example is to calculate molar fluxes of CH₄ at different points for different types of porous media. Three types of soil were used; sea sand, Ottawa sand and Kaolinite. Figure (4) shows total molar fluxes for CH₄ in the different soil samples as calculated by perturbation solution.

SUMMARY AND CONCLUSION

A perturbation method was used to solve the mass balance equations for ternary gas systems when the dusty gas model (DGM) is incorporated to calculate mole fractions and molar fluxes of the components of the system. Steady-state conditions, isobaric, isothermal and non reactive system were assumed. The straightforward expansion method to the second-order approximation was implemented in the solution. The perturbation parameter which was introduced into the equations, presented no physical meaning to the system. The solution was expressed as a closed-form solution incorporates a dimensionless length boundary conditions, and parameters of transport mechanisms. The solution was verified by a numerical solution and there was a good agreement between the two solutions. The perturbation solution was applied to different experimental and field conditions to predict mass fractions and molar fluxes of components of ternary gaseous systems.

APPENDICES

Appendix A

Details of the Perturbation Solution of the DGM

Molar fluxes of species along a given direction (i.e., the z direction) in a multicomponent gaseous system are given by Equation (15). For steady-state diffusive mass transport, it is commonly assumed that viscous flow and surface diffusion are insignificant (Farmer et al., 1980; Karimi et al., 1987; Baehar and Bruell, 1990; Voudrious and Li, 1992). Therefore, the first and third terms of the right hand side of Equation (15) may be neglected. Using Equations (15), (16) and the relations: $P_i=X_i P$ and $C_i = P_i/RT$, the molar fluxes of a three-component gaseous system can be given as (i.e., Equation 17):

$$\begin{bmatrix} N_1 \\ N_2 \\ N_3 \end{bmatrix} = - \begin{bmatrix} \frac{1}{D_1^K} + \frac{X_2}{D_{12}} + \frac{X_3}{D_{13}} & -\frac{X_1}{D_{12}} & -\frac{X_1}{D_{13}} \\ -\frac{X_2}{D_{21}} & \frac{1}{D_2^K} + \frac{X_1}{D_{21}} + \frac{X_3}{D_{23}} & -\frac{X_2}{D_{23}} \\ -\frac{X_3}{D_{31}} & -\frac{X_3}{D_{32}} & \frac{1}{D_3^K} + \frac{X_1}{D_{31}} + \frac{X_2}{D_{32}} \end{bmatrix}^{-1} \begin{bmatrix} \frac{P}{RT} \dot{X}_1 \\ \frac{P}{RT} \dot{X}_2 \\ \frac{P}{RT} \dot{X}_3 \end{bmatrix} \tag{A-1}$$

Dots in the above equation represent the derivative with respect to z . For formulation convenience, let:

$$A = \frac{1}{D_1^K}; B = \frac{1}{D_2^K}; E = \frac{1}{D_3^K}; H = \frac{1}{D_{12}}; G = \frac{1}{D_{13}}; Q = \frac{1}{D_{23}} \tag{A-2}$$

where gaseous components 1, 2 and 3 are chosen so that $M_1 < M_2 < M_3$ (M_i is the molecular weight of component i).

The total molar flux equation for each component is obtained by substitution of Equation (A-1) in the mass balance Equations and utilizing $\sum_{i=1}^n x_i = 1.0$. The total molar fluxes for component one, two and three are given by the Equations (A-3), (A-4) and (A-5), respectively.

$$\begin{aligned} \nabla \cdot N_j^T &= 0 \\ \alpha_1 \dot{X}_2^2 + \alpha_2 X_2 \dot{X}_2^2 + \alpha_3 X_2^2 \dot{X}_2^2 + \alpha_4 X_3 \dot{X}_2^2 + \alpha_5 X_2 X_3 \dot{X}_2^2 + \alpha_6 X_3^2 \dot{X}_2^2 + \alpha_7 \dot{X}_2 \dot{X}_3 + \\ \alpha_8 X_2 \dot{X}_2 \dot{X}_3 + \alpha_9 X_2^2 \dot{X}_2 \dot{X}_3 + \alpha_{10} X_3 \dot{X}_2 \dot{X}_3 + \alpha_{11} X_2 X_3 \dot{X}_2 \dot{X}_3 + \alpha_{12} X_3^2 \dot{X}_2 \dot{X}_3 + \\ \alpha_{13} \dot{X}_3^2 + \alpha_{14} X_2 \dot{X}_3^2 + \alpha_{15} X_2^2 \dot{X}_3^2 + \alpha_{16} X_3 \dot{X}_3^2 + \alpha_{17} X_2 X_3 \dot{X}_2 + \alpha_{18} X_3^2 \dot{X}_3^2 + \alpha_{19} \ddot{X}_2 + \\ \alpha_{20} X_2 \ddot{X}_2 + \alpha_{21} X_2^2 \ddot{X}_2 + \alpha_{22} X_2^3 \ddot{X}_2 + \alpha_{23} X_3 \ddot{X}_2 + \alpha_{24} X_2 X_3 \ddot{X}_3 + \alpha_{25} X_2^2 X_3 \ddot{X}_2 + \\ \alpha_{26} X_3^2 \ddot{X}_2 + \alpha_{27} X_2 X_3^2 \ddot{X}_2 + \alpha_{28} X_3^3 \ddot{X}_2 + \alpha_{29} \ddot{X}_3 + \alpha_{30} X_2 \ddot{X}_3 + \alpha_{31} X_2^2 \ddot{X}_3 + \alpha_{32} X_2^3 \ddot{X}_3 + \\ \alpha_{33} X_3 \ddot{X}_3 + \alpha_{34} X_2 X_3 \ddot{X}_3 + \alpha_{35} X_2^2 X_3 \ddot{X}_3 + \alpha_{36} X_3^2 \ddot{X}_3 + \alpha_{37} X_2 X_3^2 \ddot{X}_3 + \alpha_{38} X_3^3 \ddot{X}_3 = 0 \end{aligned} \tag{A-3}$$

$$\nabla \cdot N_2^T = 0$$

$$\begin{aligned} & \alpha_{39} \dot{X}_2^2 + \alpha_{40} X_2 \dot{X}_2^2 + \alpha_{41} X_2^2 \dot{X}_2^2 + \alpha_{42} X_3 \dot{X}_2^2 + \alpha_{43} X_2 X_3 \dot{X}_2^2 + \alpha_{44} X_3^2 \dot{X}_2^2 + \alpha_{45} \dot{X}_2 \dot{X}_3 + \\ & \alpha_{46} X_2 \dot{X}_2 \dot{X}_3 + \alpha_{47} X_2^2 \dot{X}_2 \dot{X}_3 + \alpha_{48} X_3 \dot{X}_2 \dot{X}_3 + \alpha_{49} X_2 X_3 \dot{X}_2 \dot{X}_3 + \alpha_{50} X_3^2 \dot{X}_2 \dot{X}_3 + \\ & \alpha_{51} X_2 \dot{X}_3^2 + \alpha_{52} X_2^2 \dot{X}_3^2 + \alpha_{53} X_2 X_3 \dot{X}_3^2 + \alpha_{54} \ddot{X}_2 + \alpha_{55} X_2 \ddot{X}_2 + \alpha_{56} X_2^2 \ddot{X}_2 + \alpha_{57} X_2^3 \ddot{X}_2 + \\ & \alpha_{58} X_3 \ddot{X}_2 + \alpha_{59} X_2 X_3 \ddot{X}_2 + \alpha_{60} X_2^2 X_3 \ddot{X}_2 + \alpha_{61} X_3^2 \ddot{X}_2 + \alpha_{62} X_2 X_3^2 \ddot{X}_2 + \alpha_{63} X_3^3 \ddot{X}_2 + \\ & \alpha_{64} X_2 \ddot{X}_3 + \alpha_{65} X_2^2 \ddot{X}_3 + \alpha_{66} X_2^3 \ddot{X}_3 + \alpha_{67} X_2 X_3 \ddot{X}_3 + \alpha_{68} X_2^2 X_3 \ddot{X}_3 + \alpha_{69} X_2 X_3^2 \ddot{X}_3 = 0 \end{aligned} \tag{A-4}$$

$$\nabla \cdot N_3^T = 0$$

$$\begin{aligned} & \alpha_{70} X_3 \dot{X}_2^2 + \alpha_{71} X_2 X_3 \dot{X}_2^2 + \alpha_{72} X_3^2 \dot{X}_2^2 + \alpha_{73} \dot{X}_2 \dot{X}_3 + \alpha_{74} X_2 \dot{X}_2 \dot{X}_3 + \alpha_{75} X_2^2 \dot{X}_2 \dot{X}_3 + \\ & \alpha_{76} X_3 \dot{X}_2 \dot{X}_3 + \alpha_{77} X_2 X_3 \dot{X}_2 \dot{X}_3 + \alpha_{78} X_3^2 \dot{X}_2 \dot{X}_3 + \alpha_{79} \dot{X}_3^2 + \alpha_{80} X_2 \dot{X}_3^2 + \alpha_{81} X_2^2 \dot{X}_3^2 + \\ & \alpha_{82} X_3 \dot{X}_3^2 + \alpha_{83} X_2 X_3 \dot{X}_3^2 + \alpha_{84} X_3^2 \dot{X}_3^2 + \alpha_{85} X_3 \ddot{X}_3 + \alpha_{86} X_2 X_3 \ddot{X}_2 + \alpha_{87} X_2^2 X_3 \ddot{X}_2 + \\ & \alpha_{88} X_3^2 \ddot{X}_2 + \alpha_{89} X_2 X_3^2 \ddot{X}_2 + \alpha_{90} X_3^3 \ddot{X}_2 + \alpha_{91} \ddot{X}_3 + \alpha_{92} X_2 \ddot{X}_3 + \alpha_{93} X_2^2 \ddot{X}_3 + \alpha_{94} X_2^3 \ddot{X}_3 + \\ & \alpha_{95} X_3 \ddot{X}_3 + \alpha_{96} X_2 X_3 \ddot{X}_3 + \alpha_{97} X_2^2 X_3 \ddot{X}_3 + \alpha_{98} X_3^2 \ddot{X}_3 + \alpha_{99} X_2 X_3^2 \ddot{X}_3 + \alpha_{100} X_3^3 \ddot{X}_3 = 0 \end{aligned} \tag{A-5}$$

where α_i is a coefficient function of D_i^K and D_{ij} , values of α_i are given in the Appendix. Note from Equation (11), for an n -component gaseous system, that there are $n-1$ independent total molar flux equations. Therefore, one equation out of Equations (A-3), (A-4) and (A-5) is redundant. Equations (A-4) and (A-5) were chosen to solve for the concentrations of the components. As mentioned earlier, the fundamental idea behind perturbation is to turn a difficult problem to a simple one; this can be achieved by identifying terms in Equations (A-4) and (A-5) that contribute insignificantly to the equations. The less significant terms are then removed from the equations to reduce the non-linearity of the equations. The relative importance of the terms in Equations (A-4) and (A-5) were examined by calculating the coefficients of the equations (i.e., α_i) for different ternary gaseous representing typical subsurface contaminates and having widely different molecular weights. Upon neglecting the insignificant terms, Equations (A-4) and (A-5) are reduced to Equations (A-6) and (A-7), respectively.

$$\nabla \cdot N_2^T = 0$$

$$\begin{aligned} & \alpha_{39} \dot{X}_2^2 + \alpha_{42} X_3 \dot{X}_2^2 + \alpha_{45} \dot{X}_2 \dot{X}_3 + \alpha_{46} X_2 \dot{X}_2 \dot{X}_3 + \alpha_{48} X_3 \dot{X}_2 \dot{X}_3 + \alpha_{49} X_2 X_3 \dot{X}_2 \dot{X}_3 + \\ & \alpha_{50} X_3^2 \dot{X}_2 \dot{X}_3 + \alpha_{51} X_2 \dot{X}_3^2 + \alpha_{53} X_2 X_3 \dot{X}_3^2 + \alpha_{54} \ddot{X}_2 + \alpha_{55} X_2 \ddot{X}_2 + \alpha_{58} X_3 \ddot{X}_2 + \\ & \alpha_{59} X_2 X_3 \ddot{X}_2 + \alpha_{60} X_2^2 X_3 \ddot{X}_2 + \alpha_{61} X_3^2 \ddot{X}_2 + \alpha_{62} X_2 X_3^2 \ddot{X}_2 + \alpha_{63} X_3^3 \ddot{X}_2 + \alpha_{64} X_2 \ddot{X}_3 + \\ & \alpha_{67} X_2 X_3 \ddot{X}_3 + \alpha_{69} X_2 X_3^2 \ddot{X}_3 = 0 \end{aligned} \tag{A-6}$$

$$\nabla \cdot N_3^T = 0$$

$$\begin{aligned} &\alpha_{73} \dot{X}_2 \dot{X}_3 + \alpha_{76} X_3 \dot{X}_2 \dot{X}_3 + \alpha_{78} X_3^2 \dot{X}_2 \dot{X}_3 + \alpha_{79} \dot{X}_3^2 + \alpha_{80} X_2 \dot{X}_3^2 + \alpha_{82} X_3 \dot{X}_3^2 + \alpha_{83} X_2 X_3 \dot{X}_3^2 + \\ &\alpha_{84} X_3^2 \dot{X}_3^2 + \alpha_{88} X_3^2 \ddot{X}_2 + \alpha_{91} \ddot{X}_3 + \alpha_{92} X_2 \ddot{X}_3 + \alpha_{95} X_3 \ddot{X}_3 + \alpha_{96} X_2 X_3 \ddot{X}_3 + \alpha_{98} X_3^2 \ddot{X}_3 + \\ &\alpha_{99} X_2 X_3^2 \ddot{X}_3 + \alpha_{100} X_3^3 \ddot{X}_3 = 0 \end{aligned} \tag{A-7}$$

The variables in Equations (A-6) and (A-7) are X_2, X_3 and z (X_2 and X_3 are dimensionless and z has a length unit). To obtain dimensionless forms of Equations (A-6) and (A-7), the following variables are introduced:

$$Z^* = \frac{z}{L}; \quad X_2^* = X_2; \quad X_3^* = X_3 \tag{A-8}$$

The star in Equation (A-8) represents a dimensionless variable.

$$\frac{dX_2}{dz} = \frac{dX_2^*}{dZ^*} \frac{dZ^*}{dz}, \text{ Therefore:}$$

$$\frac{dX_2}{dz} = \frac{1}{L} \frac{dX_2^*}{dZ^*}; \text{ and } \frac{d^2 X_2}{dz^2} = \frac{1}{L^2} \frac{d^2 X_2^*}{dZ^{*2}} \tag{A-9}$$

Similarly, \dot{X}_3 and \ddot{X}_3 can be expressed as:

$$\frac{dX_3}{dz} = \frac{1}{L} \frac{dX_3^*}{dZ^*}; \text{ and } \frac{d^2 X_3}{dz^2} = \frac{1}{L^2} \frac{d^2 X_3^*}{dZ^{*2}} \tag{A-10}$$

Dimensionless forms of Equations (A-6) and (A-7) are obtained by the following steps: (1) substituting Equations (A-9) and (A-10) into Equations (A-6) and (A-7); (2) multiplying both sides of Equations (A-6) and (A-7) by L^2 ; and (3) dividing Equations (A-6) and (A-7) by α_{95} , a relatively large coefficient chosen arbitrary to define a small dimensionless perturbation parameter ϵ as:

$$\epsilon = \frac{\alpha_{80}}{\alpha_{95}} \tag{A-11}$$

Note that the perturbation parameter in this case has no physical meaning; it is artificially introduced into the equation to reduce non-linearity. The dimensionless forms of Equations (A-6) and (A-7) are given by Equations (A-12) and (A-13), respectively:

$$\begin{aligned} &k_1 \dot{X}_2^2 + k_{34} \in X_3 \dot{X}_2^2 + k_{35} \in \dot{X}_2 \dot{X}_3 + k_{36} \in X_2 \dot{X}_2 \dot{X}_3 + k_{37} \in X_3 \dot{X}_2 \dot{X}_3 + k_{38} \in X_2 X_3 \dot{X}_2 \dot{X}_3 + \\ &k_{39} \in X_3 \dot{X}_2 \dot{X}_3 + k_{40} \in X_2 \dot{X}_3^2 + k_{41} \in X_2 X_3 \dot{X}_3^2 + k_{10} \ddot{X}_2 + K_{11} X_2 \ddot{X}_2 + k_{43} \in X_3 \ddot{X}_2 + \\ &k_{44} \in X_2 X_3 \ddot{X}_2 + k_{45} \in X_3 \ddot{X}_2 + k_{46} \in X_2 X_3 \ddot{X}_2 + k_{47} \in X_3 \ddot{X}_2 + k_{48} \in X_2 \ddot{X}_3 + \\ &k_{49} \in X_2 X_3 \ddot{X}_3 + k_{50} \in X_2 X_3^2 \ddot{X}_3 = 0 \end{aligned} \tag{A-12}$$

$$\begin{aligned}
 k_{51} \in \dot{X}_2 \dot{X}_3 + k_{52} \in X_3 \dot{X}_2 \dot{X}_3 + k_{53} \in X_3 \dot{X}_2 \dot{X}_3 + k_{23} \dot{X}_3^2 + \in X_2 \dot{X}_3 + k_{54} \in X_3 \dot{X}_3^2 \\
 k_{55} \in X_2 X_3 \dot{X}_3^2 + k_{56} \in X_3 \dot{X}_3^2 + k_{57} \in X_3 \ddot{X}_2 + k_{28} \ddot{X}_3 + k_{59} \in X_2 \ddot{X}_3 + X_3 \ddot{X}_3 + \\
 k_{60} \in X_2 X_3 \ddot{X}_3 + k_{61} \in X_3 \ddot{X}_3 + k_{62} \in X_2 X_3 \ddot{X}_3 + k_{63} \in X_3 \ddot{X}_3 = 0
 \end{aligned}
 \tag{A-13}$$

where k_i are dimensionless coefficients given in the Appendix. Note that X_2 , X_3 and Z are dimensionless and the star is removed from the notation for convenience. The second-order approximation of X_2 and X_3 are given by Equations (A-14) and (A-15), respectively:

$$X_2(Z; \in) = X_{20} + \in X_{21} + O(\in^2) \tag{A-14}$$

$$X_3(Z; \in) = X_{30} + \in X_{31} + O(\in^2) \tag{A-15}$$

where X_{i0} and X_{i1} are the zero-order and first-order approximations of X_i , respectively.

Substitution of Equations (A-14) and (A-15) into equations (A-12) and (A-13) and expansion of all terms give the following equations:

$$\begin{aligned}
 k_1 \dot{X}_{20}^2 + 2k_1 \in \dot{X}_{21} \dot{X}_{20} + k_{34} \in X_{30} \dot{X}_{20}^2 + k_{35} \in \dot{X}_{20} \dot{X}_{30} + k_{36} \in X_{20} \dot{X}_{20} \dot{X}_{30} + k_{37} \in X_{30} \dot{X}_{20} \dot{X}_{30} + \\
 k_{38} \in X_{20} X_{30} \dot{X}_{20} \dot{X}_{30} + k_{39} \in X_{30} \dot{X}_{20} \dot{X}_{30} + k_{40} \in X_{20} \dot{X}_{30}^2 + k_{41} \in X_{20} X_{30} \dot{X}_{30}^2 + k_{10} \ddot{X}_{20} + \\
 K_{10} \in \ddot{X}_{21} + k_{11} X_{20} \ddot{X}_{20} + k_{11} \in X_{20} \ddot{X}_{21} + k_{11} \in X_{21} \ddot{X}_{20} + k_{43} \in X_{30} \ddot{X}_{20} + k_{44} \in X_{20} X_{30} \ddot{X}_{20} + \\
 k_{45} \in X_{30} \ddot{X}_{20} + k_{46} \in X_{20} \ddot{X}_{20} X_{30} + k_{47} \in X_{30} \ddot{X}_{20} + k_{48} \in X_{20} \ddot{X}_{30} + k_{49} \in X_{20} X_{30} \ddot{X}_{30} + \\
 k_{50} \in X_{20} X_{30} \ddot{X}_{30} + O(\in^2) = 0
 \end{aligned}
 \tag{A-16}$$

$$\begin{aligned}
 k_{51} \in \dot{X}_{20} \dot{X}_{30} + k_{52} \in X_{30} \dot{X}_{20} \dot{X}_{30} + k_{53} \in X_{30} \dot{X}_{20} \dot{X}_{30} + k_{23} \dot{X}_{30}^2 + \in X_{20} \dot{X}_{30} + k_{54} \in X_{30} \dot{X}_{30}^2 \\
 2 \in k_{23} \dot{X}_{30} \dot{X}_{31} + k_{55} \in X_{20} X_{30} \dot{X}_{30} + k_{56} \in X_{30} \dot{X}_{30}^2 + k_{57} \in X_{30} \ddot{X}_{20} + k_{28} \ddot{X}_{30} + k_{28} \in \ddot{X}_{31} + \\
 k_{59} \in X_{20} \ddot{X}_{30} + X_{30} \ddot{X}_{30} + \in X_{30} \ddot{X}_{31} + \in X_{31} \ddot{X}_{30} + k_{60} \in X_{20} X_{30} \ddot{X}_{30} + k_{61} \in X_{30} \ddot{X}_{30} + \\
 k_{62} \in X_{20} X_{30} \ddot{X}_{30} + k_{63} \in X_{30} \ddot{X}_{30} + O(\in^2) = 0
 \end{aligned}
 \tag{A-17}$$

Equating terms of like powers of \in in Equations (A-16) and (A-17) to zero gives two sets of equations: (1) when the power of \in equals zero, Equations (A-18) and (A-19) are obtained; and (2) when the power of \in equals one, Equations (A-20) and (A-21) are obtained.

$$k_1 \dot{X}_{20}^2 + k_{10} \ddot{X}_{20} + k_{11} X_{20} \ddot{X}_{20} = 0 \tag{A-18}$$

$$k_{23} \dot{X}_{30}^2 + k_{28} \ddot{X}_{30} + X_{30} \ddot{X}_{30} = 0 \tag{A-19}$$

$$\begin{aligned}
 &2k_1 \dot{X}_{21} \dot{X}_{20} + k_{34} X_{30} \dot{X}_{20}^2 + k_{35} \dot{X}_{20} \dot{X}_{30} + k_{36} X_{20} \dot{X}_{20} \dot{X}_{30} + k_{37} X_{30} \dot{X}_{20} \dot{X}_{30} + k_{40} X_{20} \dot{X}_{30}^2 + \\
 &k_{38} X_{20} X_{30} \dot{X}_{20} \dot{X}_{30} + k_{39} X_{30} \dot{X}_{20} \dot{X}_{30}^2 + k_{41} X_{20} X_{30} \dot{X}_{30}^2 + k_{10} \ddot{X}_{20} + K_{10} \ddot{X}_{21} + k_{11} X_{20} \ddot{X}_{21} + \\
 &k_{11} X_{21} \ddot{X}_{20} + k_{43} X_{30} \ddot{X}_{20} + k_{44} X_{20} X_{30} \ddot{X}_{20} + k_{45} X_{30} \ddot{X}_{20}^2 + k_{46} X_{20} \ddot{X}_{20} \ddot{X}_{30} + k_{47} X_{30} \ddot{X}_{20}^3 + \\
 &k_{48} X_{20} \ddot{X}_{30} + k_{49} X_{20} X_{30} \ddot{X}_{30} + k_{50} X_{20} X_{30} \ddot{X}_{30}^2 = 0
 \end{aligned} \tag{A-20}$$

$$\begin{aligned}
 &k_{51} \dot{X}_{20} \dot{X}_{30} + k_{52} X_{30} \dot{X}_{20} \dot{X}_{30} + k_{53} X_{30} \dot{X}_{20} \dot{X}_{30}^2 + X_{20} \dot{X}_{30}^2 + k_{54} X_{30} \dot{X}_{30}^2 + 2k_{23} \dot{X}_{30} \dot{X}_{31} + \\
 &k_{55} X_{20} X_{30} \dot{X}_{30}^2 + k_{56} X_{30} \dot{X}_{30}^2 + k_{57} X_{30} \ddot{X}_{20} + k_{28} \ddot{X}_{31} + k_{59} X_{20} \ddot{X}_{30} + X_{30} \ddot{X}_{31} + X_{31} \ddot{X}_{30} + \\
 &k_{60} X_{20} X_{30} \ddot{X}_{30} + k_{61} X_{30} \ddot{X}_{30}^2 + k_{62} X_{20} X_{30} \ddot{X}_{30}^2 + k_{63} X_{30} \ddot{X}_{30}^3 = 0
 \end{aligned} \tag{A-21}$$

The general solution of Equation (A-18) can be obtained as follows:

$$\text{Let } w = \dot{X}_{20} = \frac{dX_{20}}{dZ} \tag{A-22}$$

By the chain rule:

$$\frac{d^2 X_{20}}{dZ^2} = \frac{dw}{dZ} = \frac{dw}{dX_{20}} \frac{dX_{20}}{dZ} = w \frac{dw}{dX_{20}} \tag{A-23}$$

substitution of $\frac{dX_{20}}{dZ}$ and $\frac{d^2 X_{20}}{dZ^2}$ in Equation (A-18) gives:

$$\frac{dw}{dX_{20}} (k_{11} X_{20} + k_{10}) = -k_1 w \tag{A-24}$$

Integration of the above equation gives w as:

$$w = \psi_1 (k_{11} X_{20} + k_{10})^{\left(\frac{-k_1}{k_{11}}\right)} \tag{A-25}$$

where ψ_1 is an arbitrary integration constant.

Substituting $\frac{dX_{20}}{dZ}$ for w gives the following equation:

$$\frac{dX_{20}}{dZ} = \psi_1 (k_{11} X_{20} + k_{10}) \tag{A-26}$$

From Equation (42), X_{20} is obtained as:

$$X_{20} = \frac{1}{k_{11}} \left(\frac{(Z + \psi_2)(k_1 + k_{11})}{\psi_1} \right)^{k_{11}/(k_1 + k_{11})} - \frac{k_{10}}{k_{11}} \tag{A-27}$$

where ψ_2 is an arbitrary integration constant. In similar manner, using the same procedure used to obtain the general solution of Equation (A-18) (i.e., Equations A-22- A-27), the general solution of Equation (A-19) can be obtained as:

$$X_{30} = \left(\frac{(Z + \psi_4)(k_{23} + 1)}{\psi_3} \right)^{(k_{23} + 1)^{-1}} - k_{28} \tag{A-28}$$

where ψ_3 and ψ_4 are arbitrary integration constants determined from boundary conditions. Substitution of Equations (A-27), (A-28) and their derivatives in Equation (A-20) gives the following equation:

$$\begin{aligned} \ddot{X}_{21} + \frac{2k_1}{\psi_1} [k_{81}Z + k_{82}]^{-1} \dot{X}_{21} - \frac{2k_1k_{11}}{\psi_1^2} [k_{81}Z + k_{82}]^{-2} X_{21} = \\ k_{64} [k_{83}Z + k_{84}]^{(k_{23}+1)^{-1}} [k_{81}Z + k_{82}]^{-(k_{11}+2k_1)/(k_1+k_{11})} + k_{65} [k_{81}Z + k_{82}]^{-(k_{11}+2k_1)/(k_1+k_{11})} + \\ k_{66} [k_{81}Z + k_{82}]^{-1} [k_{83}Z + k_{84}]^{-k_{23}/(k_{23}+1)} + k_{67} [k_{81}Z + k_{82}]^{-k_1/(k_1+k_{11})} [k_{83}Z + k_{84}]^{-k_{23}/(k_{23}+1)} + \\ k_{68} [k_{81}Z + k_{82}]^{-1} [k_{83}Z + k_{84}]^{(1-k_{23})/(k_{23}+1)} + k_{69} [k_{81}Z + k_{82}]^{-k_1/(k_1+k_{11})} [k_{83}Z + k_{84}]^{(1-k_{23})/(k_{23}+1)} + \\ k_{70} [k_{81}Z + k_{82}]^{-1} [k_{83}Z + k_{84}]^{(2-k_{23})/(k_{23}+1)} + k_{71} [k_{83}Z + k_{84}]^{-2k_{23}/(k_{23}+1)} + \\ k_{72} [k_{81}Z + k_{82}]^{-k_{11}/(k_1+k_{11})} [k_{83}Z + k_{84}]^{-2k_{23}/(k_{23}+1)} + k_{73} [k_{83}Z + k_{84}]^{(1-2k_{23})/(k_{23}+1)} + \\ k_{74} [k_{81}Z + k_{82}]^{-k_{11}/(k_1+k_{11})} [k_{83}Z + k_{84}]^{(1-2k_{23})/(k_{23}+1)} + k_{75} [k_{81}Z + k_{82}]^{-2} [k_{83}Z + k_{84}]^{1/(k_{23}+1)} + \\ k_{76} [k_{81}Z + k_{82}]^{-2} + k_{77} [k_{81}Z + k_{82}]^{-2} [k_{83}Z + k_{84}]^{2/(k_{23}+1)} + k_{78} [k_{81}Z + k_{82}]^{-2} [k_{83}Z + k_{84}]^{3/(k_{23}+1)} + \\ k_{79} [k_{83}Z + k_{84}]^{-(2k_{23}+1)/(k_{23}+1)} + k_{80} [k_{81}Z + k_{82}]^{-k_{11}/(k_1+k_{11})} [k_{83}Z + k_{84}]^{-(2k_{23}+1)/(k_{23}+1)} \end{aligned} \tag{A-29}$$

where k_i are dimensionless coefficients given in the Appendix. In the homogenous part of Equation (A-29), define the following functions:

$$p(Z) = \frac{2k_1}{\psi_1(k_{81}Z + k_{82})} \tag{A-30}$$

$$q(Z) = \frac{-2k_1k_{11}}{\psi_1^2(k_{81}Z + k_{82})^2} \tag{A-31}$$

Since $p(Z)$ and $q(Z)$ are analytic and $Z=0$ is an ordinary point of Equation (A-29), the particular solution of Equation (A-29) is given by the following form:

$$X_{21}(Z) = \sum_{j=0}^{\infty} \beta_j Z^j \tag{A-32}$$

Substitution of Equation (A-32) in Equation (A-29) gives:

$$\begin{aligned} \sum_{j=0}^{\infty} \left(-\frac{2k_1k_{11}}{\psi_1^2} \right) \beta_j Z^j + \sum_{j=1}^{\infty} \left(\frac{2k_1k_{82}}{\psi_1} \right) j \beta_j Z^{j-1} + \sum_{j=1}^{\infty} \left(\frac{2k_1k_{81}}{\psi_1} \right) j \beta_j Z^j + \sum_{j=2}^{\infty} (k_{81}^2) j(j-1) \beta_j Z^j + \\ \sum_{j=2}^{\infty} (k_{82}^2) j(j-1) \beta_j Z^{j-2} + \sum_{j=2}^{\infty} (2k_{81}k_{82}) j(j-1) \beta_j Z^{j-1} = NHS \end{aligned} \tag{A-33}$$

Note that **NHS** represents the non-homogenous side of Equation (A-29) (i.e., the right-hand side). Substitution of $\eta = j$ in the first, fourth and sixth summations, $\eta = j - 2$ in the second summations, and $\eta = j - 1$ in the third and fifth summations of Equation (A-33) gives the following equation:

$$\begin{aligned} \sum_{\eta=2}^{\infty} (k_{81}^2) \eta(\eta-1) \beta_{\eta} Z^{\eta} + \sum_{\eta=0}^{\infty} (k_{82}^2) (\eta+2)(\eta+1) \beta_{\eta+2} Z^{\eta} + \sum_{\eta=1}^{\infty} (2k_{81}k_{82}) (\eta+1) (\eta) \beta_{\eta+1} Z^{\eta} + \\ \sum_{\eta=1}^{\infty} \left(\frac{2k_1k_{81}}{\psi_1} \right) \eta \beta_{\eta} Z^{\eta} + \sum_{\eta=0}^{\infty} \left(\frac{2k_1k_{82}}{\psi_1} \right) (\eta+1) \beta_{\eta+1} Z^{\eta} + \sum_{\eta=0}^{\infty} \left(\frac{-2k_1k_{11}}{\psi_1^2} \right) \beta_{\eta} Z^{\eta} = NHS \end{aligned} \tag{A-34}$$

Separating the terms corresponding to $\eta = 0$, $\eta = 1$, and combining the rest under one summation, gives:

$$\begin{aligned}
 & (2k_{82}^2)\beta_2 + \left(\frac{2k_1k_{82}}{\psi_1}\right)\beta_1 + \left(\frac{-2k_1k_{11}}{\psi_1^2}\right)\beta_0 + \\
 & \left((6k_{82}^2)\beta_3 + \left(4k_{81}k_{82} + \frac{4k_1k_{82}}{\psi_1}\right)\beta_2 + \left(\frac{2k_1k_{81}}{\psi_1} - \frac{2k_1k_{11}}{\psi_1^2}\right)\beta_1 \right)Z + \\
 & \sum_{\eta=2}^{\infty} \left((k_{82}^2)(\eta+2)(\eta+1)\beta_{\eta+2} + \left((2k_{81}k_{82})(\eta+1)(\eta) + \frac{2k_1k_{82}}{\psi_1}(\eta+1) \right)\beta_{\eta+1} + \right. \\
 & \left. \left((k_{81}^2)(\eta-1)\eta + \left(\frac{2k_1k_{81}}{\psi_1}\right)\eta + \left(\frac{-2k_1k_{11}}{\psi_1^2}\right)\beta_{\eta} \right)Z^{\eta} \right) = NHS
 \end{aligned}
 \tag{A-35}$$

Equating the coefficients of like powers of Z on both sides of Equation (A-35) gives Equations (A-36 –A-38):

$$(2k_{82}^2)\beta_2 + \left(\frac{2k_1k_{82}}{\psi_1}\right)\beta_1 + \left(\frac{-2k_1k_{11}}{\psi_1^2}\right)\beta_0 = k_{76}
 \tag{A-36}$$

$$(6k_{82}^2)\beta_3 + \left(4k_{81}k_{82} + \frac{4k_1k_{82}}{\psi_1}\right)\beta_2 + \left(\frac{2k_1k_{81}}{\psi_1} - \frac{2k_1k_{11}}{\psi_1^2}\right)\beta_1 = 0
 \tag{A-37}$$

$$\begin{aligned}
 & (k_{82}^2)(\eta+2)(\eta+1)\beta_{\eta+2} + \left((2k_{81}k_{82})(\eta+1)(\eta) + \left(\frac{2k_1k_{82}}{\psi_1}\right)(\eta+1) \right)\beta_{\eta+1} + \\
 & \left((k_{82}^2)(\mu-1)\eta + \left(\frac{2k_1k_{81}}{\psi_1}\right)\eta + \left(\frac{-2k_1k_{11}}{\psi_1^2}\right) \right)\beta_{\eta} = 0, \quad \eta \geq 2
 \end{aligned}
 \tag{A-38}$$

where β_j , $j = 1, \dots, \eta$ is an arbitrary constant. Solving Equations (A-36 –A-38) for β_2 , β_3 and β_4 in terms of β_0 and β_1 gives:

$$\beta_2 = \left(\frac{k_{76}}{2k_{82}^2}\right) + \left(\frac{k_1k_{11}}{\psi_1^2k_{82}^2}\right)\beta_0 + \left(\frac{-k_1}{\psi_1k_{82}}\right)\beta_1
 \tag{A-39}$$

$$\begin{aligned}
 \beta_3 = & \left(\frac{-2k_1k_{11}k_{81}}{3\psi_1^2k_{82}^3} - \frac{2k_1^2k_{11}}{3\psi_1^3k_{82}^3}\right)\beta_0 + \left(\frac{2k_{81}k_1}{3\psi_1k_{82}^2} + \frac{2k_1^2}{3\psi_1^2k_{82}^2} + \frac{-\psi_1k_1k_{81} + k_1k_{11}}{3\psi_1^2k_{82}^2}\right)\beta_1 + \\
 & \left(\frac{-k_{76}k_{81}}{3k_{82}^3} - \frac{k_1k_{76}}{3\psi_1k_{82}^3}\right)
 \end{aligned}
 \tag{A-40}$$

$$\beta_4 = \left(\frac{k_{81}^2 k_{76}}{3k_{82}^4} + \frac{k_1 k_{76} k_{81}}{3\psi_1 k_{82}^4} + \frac{k_1 k_{76} k_{81}}{6\psi_1 k_{82}^4} + \frac{k_1^2 k_{76}}{6\psi_1^2 k_{82}^4} - \frac{k_{76} k_{81}^2}{12k_{82}^4} - \frac{k_1 k_{76} k_{81}}{6\psi_1 k_{82}^4} + \frac{k_1 k_{11} k_{76}}{12\psi_1^2 k_{82}^4} \right) + \left(\frac{2k_1 k_{11} k_{81}^2}{3\psi_1^2 k_{82}^4} + \frac{2k_1^2 k_{11} k_{81}}{3\psi_1^3 k_{82}^4} + \frac{k_1^2 k_{11} k_{81}}{3\psi_1^3 k_{82}^4} + \frac{k_1^3 k_{11}}{3\psi_1^4 k_{82}^4} - \frac{k_1 k_{11} k_{81}^2}{6\psi_1^2 k_{82}^4} - \frac{k_1^2 k_{11} k_{81}}{3\psi_1^3 k_{82}^4} + \frac{k_1^2 k_{11}^2}{6\psi_1^4 k_{82}^4} \right) \beta_0 + \left(\frac{-2k_{81}^2 k_1}{3\psi_1 k_{82}^3} - \frac{2k_1^2 k_{81}}{3\psi_1^2 k_{82}^3} + \frac{k_1 k_{81}^2}{3\psi_1^2 k_{82}^3} - \frac{k_1 k_{11} k_{81}}{3\psi_1^2 k_{82}^3} - \frac{k_1^2 k_{81}}{3\psi_1^2 k_{82}^3} - \frac{k_1^3}{3\psi_1^3 k_{82}^3} + \frac{k_1^2 k_{81}}{6\psi_1^2 k_{82}^3} - \frac{k_1^2 k_{11}}{6\psi_1^3 k_{82}^3} + \frac{k_1 k_{81}}{6\psi_1^2 k_{82}^3} + \frac{k_1^2 k_{81}}{3\psi_1^2 k_{82}^3} - \frac{k_1^2 k_{11}}{6\psi_1^3 k_{82}^3} \right) \beta_1 \quad (A-41)$$

The general solution of Equation (A-29) can be expressed as:

$$X_{21} = \beta_0 (1 + m_1 Z^2 + m_2 Z^3 + m_3 Z^4 + \dots) + \beta_1 (Z + m_4 Z^2 + m_5 Z^3 + m_6 Z^4 + \dots) + (m_7 Z^2 + m_8 Z^3 + m_9 Z^4 + \dots) \quad (A-42)$$

where m_i are coefficients function of properties of system components (i.e., gases) given in the Appendix, β_0 and β_1 are arbitrary constants. Only the particular solution of Equation (A-29) is of interest, therefore, from Equation (A-42), X_{21} can be given as:

$$X_{21} = m_7 Z^2 + m_8 Z^3 + m_9 Z^4 \quad (A-43)$$

Substitution of Equations (A-27) and (A-43) in Equation (A-14) gives the first-order approximate solution of X_2 as:

$$X_2 = \frac{1}{k_{11}} \left(\frac{(Z + \psi_2)(k_1 + k_{11})}{\psi_1} \right)^{k_{11}/(k_1 + k_{11})} - \frac{k_{10}}{k_{11}} + \frac{\alpha_{80}}{\alpha_{95}} (m_7 Z^2 + m_8 Z^3 + m_9 Z^4) \quad (A-44)$$

The first-order approximate solution of X_3 can be found using the same procedure used to solve for X_2 . X_3 is given as:

$$X_3 = \left(\frac{(Z + \psi_4)(k_{23} + 1)}{\psi_3} \right)^{1/(k_{23} + 1)} - k_{28} + \frac{\alpha_{80}}{\alpha_{95}} (m_{16} Z^2 + m_{17} Z^3 + m_{18} Z^4) \quad (A-45)$$

For ternary gaseous system, Equation (A-46) is used to solve for X_1 :

$$\sum_{i=1}^n X_i = 1.0 \quad (A-46)$$

Note that Z in Equations (A-44) and (A-45) is a dimensionless parameter: $Z = l/L$, where l is a distance along the diffusion path at which the concentrations to be calculated (measured from the boundary), and L is the total length of diffusion path.

$$\alpha_{39} = (-A^2 E^2 H + ABE^2 H - 2A^2 EHG + 2ABEHG - A^2 HG^2 + ABHG^2).$$

$$\alpha_{54} = (-A^2 BE^2 - A^2 E^2 H - 2A^2 BEG - 2A^2 EHG - A^2 BG^2 - A^2 HG^2).$$

$$\alpha_{55} = (A^2 E^2 H - ABE^2 H - 2A^2 BEQ - 2A^2 EQG + 2A^2 BEG + 4A^2 EHG - 2ABEHG - 2A^2 BQG - 2A^2 HQG + 2A^2 BG^2 + 3A^2 HG^2 - ABHG^2).$$

$$\alpha_{58} = (A^2 E^2 H - A^2 E^2 Q + 2A^2 BE - 2ABE^2 G + 4A^2 EHG - 2AE^2 HG - 2A^2 EQG + 2A^2 BG^2 - 2ABEG^2 + 3A^2 HG^2 - 2AEHG^2 - A^2 QG^2).$$

$$\alpha_{59} = (2A^2 EQG - AE^2 HQ - A^2 EQ^2 - 4A^2 EHG + 2ABEHG + 2AE^2 HG - BE^2 HG + 2A^2 BQG + 2A^2 EQG - 3ABEQG + 4A^2 HQG - 3AEHQG - A^2 Q^2 G - 2A^2 BG^2 + 2ABEG^2 - A^2 HG^2 + 2ABHG^2 + 4AEHG^2 - BEHG^2 + 2A^2 QG^2 - ABQG^2).$$

$$\alpha_{61} = (-2A^2 EHG + 2AE^2 HG + 2A^2 EQG - 2AE^2 QG - A^2 BG^2 + 2ABEG^2 - BE^2 G^2 - 3A^2 HG^2 + 4AEHG^2 -$$

$$E^2HG^2+2A^2QG^2-2AEQG^2).$$

$$\alpha_{62}= (-2A^2HQG+3AEHQG-E^2HQG+A^2Q^2G-AEQ^2G+3A^2HG^2-ABHG^2-4AEHG^2+BEHG^2+E^2HG^2-2A^2QG^2+ABQG^2+2AEQG^2-BEQG^2).$$

$$\alpha_{63}= (A^2HG^2-2AEHG^2+E^2HG^2-A^2QG^2+2AEQG^2-E^2QG^2).$$

$$\alpha_{79}= (-A^2B^2G+AB^2EG-2A^2BHG+2ABEHG-A^2H^2G+AEH^2G).$$

$$\alpha_{80}= (ABEHQ+AEH^2Q-A^2BQ^2-A^2HQ^2+2A^2BHG-2AB^2HG-2ABEHG+B^2EHG+2A^2H^2G-2ABH^2G-2AEH^2G+BEH^2G+AB^2QG+ABHQG).$$

$$\alpha_{91}= (-A^2B^2E-2A^2BEH-A^2EH^2-A^2B^2G-2A^2BHG-A^2H^2G).$$

$$\alpha_{92}= (2A^2BEH-2AB^2EH+2A^2EH^2-2ABEH^2-A^2B^2Q-2A^2BHQ-A^2H^2Q+A^2B^2G+4A^2BHG-2AB^2HG+3A^2H^2G-2ABH^2G).$$

$$\alpha_{95}= (2A^2BEH+2A^2EH^2-2A^2BEQ-2A^2EHQ+A^2B^2G-AB^2EG+4A^2BHG-2ABEHG+3A^2H^2G-AEH^2G-2A^2BQG-2A^2HQG).$$

$$\alpha_{96}= (2A^2EH^2+2ABEH^2+2A^2BHQ+2A^2EHQ-3ABEHQ+2A^2H^2Q-AEH^2Q-A^2BQ^2-A^2HQ^2-A^2BHG+2AB^2HG+2ABEHG-B^2EHG-6A^2H^2G+4ABH^2G+2AEH^2G-BEH^2G+2A^2BQG-AB^2QG+4A^2HQG-3ABHQG).$$

$$\alpha_{98}= (-A^2EH^2+2A^2EHQ-A^2EQ^2-2A^2BHG+2ABEHG-3A^2H^2G+2AEH^2G+2A^2BQG-2ABEQG+4A^2HQG-2AEHQG-A^2Q^2G).$$

$$\alpha_{99}= (-A^2H^2Q+AEH^2Q+A^2HQ^2+AEH^2Q+3A^2H^2G-2ABH^2G-2AEH^2G+BEH^2G-4A^2HQG+3ABHQG+2AEHQG-BEHQG+A^2Q^2G-ABQ^2G).$$

$$\alpha_{100}= (A^2H^2G-AEH^2G-2A^2HQG+2AEHQG+A^2Q^2G+AEQ^2G).$$

$$k_1 = \alpha_{39} / \alpha_{95}$$

$$k_{10} = \alpha_{54} / \alpha_{95}$$

$$k_{11} = \alpha_{55} / \alpha_{95}$$

$$k_{23} = \alpha_{79} / \alpha_{95}$$

$$k_{28} = \alpha_{91} / \alpha_{95}$$

$$k_{43} = \alpha_{58} / \alpha_{80}$$

$$k_{44} = \alpha_{59} / \alpha_{80}$$

$$k_{45} = \alpha_{61} / \alpha_{80}$$

$$k_{46} = \alpha_{62} / \alpha_{80}$$

$$k_{47} = \alpha_{63} / \alpha_{80}$$

$$k_{59} = \alpha_{92} / \alpha_{80}$$

$$k_{60} = \alpha_{96} / \alpha_{80}$$

$$k_{61} = \alpha_{98} / \alpha_{80}$$

$$k_{62} = \alpha_{99} / \alpha_{80}$$

$$k_{63} = \alpha_{100} / \alpha_{80}$$

$$k_{76} = \left(-\frac{k_{43}k_{28}k_1}{\psi_1^2} + \frac{k_{10}k_{44}k_1k_{28}}{k_{11}\psi_1^2} + \frac{k_{28}^2k_{45}k_1}{\psi_1^2} - \frac{k_{10}k_{46}k_1k_{28}^2}{k_{11}\psi_3^2} - \frac{k_{47}k_{28}^3k_1}{\psi_1^2} \right)$$

$$k_{81} = \left(\frac{k_1 + k_{11}}{\psi_1} \right)$$

$$k_{82} = \frac{\psi_2}{\psi_1} (k_1 + k_{11})$$

$$k_{83} = \frac{(k_{23} + 1)}{\psi_3}$$

$$k_{84} = \frac{\psi_4}{\psi_3} (k_{23} + 1)$$

$$k_{97} = \left(\frac{k_{10}k_{59}k_{23}}{k_{11}\psi_3^2} - \frac{k_{10}k_{60}k_{28}k_{23}}{k_{11}\psi_3^2} + \frac{k_{63}k_{28}^3k_{23}}{\psi_3^2} - \frac{k_{28}^2k_{23}k_{61}}{\psi_3^2} + \frac{k_{10}k_{62}k_{28}^2k_{23}}{k_{11}\psi_3^2} \right)$$

$$m_7 = \left(\frac{k_{76}}{2k_{82}^2} \right)$$

$$m_8 = \left(\frac{-k_{76}k_{81}}{3k_{82}^3} - \frac{k_1 k_{76}}{3\psi_1 k_{82}^3} \right)$$

$$m_9 = \left(\frac{k_{81}^2 k_{76}}{3k_{82}^4} + \frac{k_1 k_{76} k_{81}}{3\psi_1 k_{82}^4} + \frac{k_1^2 k_{76}}{6\psi_1^2 k_{82}^4} - \frac{k_{76} k_{81}^2}{12k_{82}^4} + \frac{k_1 k_{11} k_{76}}{12\psi_1^2 k_{82}^4} \right)$$

$$m_{16} = \left(\frac{k_{97}}{2k_{84}^2} \right)$$

$$m_{17} = \left(\frac{-k_{83}k_{97}}{3k_{84}^3} - \frac{k_{23}k_{97}}{3\psi_3 k_{84}^3} \right)$$

$$m_{18} = \left(\frac{k_{83}^2 k_{97}}{3k_{84}^4} + \frac{k_{23}k_{97}k_{83}}{3\psi_3 k_{84}^4} + \frac{k_{23}^2 k_{97}}{6\psi_3^2 k_{84}^4} - \frac{k_{97}k_{83}^2}{12k_{84}^4} + \frac{k_{97}k_{23}}{24\psi_1^2 k_{84}^4} \right)$$

Table 1: Properties and boundary conditions of the system used to verify the perturbation Solution.

Component <i>i</i>	M_i g/mole	D_i^k cm ² /sec	D_{ij} cm ² /sec	Boundary Concentrations	
				$z = 0$	$z = L$
A = He	4.003	0.837207	$D_{AB} = 1.126$	$X_{A0} = 0.5$	$X_{AL} = 0.0$
B = Ne	20.183	0.372868	$D_{AC} = 0.729$	$X_{B0} = 0.0$	$X_{BL} = 0.5$
C = Ar	39.944	2.65033	$D_{BC} = 0.322$	$X_{C0} = 0.5$	$X_{CL} = 0.5$

Table 2: Properties and boundary conditions of the system given in Example 1.

Component <i>i</i>	M_i g/mole	D_{ij} cm ² /sec	$D_{ij}^e \dagger$ cm ² /sec	Boundary Concentrations	
				$z = 0$	$z = L$ (10m)
A = CH ₄	16.043	$D_{AB} = 0.2137$	$D_{AB} = 0.02137$	$X_{A0} = 1.0$	$X_{AL} = 0.0$
B = N ₂	28.013	$D_{AC} = 0.2263$	$D_{AC} = 0.02263$	$X_{B0} = 0.0$	$X_{BL} = 0.78$
C = O ₂	31.999	$D_{BC} = 0.2083$	$D_{BC} = 0.02083$	$X_{C0} = 0.0$	$X_{CL} = 0.22$

$\dagger D_{ij}^e$ is calculated as $D_{ij}^e = 0.1D_{ij}$.

Table 3: Properties and boundary conditions of the system given in Example 2.

Component <i>i</i>	M_i g/mole	$D_i^k \dagger$ cm ² /sec	$D_{ij} \ddagger$ cm ² /sec	$D_{ij}^e \S$ cm ² /sec	Boundary Concentrations	
					$z = 0$	$z = L$ ($L = 2.54$ cm)
A = N ₂	28.013	0.0125	$D_{AB} = 0.284$	0.0426	$X_{A0} = 0.702$	$X_{AL} = 1.0$
B = O ₂	31.999	0.0117	$D_{AC} = 0.107$	0.0161	$X_{B0} = 0.198$	$X_{BL} = 0.0$
C = C ₆ H ₆	78.114	0.0075	$D_{BC} = 0.100$	0.0150	$X_{C0} = 0.10$	$X_{CL} = 0.0$

$\dagger D_i^k$ is calculated using Eq. 3 ($\bar{r} = 4 \times 10^{-7}$ cm for clayey soil (Abriola et al., 1990), $T = 20^\circ\text{C}$).

\ddagger Data from Abu-El-Sha'r, 1993.

$\S D_{ij}^e$ is calculated using Eqn. (8) and (9), assuming $T_p = 0.45$.

Table 4: Properties and boundary conditions of the system given in Example 3.

Soil	Porosity	Q_m	Q_p (cm)	gas	M_i g/mole	D_i^k † cm ² /sec	D_{ij} cm ² /sec	D_{ij}^e ‡ cm ² /sec
Sea Sand	0.46	0.22	0.0109	A=CH ₄	16.043	424.7	D_{AB}^- 0.2137	0.0470
				B=N ₂	28.013	321.4	D_{AC}^- 0.2263	0.0497
				C=O ₂	31.999	300.74	D_{BC}^- 0.2083	0.0458
Ottawa sand	0.36	0.17	0.0303	A=CH ₄	16.043	1180.7	D_{AB}^- 0.2137	0.0363
				B=N ₂	28.013	893.5	D_{AC}^- 0.2263	0.0384
				C=O ₂	31.999	836.01	D_{BC}^- 0.2083	0.0354
Kaolinite	0.85	0.41	0.0008	A=CH ₄	16.043	31.17	D_{AB}^- 0.2137	0.0876
				B=N ₂	28.013	23.59	D_{AC}^- 0.2263	0.0927
				C=O ₂	31.999	22.07	D_{BC}^- 0.2083	0.0850

† D_i^k is calculated using Eqn. (2) ($T=20\text{ }^\circ\text{C}$).

‡ D_{ij}^e is calculated using Eqn. (8).

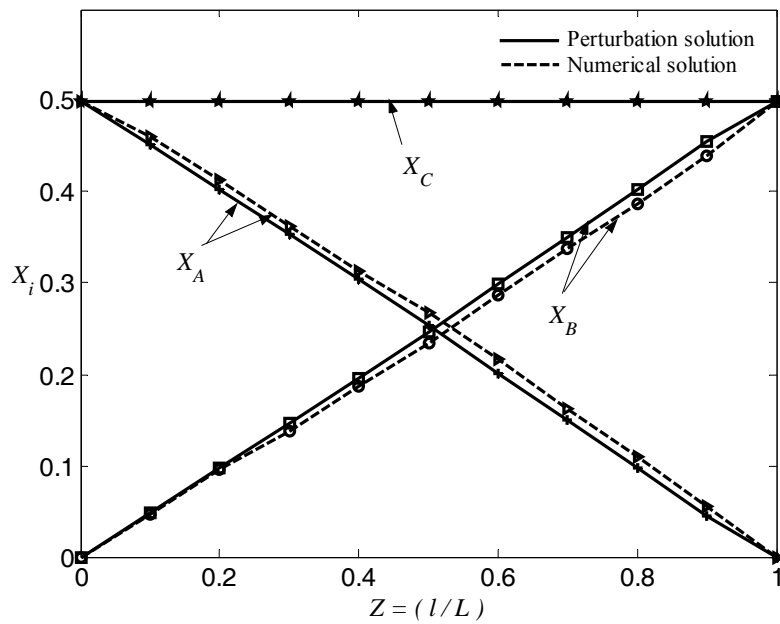


Figure 1: Comparison between perturbation and numerical solutions for a ternary gaseous system.

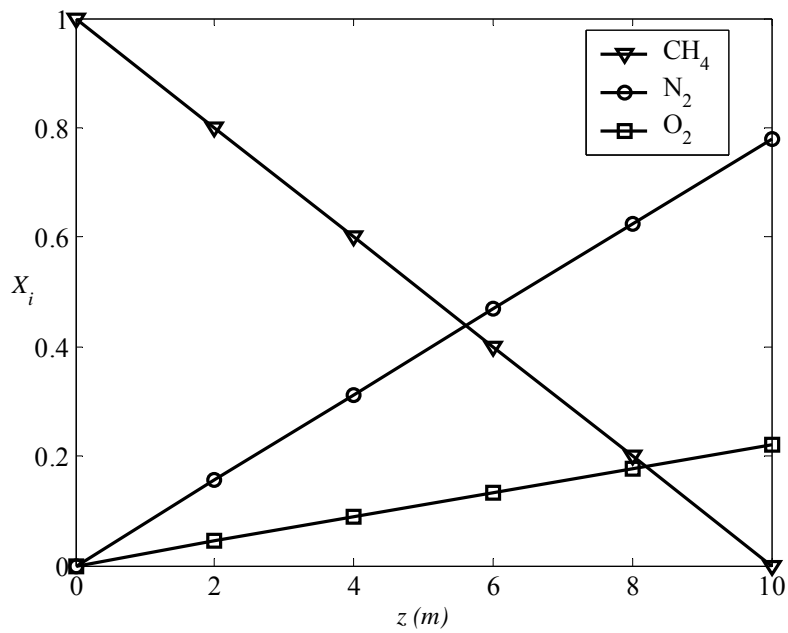


Figure 2: Mole fractions of the components of the system given in Example 1 as calculated by perturbation solution.

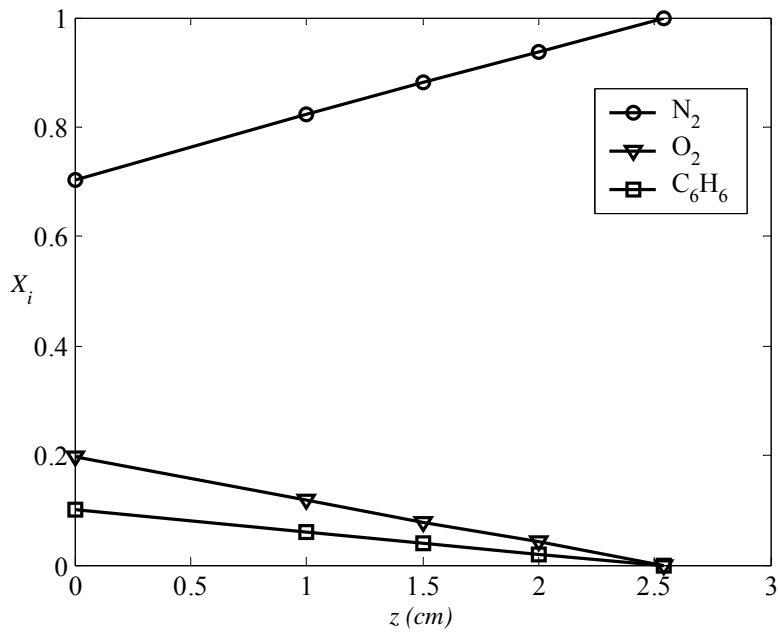


Figure 3: Mole fractions of the components of the system given in Example 2 as calculated by perturbation solution.

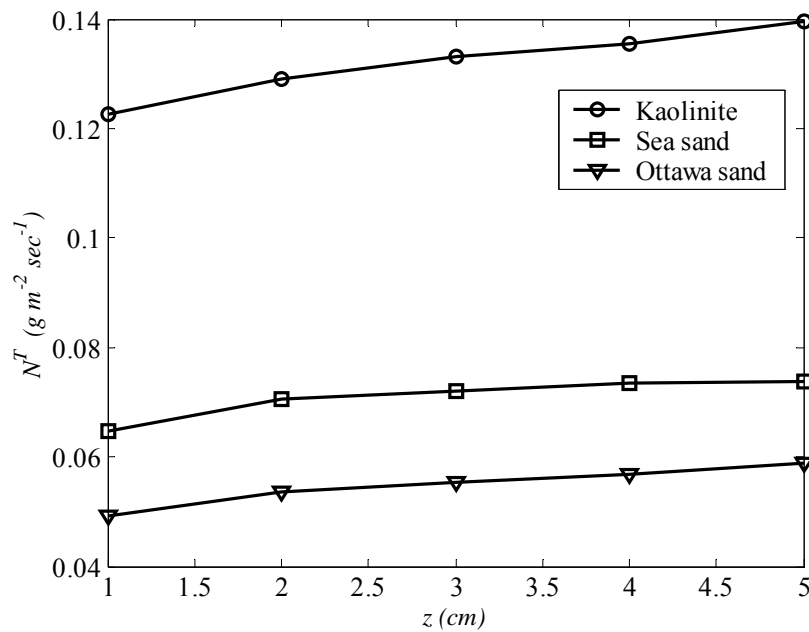


Figure 4: Total molar fluxes of CH₄ in different porous media systems given in Example 3 as calculated by perturbation solution.

Notation

- A coefficient ($L^2 t^{-1}$)
- B coefficient ($L^2 t^{-1}$)
- c total molar concentration (mole L^{-3})
- c_i molar concentration of component i (mole L^{-3})
- D_{ij} free binary diffusivity of gases i and j ($L^2 t^{-1}$)
- D_{ij}^e effective binary diffusion coefficient of gases i and j ($L^2 t^{-1}$)
- D_i^K Knudsen diffusivity (Knudsen diffusion coefficient) of gas i ($L^2 t^{-1}$)
- $D_i^K(r)$ Knudsen diffusivity of gas i in a pore of radius r ($L^2 t^{-1}$)
- $D_{is}(r)$ effective surface diffusivity of component i in a pore of radius r ($L^2 t^{-1}$)
- E coefficient ($L^2 t^{-1}$)
- G coefficient ($L^2 t^{-1}$)
- H coefficient ($L^2 t^{-1}$)
- i index
- j index
- k intrinsic permeability (L^2)
- k_i coefficient

L	length (L)
M_i	molecular weight of component i ($M \text{ mole}^{-1}$)
m_i	coefficient
n	number of gas components
n'	molar density of gas and particles ($\text{mole } L^{-3}$)
N_i^D	total molar diffusive flux of component i ($\text{mole } L^{-2} t^{-1}$)
N_i^K	Knudsen molar flux of component i ($\text{mole } L^{-2} t^{-1}$)
N_i^T	total molar flux of component i ($\text{mole } L^{-2} t^{-1}$)
N^v	molar viscous flux ($\text{mole } L^{-2} t^{-1}$)
$[N_z]$	column vector with elements N_{iz}, \dots, N_{nz}
P	pressure ($M L^{-1} t^{-2}$)
Q	coefficient ($L^2 t^{-1}$)
Q_m	obstruction factor (diffusivity)
Q_p	obstruction factor for Knudsen diffusivity (the effective Knudsen radius) (L)
R	ideal gas constant ($M L^2 t^{-2} T^{-1} \text{ mole}^{-1}$)
R_{vi}	reaction rate of component i per unit volume of porous media ($M^3 t^{-1} L^{-3}$)
r	pore radius (L)
\bar{r}	average pore radius (L)
T	temperature (T)
t	time (t)
T_p	total porosity of the porous media
X_i	mole fraction of component i
\dot{X}	dimensionless mole fraction
Z	dimensionless length, l/L
\dot{Z}	dimensionless length
z	length (L)
DGM	dusty gas model
$VOCs$	volatile organic compounds
NHS	nonhomogenous side
α_i	coefficient
α_{ij}	generalized thermal diffusivity
β_i	coefficient
η	index

ϵ	perturbation parameter
ε	void fraction
μ	dynamic viscosity ($ML^{-1}t^{-1}$)
ψ_i	integration constant
ΣV	sum of atomic diffusion volumes
∞	infinity
∇	gradient operator

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