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Reservoir Engineering Research Institute

PROJECT 3 - AREAL AND VERTICAL COMPOSITIONAL VARIATION IN HYDROCARBON RESERVOIRS

Part I- Problem Formulation, and Thermal Diffusion and Gravity Segregation

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Very large compositional variation both areally and vertically has been observed in some hydrocarbon reservoirs. Several mechanisms are believed to contribute to such variations. These include: 1) gravitational segregation, 2) molecular diffusion, 3) thermal diffusion, and 4) thermal convection. At isothermal conditions only gravitational segregation and molecular diffusion contribute to vertical compositional grading. The Gibbs segregation concept can properly account for this process. Under nonisothermal conditions, which is often the case, the process is thermodynamically irreversible and therefore Gibbs criteria of equilibrium cannot be invoked.

The current literature often combines the Gibbs segregation concept and the natural convection process to formulate the interaction of convection and gravity segregation for multicomponent systems at nonisothermal conditions. The Dary law is also used without the modification of the velocity weighing for multicomponent systems. Such a formulation may not describe the process properly. In this report, we will first formulate compositional variation in hydrocarbon reservoirs at nonisothermal condition. The results for the special case of gravity and thermal diffusion are also presented.

INTRODUCTION

In some hydrocarbon reservoirs, very large compositional variation has been observed both areally and vertically. As an example, the areal variation of composition of H2S in a reservoir in Abu Dhabi is from zero to 10 percent1 (It is believed that there is no barrier across the reservoir). In the vertical direction, the variation of composition could be even more pronounced.2

A number of papers have addressed the subject of compositional variation in hydrocarbon reservoirs. Those papers which focus on gravitational equilibrium demonstrate a fair degree of success. Our work2 is perhaps the most recent attempt to study gravitational equilibrium under isothermal conditions.

There is generally a temperature gradient in hydrocarbon reservoirs in the vertical direction. In some reservoirs, there may also be a small temperature gradient in the areal direction (say 1 °F/mile). Temperature gradients as small as 1 °F/mile may have significant effects on areal composition variation. The areal temperature gradient always induces both thermal convection and thermal diffusion. The vertical temperature gradient causes thermal diffusion but may or may not induce thermal convection. To our knowledge, Jacqmin's work3 is the main investigation for integrating gravity segregation and thermal convection in oil and gas reservoirs. He assumed that with thermal convection, the criterion of Gibbs gravity equilibrium (\( d\mu_i = -M_i g dz \), \( z \) is positive upward, \( \mu \) is the chemical potential, \( M \) is the molecular weight, and \( z \) is the vertical distance) is valid. At nonisothermal conditions, the Gibbs criterion of gravity equilibrium due to entropy production cannot be invoked. Apparently, Jacqmin
also assumed that the velocity in the Darcy equation and the diffusion equation are the same for multicomponent systems. There are a number of studies on the interaction of gravity segregation and thermal diffusion. Examples include the work of Holt, et al.4, Belery and da Silva5, and the recent work by Faissat, et al6. These authors basically begin their formulation with the thermodynamics of irreversible processes. Based on a numerical example, Holt, et al. show that thermal diffusion significantly enhances the composition gradient in the vertical direction. The results presented in Ref. 5 also reveal that thermal diffusion enhances the vertical variation of composition. The study by Faissat et al. provides a background on thermal diffusion and gravity segregation processes. In the work of the above authors, it has not been established whether thermal diffusion enhances composition variation in the vertical direction. On a more fundamental level, there is a need for a simple formulation with clear physical meaning of the contribution of various mechanisms.

The purpose of our work is the study of variation of composition in oil and gas reservoirs and the investigation of the major mechanisms that affect such a variation. The first step towards this end, is problem formulation. The second step consists of the study of the composition variation in a two-component model reservoir fluid to assess the significance of various mechanisms. The third step is the generalization of the model to multicomponent complex reservoir fluid systems. The ultimate goal of the work is to develop a general model to be used in characterizing a reservoir from the initial fluid distribution and compare the model results to field data. Such a model will also help in locating the gas oil contact (GOC).

PROBLEM FORMULATION

The continuity equation for each component may be written as,

\[ \nabla \cdot \bar{n}_i = -\phi \frac{\partial}{\partial t} (\rho \omega_i) \quad \text{for} \quad i = 1, 2 \tag{1} \]

where \( \bar{n}_i \) is the mass flux of component \( i \), \( \phi \) is the porosity, \( \rho \) is the mass density, and \( \omega_i \) is the mass fraction of component \( i \). In this report, the work will be limited to a two-component system in order to avoid complications which arise from diffusion coefficients in multicomponent systems. (In binary systems \( D_{12} = D_{21} \), where \( D \) is the diffusion coefficient, and 1 and 2 are component indices; in ternary and multicomponent systems \( D_{ij} \) and \( D_{ji} \) are not in general equal).

The mass flux \( \bar{n}_i \) is given by,

\[ \bar{n}_i = \rho \omega_i \bar{v} + \bar{j}^{(1)}_i \quad \text{for} \quad i = 1, 2 \tag{2} \]

where \( \bar{v} \) is the mass-averaged velocity, and \( \bar{j}^{(1)}_i \) is the total diffusion mass flux (non-convective) of component \( i \). In Eq. 2 the first term is the convective mass flux. The Darcy equation provides the velocity,
\[
\dot{V}_d = -\frac{k}{\phi\mu} (\nabla P + \rho g \nabla z)
\]  

(3)

where \(k\) is the permeability, \(\mu\) is the viscosity and \(P\) is the pressure. In the above equation, \(\dot{V}_d\) is the overall volumetric velocity which in the absence of diffusive fluxes, is the same as the mass-averaged velocity, \(\bar{v}\). However, when diffusive and convective fluxes are present, \(\bar{v}\) and \(\dot{V}_d\) are generally different. They are related by,

\[
\dot{V}_d = \bar{v} - (\frac{\nabla_2}{M_2} - \frac{\nabla_1}{M_1}) \dot{\bar{v}}(t)
\]  

(4)

In Eq. 4, \(M_i\) is the molecular weight and \(\nabla_i\) is the partial molar volume of component \(i\) (the derivation is provided in Appendix A).

Combining Eqs 1, and 2, and substituting for \(\omega_i = x_i n_i / \rho\),

\[
\nabla \cdot (x_i M_i \bar{v} + \dot{\bar{v}}(t)) = -\phi \frac{\partial}{\partial t} (x_i M_i n) \quad i = 1, 2
\]  

(5)

where \(x_i\) is the mole fraction and \(n\) is total molar density.

The expression for the total diffusive flux in a binary system for component 1 is given by \(^8\),

\[
\dot{\bar{v}}_{1}(t) = -\left(\frac{n^2}{\rho}\right) M_1 M_2 D_{12} \left[ \left( \frac{\partial \ln f_i}{\partial \ln x_1} \right)_{T,P} \nabla x_1 + \frac{M_i x_1}{RT} \left( \frac{\nabla_1}{M_1} \nabla P + g \nabla z \right) + k_T \nabla \ln T \right]
\]  

(6)

where \(D_{12}\) is the molecular diffusion coefficient of components 1 and 2, \(f\) is the fugacity, \(T\) is the temperature, and \(k_T\) is the thermal diffusion ratio of components 1 and 2. The evaluation of \(k_T\) is a major task in our study. It will be later discussed separately. For an isothermal process at steady state, Eq. 6 will give the condition of thermodynamic equilibrium (see Appendix B).

Three diffusion processes are included in Eq. 6; the first term represents the molecular diffusion, the second term is for pressure diffusion which under the influence of gravity leads to gravity segregation, and the last term represents thermal diffusion. Note that the second term on the right hand side of Eq. 6 appears differently from the corresponding equation in Bird, Stewart, and Lightfoot\(^8\) (see Eq. 18.4 -15, Ref. 8). Our modified equation for the total diffusion flux is applicable to both convective - diffusive flow as well as diffusive flow, while the original equation in Ref. 8 may not be valid for convective - diffusive flow. A very interesting feature of Eq. 6 is that in the absence of temperature gradient, it simplifies to the Gibbs segregation equation (see Appendix B). As it
was stated before, with thermal diffusion and even without convection, the equation \( d\mu_i = M_i g dz \) does not hold.

Combining Eqs 5 and 6, one obtains,

\[
\nabla \cdot n_1 \nabla - \nabla \left[ \left( \frac{n^2}{\rho} \right) M_2 D_{12} \left( \frac{\partial \ln f_1}{\partial \ln x_1} \right)_{T,P} \nabla x_1 + \frac{M_1 x_1}{RT} \left( \frac{\nabla V}{M_1} V + g \nabla z \right) + k_T \nabla \ln T \right] = \phi \frac{\partial}{\partial t} (x_1 n)
\]

(7)

Eq. 7 can be written for component 2, but it is simpler to write Eq. 7 for components 1 and 2 and then by adding them one obtains,

\[
\nabla \cdot n \nabla = -\phi \frac{\partial}{\partial t} (n)
\]

(8)

since \( j_1^{(1)} \) & \( j_2^{(1)} \) = 0.

We need to write the following constraint equation,

\[
x_1 + x_2 = 1
\]

(9)

and the equation of state (EOS),

\[
n = \frac{P}{ZRT}
\]

(10)

to complete the formation.

In this work, we will use the Peng-Robinson EOS\(^9\) to calculate fugacity derivatives, partial molar volume, and the density.

In a two - D space (x, z) with two components, the six unknowns are \( V_x \), \( V_y \), \( V_{dz} \), \( V_{dy} \), \( x_1 \), and \( p \). There are also six equations; Eqs. 3, 4, for x and z directions, and Eqs 7 and 8. If we assume zero convection (for vertical direction, or zero temperature gradient in the horizontal direction) the unknowns reduce to 2: \( x_1 \) and \( P \). For this case, one can write Eq. 7 for components 1 and 2 to obtain both \( x_1 \) and \( P \). A simpler alternative would be to use \( j_1^{(1)} + j_2^{(1)} = 0 \), and the Gibbs-Duhem relationship to obtain \( \nabla P = \rho g \nabla z \) which is valid for both isothermal and nonisothermal conditions. Note that Eq. 3 with \( \nabla d = 0 \) one obtains \( \nabla P = \rho g \nabla z \). Use of Eqs 7 and \( \nabla P = \rho g \nabla z \) also provides \( P \) and \( x_1 \).
Boundary and Initial Conditions - The boundary conditions in the general case are:

\[ j_{1z} = 0 \quad \text{and} \quad \nu_z = 0 \quad @ \quad z = 0, \quad 0 \leq x \leq l_x \]  
\[ j_{1z} = 0 \quad \text{and} \quad \nu_z = 0 \quad @ \quad z = l_z, \quad 0 \leq x \leq l_x \]  
\[ j_{1x} = 0 \quad \text{and} \quad \nu_x = 0 \quad @ \quad x = 0, \quad 0 \leq z \leq l_z \]  
\[ j_{1x} = 0 \quad \text{and} \quad \nu_x = 0 \quad @ \quad x = l_x, \quad 0 \leq z \leq l_z \]  

With the above boundary conditions, the normal velocity and the normal mass flux are zero. For unsteady state, the initial conditions may be specified as,

\[ x_1(t=0, x, z) = x_1^0 \]  
\[ P(t=0, x, z) = -\rho gz + P^0 \]  

THERMAL DIFFUSION AND GRAVITY SEGREGATION

We can study the combined effect of thermal diffusion and gravity segregation in one-dimensional vertical direction at steady state by writing \( j_{1z}^{(t)} = 0 \) and,

\[ \frac{dP}{dz} = -\rho g \]  

From Eq. 6, one can derive,

\[ \frac{dx_1}{dz} = \left( \frac{\partial \ln x_1}{\partial \ln f_1} \right)_{T,P} \left[ \frac{M_2\sqrt{\nu_2} - M_1\sqrt{\nu_1}}{\nu_1(x_1\sqrt{\nu_1}) + \nu_2(x_2\sqrt{\nu_2})} \rho \frac{g}{RT} - k_T \frac{d\ln T}{dz} \right] \]  

by using \( \rho = \left( \frac{2}{\sum_{i=1}^2 x_i M_i} \right) / \left( \frac{2}{\sum_{i=1}^2 x_i \sqrt{\nu_i}} \right) \). These two equations provide \( x_1 \) and \( P \) by using a numerical scheme, say Euler's scheme. There is a need to specify pressure and composition at a give depth. Vertical temperature gradient has also to be specified. The PR-EOS can be used to calculate \( (\partial \ln x_1 / \partial \ln f_1)_{T,P}, \nu_1, \nu_2, \) and \( \rho \). In the following, the results of several numerical examples will be presented. These examples will illustrate the contribution of gravity and thermal diffusion to vertical composition variation.
**C1-C3 Column**

Figs. 1a, 2, and 3 provide the variation of composition vs. depth for the C1/C3 binary system in the single phase state. The temperature gradient in this and subsequent examples is 1.8 °F/100 ft.

Fig. 1a shows the variation of composition for methane along a depth of 2000 ft. The composition, pressure, and temperature at zero depth are fixed at 30 percent methane, 1050 psia, and 163 °F, respectively. The calculated results presented in the figure reveal that gravity segregation at isothermal conditions is pronounced (when gravity alone is considered temperature is held constant.) The thermal diffusion at nonisothermal conditions causes a further increase in the variation of composition with depth. Fig. 1b shows the pressure composition plot along the hydrocarbon column and the phase envelope at 160 °F. This figure reveals that the fluid at the top at depth=0 is close to the critical point and it is in the liquid state. Around the critical point, both gravity and thermal diffusion have a pronounced effect on composition variation as expected. Fig. 2 presents the composition variation vs. depth for a fluid in a gas state away from the critical point. The composition, pressure and temperature at depth=0 are 33.5 percent methane, 587 psia, and 163 °F, respectively. This figure reveals that thermal diffusion has a very significant effect on the increase of composition with depth.

Fig. 3 depicts the variation of composition with depth for a binary liquid mixture away from the critical point. Gravity segregation has a mild effect on segregation. The combination of thermal diffusion and gravity results in a weak change of composition with depth. Note that thermal diffusion reduces the compositional variation for this case.

**C1-C4 Column**

Fig. 4 provides the variation of methane composition vs. depth for a liquid binary liquid mixture of C1/nC4. The composition, pressure, and temperature at depth=0 are 27.25 mole percent C1, 1300 psia, and 200 °F, respectively. Both gravity and thermal diffusion result in variation of composition with depth.

Fig. 5 shows the composition variation with depth for binary gas mixture of C1/nC4 system away from the critical point. As expected gravity has a small effect. However, thermal diffusion provides a significant composition variation.

**C1-C10 System**

Fig. 6a presents the result for a binary liquid mixture of C1/nC10 away from the critical point. Gravity affects the segregation, but thermal diffusion in combination with gravity provides an increase of the light component, methane, with depth. The composition, pressure, and temperature at depth=0 are chosen as 50 mole percent methane, 3000 psia, and 160 °F, respectively. Fig. 6b provides the pressure composition profile as well as the C1/nC10 phase diagram at 160 °F.
Several binary mixtures of two heavy hydrocarbons were also studied. For all of those systems, gravity causes a weak segregation. Thermal diffusion effect is also not pronounced. Fig. 7 provides the results for the nC7-nC16 binary liquid mixture. At depth=0, nC7 mole percent is 75 percent, pressure=2000 psi, and temperature=95 °F. This figure reveals that C7 mole fraction decreases slightly with depth. The combine effect of gravity and thermal diffusion provides a mild increase of C7 fractions with depth. Note that for the gravity mechanism, the mole fraction of the lighter component (i.e., C7) does increase with depth which suggests that molecular weight alone may not cause segregation; the partial molar volume is also important.

In addition to the results presented in Figs. 1-7, calculation for some other binary systems revealed that as the critical region is approached both the gravity and thermal diffusion strongly affect composition variation. For thermal diffusion, one could expect either an increase or a decrease of composition with depth.

ESTIMATION OF THERMAL DIFFUSION RATIO

In this section we will, in some detail, review the work on the estimation of thermal diffusion ratio, kT. Experimental measurements of the thermal diffusion ratio are somewhat sparse, even for binary mixtures. This is especially the case for typical reservoir condition measurements of hydrocarbon systems at elevated temperature and pressure. Furthermore, due to the relatively recent application of this theory to hydrocarbon reservoir fluids, a corresponding database of measurements has not yet been accumulated. Finally, such measurements are difficult to make, due to the small magnitude of the phenomena as well as the possible obscuring effect of thermal convection, and are thus subject to uncertainty. Even the sign of kT is uncertain, since it can be difficult to predict a priori based on molecular structure, even for binary systems, whether a component will drift with or against the thermal gradient (Jones and Foreman10, Jones and Milberger11).

It is necessary, therefore, to rely on theoretical calculations for kT. While these formulas are subject to uncertainty, especially in the absence of corroborating experimental measurements, they represent the only estimates of kT for some systems under reservoir conditions. The models described in the literature appear to fall into two major groups. The first is based on Dougherty and Drickamer's12 early work and attempts to find a value for the thermal diffusion factor, a = kT/(x1x2) in terms of the specific heats of transport of the two components in a binary mixture. These, in turn, are estimated from the "activation energy of molecular motion" which can be obtained from the
viscosity behavior of the mixture. Similar approaches have been followed later by other investigators (Tichacheck, Kmack and Drickamer\textsuperscript{13}, Whittaker and Pigford\textsuperscript{14}). The second main line of investigation considers the maximization of the partition function of an idealized two-bulb thermal diffusion apparatus (Haase\textsuperscript{15}, Kempers\textsuperscript{16}). This yields an expression for $a$ in terms of either the enthalpy difference from the standard state of the components along with a value of $a$ at low densities (which may be obtained from kinetic theory) in the case of Haase's work, or the absolute enthalpies only (Kempers). Holt\textsuperscript{4} et al., and Belery and da Silva\textsuperscript{5} have employed the first method. It is difficult to obtain experimental values for derivatives of viscosity with respect to temperature and pressure, but they may be calculated in a straightforward manner from a viscosity model, although existing viscosity models may not be reliable.

The Dougherty and Drickamer formula\textsuperscript{12}, as mentioned previously, expresses $a$ in terms of the specific heats of transport $DU_1^*$ and $DU_2^*$, for components 1 and 2 respectively, as follows,

$$a = \frac{M_1 \bar{V}_2 + M_2 \bar{V}_1}{2(M_1 x_1 + M_2 x_2) x_1} \left(\frac{DU_1^*}{\bar{V}_1} - \frac{DU_2^*}{\bar{V}_2}\right) \left(\frac{\partial x_1}{\partial \mu_1}\right)_{T,P} \tag{19}$$

Here, the convention is used that $a$ is positive when component 1 segregates with the temperature gradient.

The heats of transport are related to the activation energy for molecular movement as follows,

$$DU_i^* = \left(\frac{\partial (n DU_m^*)}{\partial n_i}\right)_{P,T,n_i} \tag{20}$$

where

$$DU_m^* = R \left[\left(\frac{\partial \ln(\mu/\rho)}{\partial (1/T)}\right)_{P, x_i} - PT \left(\frac{\partial \ln(\mu/\rho)}{\partial P}\right)_{T, x_i}\right] \tag{21}$$

This allows the use of the presumably more accurate mixture rather than pure component values for the evaluation of $DU_i^*$. In a similar way, analytical expressions for these terms can be derived from the appropriate equation of state and viscosity models once they have been selected.

The expression for the thermal diffusion factor from Kempers for a binary mixture is:
\[ \alpha = \frac{\overline{V}_1 \overline{H}_2 - \overline{V}_2 \overline{H}_1}{(\overline{V}_1 x_1 + \overline{V}_2 x_2) x_1 (\frac{d \mu_1}{dx_1})_{T,P}} \] 

(22)

where \( \overline{H}_1 \) and \( \overline{H}_2 \) are the partial molar enthalpy of components 1 and 2. We have used the above equation to compute the thermal diffusion factor of binary hydrocarbon mixtures. The experimental values of \( \alpha \), quoted by Kempers for the C_1-C_3 system are especially relevant to this study. Here the subscript 1 refers to methane, and the sign convention is as described above.

Fig. 8 shows the calculated results and data for C_1/C_3 at 163 °F and 810 psia. In our calculations, the PR-EOS was used and the interaction coefficients between C_1 and C_3 was set at 0.01. Kempers used the Soave-EOS but did not provide the parameters of this equation of state. Fig. 8 reveals that the version of the Soave-EOS used by Kempers provides better results than the PR-EOS. The data presented in Fig. 8 pertain to the gas state.

Fig. 9 depicts the results of calculations and data for the above system for a mixture containing 0.34 mole fraction methane at 163 °F and various pressures. The calculated values by Kempers in the pressure range of 600 to 800 psia are in better agreement with data than our calculated values. However, the calculated values by Kempers for pressure>1000 psia are very different from data. Our calculated value at 1123 psia is in agreement with the data while Kempers' is off by an order of magnitude. It is possible that Kempers has adjusted some parameters of the EOS; as a result the high pressure values are predicted unreliably. Fig. 10 shows the phase envelope for the C_1/C_3 system at 163 °F. The data points are also shown on the figure. It is clear that some of the data points are in the two-phase region. Kempers has used the Soave-EOS to calculate the thermal diffusion factor in the two-phase region. He may not have recognized this fact.

Fig. 11 shows the thermal diffusion factor of nC_7-nC_16 system at 95 °F and atmospheric pressure, where the fluid is a liquid. The data are from Ref. 17. This figure reveals that unlike the C_1/C_3 system, the variation of \( \alpha \) with the nC_7-nC_16 composition is small. This figure also reveals that there is a fair agreement between data and predicted results from the PR-EOS.

Fig. 12 provides a comparison of the data\(^{18}\) and calculated results of thermal diffusion factor for various hydrocarbon binary systems. In general, the agreement is fair except for C_7/C_14 and C_7/C_15 systems.

For the above calculations, we used the PR-EOS without the volume translation; with volume translation, the results did not improve.
CONCLUDING REMARKS

In this study we have formulated the problem of compositional variation in hydrocarbon reservoirs. The results for gravity and thermal diffusion show that thermal diffusion could enhance segregation. It could also reduce the effect of gravity. An important parameter of thermal diffusion is the thermal diffusion ratio. Very limited data on this parameter are available. The theory for the calculation of this parameter has to be improved.

Currently we are studying the interaction of convection with gravity and thermal diffusion. When this phase of the work is completed, multi-component systems will be investigated. At a later stage, we may resort to molecular dynamic simulations or devise a new or more physically sound theory for the calculation of thermal diffusion ratio.

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NOMENCLATURE

D - Molecular diffusion coefficient
fi - Fugacity of component i
H_i - Partial molecular molar enthalpy of component i
j_i - Total diffusion mass flux of component i
k - Permeability
k_T - Thermal diffusion ratio
M_i - Molecular weight of component i
n_i - Mass flux of component i
n - Molar density (total)
n_i - Molar density of component i
R - Gas constant
P - Pressure
T - Temperature

\bar{V} - Mass-averaged velocity
\bar{V}_i - Velocity of component i
\bar{V}_d - Volumetric-averaged velocity
\bar{V}_i - Partial molar volume of component i

\pi_i - Mole fraction of component i
x - Spacial x-coordinate
z - Spacial z-coordinate
Z - Supercompressibility factor

GREEK LETTERS

\alpha - Thermal diffusion factor
\Delta U_i - Specific heat of transport of component i
\nabla - Vector operator "nabla" or "del"
\mu - Viscosity
\mu_i - Chemical potential of component i
\rho - Mass density (total)
\rho_i - Mass density of component i
\phi - Porosity
\omega_i - Mass fraction of component i

SUPERSCRIPT

\circ - Reference point
REFERENCES


Appendix A - Mass and Volume Averaged Velocities

The mass-averaged velocity is defined as,

\[ \bar{v} = \sum \frac{\rho_i v_i}{\rho} \]  \hspace{1cm} (A-1)

where \( \rho_i \) is the mass density of component \( i \), and \( v_i \) is the velocity of component \( i \). The volume-averaged velocity is defined as,

\[ \bar{v}_d = \sum \rho_i \bar{v}_i \left( \frac{V_i}{M_i} \right) \]  \hspace{1cm} (A-2)

The volume-averaged velocity is the same as the Darcy velocity and therefore it is denoted by \( \bar{v}_d \).

But \( \bar{v}_i(t) = \rho_i(\bar{v}_i - v) \) from which,

\[ \bar{v}_i = v + \bar{v}_i(t) / \rho_i \]  \hspace{1cm} (A-3)

where \( \bar{v}_i \) is defined by Eq. 2

Combining Eqs (A-2) and (A-3) gives,
\[
\dot{\nu}_d = \dot{\nu} \left( \sum \frac{\rho_i \dot{\nu}_i}{M_i} \right) - \sum \dot{\tau}^{(t)} \left( \frac{\dot{\nu}_i}{M_i} \right)
\]

where \( \sum \frac{\rho_i \dot{\nu}_i}{M_i} = 1. \)

**Appendix B - Derivation of Thermodynamic Equilibrium Expression from Total Diffusion Flux Expression**

Let's write the expression for the total diffusion mass flux of component 1 (i.e., Eq. 6) in the z-direction for isothermal conditions,

\[
\dot{\tau}_1^{(t)} = -\left( \frac{n^2}{\rho} \right) M_1 M_2 D_1 \left[ \left( \frac{\partial \ln f_1}{\partial \ln x_1} \right) \left( \frac{\partial x_1}{\partial z} \right) + \frac{M_1 x_1}{RT} \left( \frac{\nu_1}{M_1} \frac{\partial P}{\partial z} + g \right) \right]
\]

At stationary state, \( \dot{\tau}_1^{(t)} = 0 \), and therefore

\[
\left( \frac{\partial \ln f_1}{\partial \ln x_1} \right)_{T,P} \frac{dx_1}{dz} + \frac{M_1 x_1}{RT} \left( \frac{\nu_1}{M_1} \frac{dP}{dz} + g \right) = 0
\]

But \( \frac{dP}{dz} = -\rho g \), and also \( \left( \frac{\partial \ln f_1}{\partial \ln x_1} \right)_{T,P} = x_1 \left( \frac{\partial \ln f_1}{\partial x_1} \right)_{T,P} \). Combining Eq. B-2 and the above relationships one obtains,

\[
\left( \frac{\partial \ln f_1}{\partial x_1} \right)_{T,P} \frac{dx_1}{dx} + \frac{g}{RT} (M_1 - \rho \dot{\nu}_1) = 0
\]

or

\[
\left( \frac{\partial \ln f_1}{\partial x_1} \right)_{T,P} \frac{dx_1}{dz} = \frac{g}{RT} (\rho \dot{\nu}_1 - M_1)
\]

Eq. B-4 can be also expressed in terms of chemical potential,

\[
(d\mu_1 = RT d\ln f_1)_T
\]
Eq. (B-6) can also be written for component 2. These two equations will provide pressure and composition at any depth once pressure and composition at a reference depth are specified. Eq. (B-6) can also be obtained from \( d\mu_i = -M_i gdz \) by expanding \( d\mu_i(P, x_1) \) and using \( dp = -\rho gdz \).
'Fig.1a- Depth-Composition relationship for a C1/C3 system (P=1050 psia, T=163 F).'}
Fig. 1b- Phase envelope and pressure-composition relationship for a C1/C3 system (T=163 F).
Fig. 2 - Depth-Composition relationship for a C1/C3 system (P=587 psia, T=163 F).
Fig. 3- Depth-Composition relationship for a C1/C3 system (P=1500 psia, T=163 F).
Fig. 4- Depth-Composition relationship for a C1/nC4 system (P=1300 psia, T=220 F).
Fig. 5 - Depth-Composition relationship for a C1/nC4 system
(P = 514 psia, T = 160 F).
Fig. 6a- Depth-Composition relationship for a C1/nC10 system (P=3000 psia, T=160 F).
Fig. 6b- Phase envelope and pressure-composition relationship for a C1/nC10 system (T=160 F).
Fig. 7 - Depth-Composition relationship for a nC7/nC16 system (P=2000 psia, T=95 F).
Fig. 8: Thermal diffusion coefficient for the C1/C3 binary at 163 F and 810 psia.
Fig. 9- Thermal diffusion coefficient for the C1/C3 binary at 163 F and 0.34 mole fraction C1.
Fig. 10- Phase diagram of the C1/C3 system at 163 F and the data points used by Kempers.
Fig. 11 - Thermal diffusion coefficient for the nC7/nC16 binary at atmospheric pressure and 95 F.
Fig. 12- Comparison of data and calculated results of the thermal diffusion coefficient for various hydrocarbon systems.