Two-Phase Segregation in a Thick Reservoir

SHAPIRO, Alexander A., Engineering Research Center IVC-SEP,
Technical University of Denmark

STENBY, Erling H., Engineering Research Center IVC-SEP,
Technical University of Denmark

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Abstract

We present in this paper the mathematical theory of segregation in a thick oil-gas-condensate reservoir. The theory takes into account the non-equilibrium effect of the geothermal gradient and the action of the capillary forces, due to which a two-phase transition zone between the gas cap and the oil layer is formed. Analytical solutions of the segregation equations are obtained.

INTRODUCTION

The problem of segregation is studied in order to predict the distribution of reserves and properties of hydrocarbon mixtures in a thick oil-gas-condensate reservoir. In this kind of reservoir substantial variation in the composition of the reservoir mixture with depth is observed [1-3]. This effect was realized as early as in 1938 [4] and extensively studied during the last decade (see the review in [5]). Significant compositional gradients were reported for such reservoirs as Karachaganak [1], East Painter [2], the Birba field [3], the Brent field [6-8] and others.

Segregation arises in a reservoir due to the action of the gravitational force. The two major effects of the segregation are splitting of the reservoir into oil and gas zones and formation of compositional gradients in both zones.

The picture of the distribution of hydrocarbons along a reservoir is complicated by the action of the capillary forces and of the thermal gradient of the Earth. The capillary forces lead to spreading of the gas-oil contact (GOC) and formation of a transition zone in which the saturation of oil varies from zero to unity. This zone may be quite thick and contain a significant amount of hydrocarbons [1,9,10].

Presence of the thermal gradient leads to redistribution of the components in the reservoir in accordance with the Dufour-Soret effects [11-13]. It has been

noted that non-isothermal effects may be of the same order of magnitude as gravitational effects [14]. They are necessary in order to explain deviations from the segregated state predicted by thermodynamic equilibrium models [1,5]. Additionally, the thermal field may sometimes cause instability of an equilibrium state and formation of convective fluxes [15-17].

In the present paper, we discuss the mutual effect of the capillary forces and of the thermal gradient on the state of a hydrocarbon mixture in a thick reservoir. Study has significance for the description of the two-phase transition zone between the gas cap and the oil foot. Some effects characteristic of the transition zone are of general interest and contradict the usual opinion that the reservoir fluid does not move unless the reservoir development starts.

More precisely, the usual opinion is that, if the geothermal gradient is negligible, the reservoir mixture is in the thermodynamic equilibrium state. Action of the geothermal gradient breaks the thermodynamic equilibrium, but retains the mechanical one, as long as the state of the mixture is stable with regard to convective perturbations. Convective instability is mainly characteristic of inhomogeneous high-permeable reservoirs containing light hydrocarbons. Thus, in most cases no motion of the hydrocarbon fluids before the development of the reservoir is assumed.

However, the present study shows that, due to the geothermal gradient, the mechanical equilibrium in the two-phase transition zone becomes impossible. The two-phase mixture is in a non-equilibrium stationary state with zero convective flow, but non-zero diffusion fluxes and mass exchange between phases. The intensity of these diffusion fluxes is significant as compared with geological time scales. Diffusion leads to redistribution of the components in the transition zone.

The study of compositional grading in the transition zone is based on the non-equilibrium thermodynamic model developed in [18]. The formulas for dif-

fusion fluxes in a binary mixture obtained in [18] are here generalized to a multicomponent case. The interpretation is clarified to show the impact of different mechanisms on a compositional grading in a transition zone.

EQUILIBRIUM AND NON-EQUILIBRIUM SEGREGATION

Equations of equilibrium segregation

Early studies of the phenomenon of compositional grading [4,19] are based on the model of isothermal segregation in the external (gravitational) field. Within the framework of this model, segregation of a one-phase A -component mixture is described by the following system:

$$\frac{d\mu_\alpha^i}{dz} = M_\alpha g \quad (i = l, v; \alpha = 1, A) \quad (1)$$

where M_α are the molecular weights of the components and $\mu_\alpha^i = \mu_\alpha^i(P^i, T, x_\beta^i)$ are their chemical potentials in the i th phase (liquid or vapor). The potentials depend on the phase pressures P^i and on the molar fractions of the components x_β^i ($\beta = 1, A-1$). Thus, at a constant temperature the system of equations (1) is closed and, in principle, allows us to determine distributions of all the components and of the pressure starting from the data at a single depth.

An important consequence of Eq. (1) and the Gibbs–Duhem equation is the hydrostatic distribution of the pressure:

$$\frac{dP^i}{dz} = \rho^i g \quad (2)$$

Another form of the equations of isothermal segregation may be obtained by introduction of *reduced chemical potentials* [1]:

$$\eta_\alpha^i = \frac{\mu_\alpha^i}{M_\alpha} - \frac{\mu_A^i}{M_A} \quad (\alpha = 1, A-1) \quad (3)$$

In these designations, Eq. (1) is transformed to

$$\frac{d\eta_\alpha^i}{dz} = 0 \quad (4)$$

and, since the number of equations in system (4) is only $A-1$, Eq. (2) becomes independent and may be used to complete the last system.

Two important generalizations of the above treatment were recently developed. First, it was shown that, in the absence of the specific phenomenon called *the dynamic thermodiffusion*, system (1) may be used to describe the non-isothermal segregation for the known distribution of temperature with depth $T(z)$ (for example, for a constant value of the geothermal gradient $\epsilon = dT/dz$) [12].

The second generalization was taking into account capillary forces which lead to the formation of a two-phase transition zone [10]. At constant temperature,

an equilibrium distribution in this zone obeys Eq. (1) for both phases, and, additionally, the condition of equality of the chemical potentials of vapor and liquid:

$$\mu_\alpha^v = \mu_\alpha^l \quad (\alpha = 1, A); \quad (5)$$

The liquid saturation s is found from the capillary pressure equation

$$P^v - P^l = \xi J(s) \quad (6)$$

where J is the capillary pressure (the Leverett) function, the factor ξ is expressed through the surface tension σ , the wetting angle θ and the characteristic radius of a pore $\sqrt{k/\phi}$ (k being the permeability and ϕ the porosity):

$$\xi = \frac{\sigma \cos \theta}{\sqrt{k/\phi}} \quad (7)$$

Equations of non-equilibrium segregation

Let us now consider the case where the temperature differs from constant, and there is neither mechanical, nor thermodynamic equilibrium in the transition zone. Later on we will show that breaking the equilibrium is unavoidable if the dynamic thermal diffusion cannot be neglected.

If the reservoir is closed and no inflow of gas and oil through its top and bottom boundaries is observed, the convective fluxes of both phases are equal to zero. However, diffusion fluxes in the transition zone may differ from zero and be somehow equilibrated by the component exchange between the phases. On the basis of the formalism of non-equilibrium thermodynamics, the following expressions for the diffusion fluxes can be obtained [1,18]:

$$I_\alpha^i = - \sum_{\beta=1}^{A-1} L_{\alpha\beta}^i \frac{d\eta_\beta^i}{dz} - N_\alpha^i \frac{dT}{dz} \quad (\alpha = 1, A-1) \quad (8)$$

The temperatures in the two phases are supposed to be equal to the same value $T = T(z)$, and the total non-convective heat flux is expressed as

$$Q = -s\phi \sum_{\beta=1}^{A-1} q_\beta^l \frac{d\eta_\beta^l}{dz} - (1-s)\phi \sum_{\beta=1}^{A-1} q_\beta^v \frac{d\eta_\beta^v}{dz} - r(s) \frac{dT}{dz} \quad (9)$$

In the last two equations, the values $L_{\alpha\beta}^i$, N_α^i , q_β^i , $r(s)$ are the kinetic coefficients, which, generally speaking, may depend on the thermodynamic properties of the phases. The total heat conductivity $r(s)$ is expressed through the heat conductivities of liquid, vapor and solid (the last is the reservoir rock):

$$r(s) = \phi[r^l s + r^v(1-s)] + (1-\phi)r^s \quad (10)$$

According to the definition given in [13], the terms $N_{\alpha}^i(dT/dz)$ in Eq. (8) correspond to the so-called dynamic thermodiffusion, as opposed to the static thermodiffusion, which arises as follows. Let us represent the derivatives $d\eta_{\beta}^i/dz$ as

$$\frac{d\eta_{\beta}^i}{dz} = \sum_{\gamma} \frac{d\eta_{\beta}^i}{dx_{\gamma}^i} \frac{dx_{\gamma}^i}{dz} + \frac{d\eta_{\beta}^i}{dP^i} \frac{dP^i}{dz} + \frac{d\eta_{\beta}^i}{dT} \frac{dT}{dz} \quad (11)$$

and substitute the last equation into Eq. (8). The contribution of the first term of Eq. (11) gives the usual diffusion and cross-diffusion terms, the second term in Eq. (11) expresses the barodiffusion, while the last term contributes to the thermal diffusion. This contribution, from the derivatives of the chemical potentials, has assumed the name of the static thermal diffusion [13].

As it was mentioned above, the diffusion fluxes inside the two phases are equilibrated by the mass exchange between them. On the basis of non-equilibrium thermodynamics, it can be established that the exchange u_{α} of the α th component is proportional to the differences of the reduced chemical potentials (thus, the equality (5) of the chemical potentials in the two phases is violated):

$$u_{\alpha} = \sum_{\beta=1}^{A-1} U_{\alpha\beta} (\eta_{\beta}^l - \eta_{\beta}^v) \quad (\alpha = 1, A-1) \quad (12)$$

These equations determine the mass exchanges of the first $A-1$ component. The exchange of the remaining component is expressed through the values of u_{α} due to the mass conservation law. It can be shown [18] that such an expression is equivalent to the difference of the A th chemical potential being proportional to differences of the reduced chemical potentials in both phases:

$$\mu_A^v - \mu_A^l = \sum_{\beta=1}^{A-1} e_{\alpha} (\eta_{\beta}^v - \eta_{\beta}^l) \quad (13)$$

where e_{α} are linear combinations of the kinetic coefficients of the exchange between phases.

Let us formulate a complete system of equations describing the non-equilibrium segregation. Instead of the equilibrium segregation conditions (4), we have a system of mass conservation laws for both phases:

$$\frac{d}{dz} [\phi s I_{\alpha}^l] = -u_{\alpha} \quad (14)$$

$$\frac{d}{dz} [\phi(1-s) I_{\alpha}^v] = u_{\alpha} \quad (15)$$

It can be shown that the energy equation is reduced to the condition of the constancy of the heat flux of the Earth:

$$Q = -Q_0 = \text{const} \quad (16)$$

The system of equations (14) to (16) is completed by the hydrostatic conditions (2) and the capillarity equation (6). The total number of equations in this system is $2A+2$. Correspondingly, we have $2A+2$ independent variables, which are to be chosen η_{α}^i , P^i , T , s and will be referred to as the *basic set of segregation variables*.

STATIC SOLUTION

In this section, we formulate general conditions providing an equilibrium (static) solution of the segregation problem, and discuss systems of equations from which grading in different zones of a reservoir may be evaluated.

Let us first consider a one-phase zone i . The segregated state in this zone is described by $A+1$ independent variables η_{α}^i ($\alpha = 1, A-1$), P^i , T . Since the top and the bottom of the reservoir are impermeable, the diffusion fluxes through them are equal to zero. It follows from the mass balance equations (14) and (15) (from which the terms of exchange are excluded) that the diffusion fluxes are equal to zero throughout all the one-phase zone:

$$I_{\alpha}^i = 0 \quad (17)$$

Thus, the mixture in a one-phase zone is in a mechanical equilibrium state. The system of equilibrium equations (17) is completed by Eqs. (2) and (16). From this system the geothermal gradient ϵ and gradients of the reduced chemical potentials can be determined [1]:

$$\frac{dT}{dz} = E(s) Q_0 = \epsilon \quad (18)$$

$$\frac{d\eta_{\alpha}^i}{dz} = \lambda_{\alpha}^i \epsilon \quad (19)$$

where the saturation s is equal to zero in the gas zone and to unity in the liquid zone. The coefficient $E(s)$ and the vector λ^i consisting of the values λ_{α}^i are expressed as follows:

$$\lambda^i = -(\mathbf{L}^i)^{-1} \mathbf{N}^i, \quad (20)$$

$$E(s) = \frac{1}{r(s) - (\mathbf{q}^i)^T \lambda^i}$$

The matrix $\mathbf{L}^i$ consists of the components $L_{\alpha\beta}^i$, the vectors $\mathbf{N}^i$, $\mathbf{q}^i$ of the components N_{α}^i , q_{α}^i , correspondingly¹.

Comparison of Eqs. (18) and (19) with system (4) shows contribution of the geothermal gradient to the compositional grading. It can be seen that this contribution is proportional not only to the geothermal gradient itself, but also to the coefficients of the dynamic thermodiffusion N_{α}^i . In the absence of dynamic thermodiffusion, the segregation is described by the quasi-equilibrium equations (4) in which, however, the

¹In the following, we use bold letters to denote vectors and matrices and the same italic letters for their components. An exception is made for the values denoted by greek letters.

temperature is changed in accordance with Eq. (18) [1,12].

Dynamic thermodiffusion is crucial for the possibility of equilibrium in the two-phase transition zone. Let us assume that we wanted to obtain an equilibrium solution for this zone. Such a solution would still obey $2(A-1)$ equations (19) (which follows from Eq. (17) of the absence of diffusion fluxes in vapor and liquid phases) and Eq. (18) for the geothermal gradient. The saturation s in the last equation is determined from Eqs. (2) and (6). Thus, we have already $2A+2$ equations for the basic set of $2A+2$ variables described at the end of the last section. However, it follows from Eq. (17) and the mass conservation laws (14), (15) that the component exchanges u_α must also be equal to zero in an equilibrium state, or

$$\eta_\alpha^v = \eta_\alpha^l \quad (21)$$

We obtain $A-1$ additional conditions of the equilibrium. These conditions are incompatible with Eq. (19) if the coefficients λ_α^i are different for different phases. Actually, it is beyond reason to hope that the dynamic thermodiffusion coefficients are the same in gas and liquid.

However, if the dynamic thermodiffusion can be neglected, $\lambda_\alpha^i = 0$, system (19) is simplified and reduced to the system of equations for the quasi-equilibrium segregation (4). The last system is compatible with condition (21). Thus, *in the absence of the dynamic thermodiffusion the transition zone is in the equilibrium state*. This state is described by the pressure and capillary pressure equations (2) and (6), the segregation equations (4) together with the condition (21) and the temperature distribution (18), which is simplified and transformed to

$$\frac{dT}{dz} = \epsilon(s) = Q_0/r(s) \quad (22)$$

An important property of the static solution is that this solution makes it possible to predict the distribution of the thermodynamic parameters and the location of GOC starting from data at a single depth, if equations of state for gas and liquid, heat conductivities and capillary properties of the porous medium are known. Assume, for example, that we know the mixture composition, the pressure and the temperature at some point in the gas part of the reservoir. By solving segregation equations (2) and (4) we find the distribution of the thermodynamic parameters inside the gas zone [1]. The top of the transition zone is found as the point at which conditions (5) are compatible with the capillary pressure condition:

$$P^v - P^l = \xi J(0) \quad (23)$$

This condition also determines the pressure in the liquid phase, while Eq. (21) gives the initial values for the reduced chemical potentials. If we know all the

initial values at the top of the transition zone, it is possible, by solving the static system of segregation to find distribution of all the parameters inside the transition zone and then to spread it to the one-phase oil zone of the reservoir.

Note that, in the absence of dynamic thermodiffusion, the reduced chemical potentials remain invariable throughout all the phases and all the zones of the reservoir.

DYNAMIC SOLUTION

In this section we show that the conclusion about possibility of predicting the compositional grading and the location of the gas-oil contact remains valid for the case where the dynamic thermal diffusion cannot be neglected. For this purpose we construct a non-equilibrium dynamic solution and determine diffusion fluxes of the components in the transition zone.

Boundary conditions

The system of $2A+2$ differential equations determining the dynamic solution consists of the mass balance equations (14), (15), the hydrostatic equations (2), the capillarity equation (6) and the heat equation (16). This is the second-order system with regard to reduced chemical potentials, the first-order system with regard to phase pressures and to temperature, and the zero-order system with regard to saturation². Correspondingly, for a correct statement of a boundary value problem, we need two boundary conditions for each reduced chemical potential and one condition for each pressure and temperature. Two additional conditions are to be determined to specify locations of the boundaries of the transition zone.

Let us make a list of boundary conditions which we actually have for the transition zone, after determining the distribution in the gas cap starting from the data at a single point in the cap.

Assume that the top h and the bottom H of the transition zone are known. At the top of the transition zone:

- The pressure P^v is known from the distribution in the gas cap. The value P^l is found from Eq. (23).
- The temperature is found from its distribution in the gas cap.
- The chemical potentials in the gas phase η_α^v are defined from the distribution in the gas cap.
- Diffusion fluxes in the gas phase I_α^v are equal to zero. Then Eqs. (19) determine the initial values $d\eta_\alpha^v/dz$.

At the bottom H of the transition zone

²This statement is not perfectly rigorous from the mathematical point of view, however, it clarifies the character of the system.

- The diffusion fluxes in the liquid phase $I_\alpha^l = 0$. Again, the values $d\eta_\alpha^l/dz$ may be determined from Eqs. (19) (with the geothermal gradient ϵ corresponding to unity saturation).

Additionally, we have two conditions which might be used in order to find the boundaries h , H of the transition zone:

- The saturation equals zero at the top and unity at the bottom of the transition zone.

We should not set $I_\alpha^l = 0$ at the top and $I_\alpha^v = 0$ at the bottom of the transition zone, because the saturations of the corresponding phases and, therefore, the total fluxes are equal to zero at these boundaries regardless of values of diffusion fluxes. There is no way to determine the values of η_α^l , neither at the top nor at the bottom of the transition zone, since conditions (21) are violated for the dynamic solution.

Thus, we lack boundary conditions for the reduced chemical potentials of the liquid phase. This lack is compensated for by the fact that the points $s = 0$ and $s = 1$ are the specific points of the system considered, and there is only one specific trajectory of the system connecting these specific points and obeying the formulated boundary conditions. The corresponding theorem for the binary mixture was proven in [18]. We accept without proof that this theorem is valid for a multicomponent case.

Another difficulty of the formulated boundary value problem is the necessity of combining the internal problem of determining the distributions of thermodynamic parameters inside the transition zone with the external problem of locating the boundaries of that zone. In the next section, we will formulate assumptions allowing to avoid this problem and to find an approximate solution of the system.

Such an approximate solution is necessary, because the formulated boundary problem is extremely difficult to solve numerically. The reason is not only that the coupling of the external and internal problems requires advanced iteration methods for locating the transition zone [5]. An additional difficulty is that all but one of the solutions of the diffusion problem "turn to infinity" in the very neighborhood of the specific points $s = 0$, $s = 1$, and it is probably impossible to use methods based on finite differences in order to separate the only bounded solution.

Simplifying assumptions

To proceed with constructing the approximate solution, we assume that in the transition zone we can neglect variations of the phase densities ρ^i , of the kinetic coefficients $L_{\alpha\beta}^i$, N_α^i , q_α^i , r^i and of the surface tension $\sigma \cos \theta$. Additionally, the capillary pressure function $J(s)$ is assumed to be the same at each depth. However, the porous medium may be heterogeneous, as the average pore size $\sqrt{k/\phi}$ may vary with depth.

The assumption about constancy of the densities and kinetic coefficients is validated by the fact that, along the transition zone, variations of such governing parameters as pressures and temperature are usually insignificant [1,10] and, therefore, the "secondary" changes in the coefficients of the governing equations may be neglected.

In the assumptions above, the pressure and capillarity equations (2) and (6) may be solved separately from the other system, which gives

$$P^v = P_0 + \xi(h)J(0) + \rho^v g(z - h),$$

$$P^l = P_0 + \rho^l g(z - h),$$

$$J(s) = \frac{\xi(h)J(0) - (\rho^l - \rho^v)g(z - h)}{\xi(z)} \quad (24)$$

An unknown constant $P_0 = P^v(h) - \xi(h)J(0)$ will later be found from solution of the external problem. The saturation $s(z)$ defined by the last equation is independent of P_0 and of the reduced chemical potentials. This makes it possible to use $s(z)$ as known dependence in the system (14), (15), (16) for the chemical potentials and the temperature.

The thickness of the transition zone H_{tr} is found from Eq. (24) with $s = 1$, $z = h + H_{tr}$:

$$H_{tr} = \frac{\xi(h)J(0) - \xi(h + H_{tr})J(1)}{(\rho^l - \rho^v)g} \quad (25)$$

If the reservoir is homogeneous ($\sqrt{k/\phi} = \text{const}$), then the right-hand side of the last equation is independent of H_{tr} and explicitly determines its value. However, for a sharply heterogeneous porous medium, Eq. (25) may have several solutions indicating the formation of multiple transition zones. Even if it is not the case, the saturation defined by Eq. (24) may vary in a sharply non-monotonous way.

Usually, the thickness of the transition zone is defined not as a distance between the depths of zero and unity saturations, but between those of the residual saturations of the phases, so that GOC corresponds to reaching the residual oil saturation [10]. For this definition of the transition zone, the values $J(0)$ and $J(1)$ in Eq. (25) must be replaced by $J(s_{gr})$ and $J(s_{or})$, correspondingly. The last equation serves a reasonable approximation for the thickness of the transition zone even if phase densities and surface tension vary.

Let us give an example of the estimation of the thickness of the transition zone. Assume that the vapor and liquid densities are 200 and 600 kg/m³, correspondingly, the reservoir is homogeneous and low-permeable, with the permeability 10^{-15} m² and porosity 0.1, and the difference between the least values of the Leverett function is 8. Then, for the surface tension varying from 1 to 10 mPa·m and the absolutely wetting liquid phase, the thickness of the transition zone varies from 20 to 200 m, which is quite a large

value compared with a characteristic reservoir thickness. Of course, these estimates may strongly vary depending on reservoir conditions. However, they show that the effects of the transition zone cannot be neglected without pre-evaluation.

Reduction of the system

Assuming that the dependence $s(z)$ is known, let us obtain a closed system of equations for the vector ψ defined as a difference of the vectors of reduced chemical potentials:

$$\psi = \eta^v - \eta^l \quad (26)$$

To do so, we follow the procedure suggested in [18] for a binary mixture, generalizing it to the multicomponent case. First, we add Eqs. (14) and (15), integrate the result by dz and find the constant of integration from the boundary conditions at the upper boundary of the transition zone. The result is

$$s\mathbf{I}^l + (1-s)\mathbf{I}^v = 0 \quad (27)$$

Along with the value $r(s)$ defined by Eq. (10), we introduce the designations

$$\mathbf{q}(s) = \phi\{s\mathbf{q}^l + (1-s)\mathbf{q}^v\}$$

$$\mathbf{N}(s) = \phi\{s\mathbf{N}^l + (1-s)\mathbf{N}^v\}$$

$$\mathbf{L}(s) = \phi\{s\mathbf{L}^l + (1-s)\mathbf{L}^v\}$$

$$\mathbf{D}(s) = r(s)\mathbf{L}(s) - \mathbf{N}(s)\mathbf{q}(s)^\top$$

where the sign $\top$ is used to denote the transposition of a vector (matrix), so that the product $\mathbf{N}(s)\mathbf{q}(s)^\top$ is a matrix consisting of the products of the components of the vectors $\mathbf{N}(s)$, $\mathbf{q}(s)$.

Introducing ψ instead of η^v into Eqs. (16) and (27), we transform them to the form of

$$\begin{aligned} \frac{dT}{dz} &= \frac{Q_0}{r(s)} - \frac{1}{r(s)}\mathbf{q}(s)^\top \frac{d\eta^l}{dz} \\ &\quad - \frac{\phi}{r(s)}(1-s)(\mathbf{q}^v)^\top \frac{d\psi}{dz}, \end{aligned} \quad (28)$$

$$\mathbf{L}(s)\frac{d\eta^l}{dz} + (1-s)\mathbf{L}^v\frac{d\psi}{dz} + \mathbf{N}(s)\frac{dT}{dz} = 0 \quad (29)$$

Then the value dT/dz is substituted from Eq. (28) into Eq. (29):

$$\begin{aligned} \frac{d\eta^l}{dz} &= -(1-s)\mathbf{D}(s)^{-1} \{r(s)\mathbf{L}^v - \phi\mathbf{N}(s)\mathbf{q}^v\}^\top \frac{d\psi}{dz} \\ &\quad - Q_0\mathbf{D}(s)^{-1}\mathbf{N}(s) \end{aligned} \quad (30)$$

Finally, excluding from Eq. (14) the values dT/dz , $d\eta^l/dz$ by use of Eqs. (28) and (30) we obtain the following equation for ψ :

$$\frac{d}{dz}[\mathbf{A}(z)\frac{d\psi}{dz}] - \mathbf{U}\psi = \frac{d\mathbf{R}(z)}{dz} \quad (31)$$

where

$$\begin{aligned} \mathbf{A}(z) &= \phi s(1-s) \times \\ &\quad \left\{ r(s)\left(\mathbf{L}^l - \frac{\mathbf{N}^l\mathbf{q}(s)^\top}{r(s)}\right)\mathbf{D}(s)^{-1}(\mathbf{L}^v - \frac{\phi\mathbf{N}(s)\mathbf{q}^v\top}{r(s)}) \right. \\ &\quad \left. + \frac{\phi}{r(s)}\mathbf{N}^l\mathbf{q}^v\top \right\} \end{aligned}$$

$$\begin{aligned} \mathbf{R}(z) &= \phi s\{r(s)\mathbf{L}^l - \mathbf{N}^l\mathbf{q}(s)^\top\}\mathbf{D}(s)^{-1}\mathbf{N}(s) - \mathbf{N}^l\} \\ &= \phi(1-s)\{\mathbf{N}^v - [r(s)\mathbf{L}^v - \mathbf{N}^v\mathbf{q}(s)^\top]\mathbf{D}(s)^{-1}\mathbf{N}(s)\} \end{aligned}$$

It is seen that $\mathbf{A} = 0$ at $s = 0$ or $s = 1$, so that the top and the bottom of the transition zone are really the specific points of Eq. (31). However, at the same points $\mathbf{R} = 0$ which makes possible the existence of the only bounded solution, as it was shown in [18].

Asymptotical analysis

System (31) may be considered as a system with a large parameter. In order to show this we transform Eq. (31) to a dimensionless form. For this purpose, the vertical coordinate z is substituted by $Z = (z-h)/H_{tr}$, so that Z varies from zero at the top of the transition zone to unity at its bottom. The diffusion fluxes are normalized by the characteristic value I_0 , the terms of mass exchange by the characteristic value m_0 . The corresponding dimensionless variables are denoted by the superscript $'$. Then Eq. (31) assumes the form of

$$\frac{d}{dZ}[\mathbf{A}'(Z)\frac{d\psi'}{dZ}] - \gamma\mathbf{U}'\psi' = \frac{d\mathbf{R}'(Z)}{dZ}, \quad (32)$$

$$\gamma = \frac{m_0 H_{tr}}{I_0}$$

Let us estimate the order of magnitude of the dimensionless parameter γ , which reflects the relation between the characteristic values of diffusion fluxes and the fluxes governing the exchange between phases. It is natural to assume that this exchange is also caused by the diffusion mechanism. However, this mechanism acts at characteristic distances much smaller than the thickness of the transition zone H_{tr} . Different phases in a disordered porous medium are well "mixed up", and a characteristic thickness d of a separate gas (liquid) cluster is of the order of several pore sizes. The last statement is valid even in the case where the phases form continuous systems (infinite clusters).

We have $m_0 \sim I_{eq}/d$, where I_{eq} is the diffusion flux equating potentials in the two phases, and $\gamma \sim (H_{tr}/d)(I_{eq}/I_0)$. On the other hand, $I_0 \sim D_0/H_{tr}$ and $I_{eq} \sim D_{eq}/d$, where D_0 and D_{eq} are diffusion coefficients of the corresponding processes. Assuming that $D_0 \sim D_{eq}$ we obtain $I_{eq}/I_0 \sim H_{tr}/d$. Thus, $\gamma \sim (H_{tr}/d)^2$, which is reasonably large.

The way the large parameter γ enters system (32) is of WKB type. One of its partial bounded solutions may be within γ^{-1} approximated by [20]:

$$\psi' = \frac{1}{\gamma}(\mathbf{U}')^{-1}\frac{d\mathbf{R}'(Z)}{dZ}, \text{ or } \psi = \mathbf{U}^{-1}\frac{d\mathbf{R}(z)}{dz} \quad (33)$$

Since we postulated (and partly proved [18]) the existence of the only bounded solution of the initial system (31), this solution is necessarily approximated by Eq. (33).

Note that solution (33) is of the order of γ^{-1} . The reason is that the chemical potentials in both phases are equated by the fast process of mass exchange, and the difference ψ between them must be negligibly small. It is a reasonable approximation to neglect the value of ψ in the expressions for the diffusion fluxes, the temperature and the chemical potentials. Such an approximation also makes it possible to get rid of the kinetic coefficients $U_{\alpha\beta}$ of mass exchange, which are obviously hard to determine.

Approximate solution

Solution (33) may be substituted into the expression (30) for the derivatives of chemical potentials, which gives

$$\begin{aligned} \frac{d\eta^l}{dz} = & \\ & -(1-s)D(s)^{-1} \{r(s)L^v - \phi N(s)q^{v\top}\} U^{-1} \frac{d^2 R(z)}{dz^2} \\ & - Q_0 D(s)^{-1} N(s) \end{aligned}$$

Note, however, that the first term in the right side of this equation is of the order of γ^{-1} compared to the second term. In the chosen approximation it may be neglected:

$$\frac{d\eta^l}{dz} = -Q_0 D(s)^{-1} N(s) \quad (34)$$

At $s = 1$, this expression for $d\eta^l/dz$ coincides with Eq. (19) defining the gradient of the chemical potentials in the oil zone. Thus, in the chosen approximation not only the chemical potentials, but also their gradients are continuous.

Substituting Eqs. (33) and (34) into Eq. (28) for the temperature gradient and neglecting the terms of the order of γ^{-1} , we find that

$$\frac{dT}{dz} = \frac{Q_0}{r(s)} [1 + q(s)^\top D(s)^{-1} N(s)] \quad (35)$$

The first term in the last equation corresponds to the geothermal gradient determined by Eq. (22), as the dynamic thermodiffusion is neglected. The second term expresses the correction caused by dynamic thermodiffusion. However, this correction differs from that given by Eqs. (18) and (20). The reason is that the last equations correspond to the assumption about absence of motion, while Eqs. (34) and (35) correspond to the diffusion fluxes, which differ from zero. Substituting these equations into expression (14) for the diffusion fluxes in liquid we find that

$$I^l = Q_0 [L^l - \frac{N^l q(s)^\top}{r(s)}] D(s)^{-1} N(s) - \frac{Q_0}{r(s)} N^l \quad (36)$$

A similar expression can be obtained for I^v . By simple transformations it can be shown that $I^l = 0$ when $s = 1$. Thus, diffusion fluxes in liquid disappear at the lower boundary of the transition zone. Similarly, the diffusion fluxes in the gas phase vanish at the upper boundary of that zone. Of course, the diffusion fluxes are proportional to the dynamic thermodiffusion coefficients N^l , N^v , and to the heat flux of the Earth Q_0 .

In the case of binary mixtures, all the vectors and matrices become scalars, and the equations for gradients of chemical potentials, temperature and diffusion fluxes are simplified [18]:

$$\frac{d\eta^l}{dz} = -Q_0 \frac{N(s)}{D(s)},$$

$$\frac{dT}{dz} = Q_0 \frac{L(s)}{D(s)},$$

$$I^l = Q_0 \phi(1-s) \frac{L^l N^v - L^v N^l}{D(s)}$$

Now the thickness of the transition zone and all the values inside it are found, and the remaining problem is to determine the position of the upper boundary h of the transition zone. Assume that we know the distribution of chemical potentials, pressure and temperature at any depth z in the gas cap. At the upper boundary of the transition zone chemical potentials in the liquid phase must obey the following system of equations:

$$\eta^l = \eta^v - \psi(h)$$

$$\mu_A^l = \mu_A^v - e\psi(h)$$

These equations are consequences of Eqs. (13) and (26). The value $\psi(h)$ is known from the solution of the internal problem for the transition zone. Note that, neglecting the value of ψ (which is of order γ^{-1}), we obtain the usual system of equalities of the chemical potentials:

$$\mu_\alpha^l = \mu_\alpha^v \quad (\alpha = 1, A)$$

Thus, when we know $\mu^v(z)$ we can find hypothetical $\mu^l(z)$ for any depth inside the gas cap. Then the hypothetical pressure in the liquid phase can be found from the equation of state for this phase: $P^l(z) = P^l(\mu^l(z), T(z))$. Finally, the upper boundary h of the transition zone is found to be the depth at which the capillarity equation (23) for zero saturation is valid.

Sample calculations

A remarkable property of Eqs. (34) to (36) for gradients of thermodynamic variables and diffusion fluxes is that these values do not depend on the capillary characteristics of a porous medium, but only on the saturation and kinetic coefficients. Thus, it is reasonable to study these values as functions of the saturation. The corresponding dependencies are presented in Table 1.

s	$v_d^l, 10^{-10} \text{ m/s}$	$\frac{d\eta^l}{dz}, \text{ J/(kg}\cdot\text{m)}$	$\frac{dT}{dz}, 10^{-2} \text{ K/m}$
0.0	1.48	0.62	3.30
0.2	1.39	0.87	3.27
0.4	1.28	1.24	3.25
0.6	1.11	1.85	3.25
0.8	0.80	3.01	3.29
1.0	0.	6.26	3.50

Table 1: Variations of diffusion flowrates and gradients of thermodynamic variables with saturation

The reservoir mixture of an oil-gas-condensate reservoir was split into two pseudocomponents, methane and another one approximately possessing properties of *n*-hexane. Thermodynamic properties of these mixtures were taken from [21]. The densities of gas and liquid are, correspondingly, 250 kg/m³ and 500 kg/m³. The diffusion coefficients are of the order of the molecular diffusion ($10^{-8} \text{ m}^2/\text{s}$ for gas and $10^{-7} \text{ m}^2/\text{s}$ for liquid), since there is no convective diffusion in absence of the convective flux. The thermodiffusion ratios are estimated 0.05 for liquid and 0.5 for gas [22]. These values are used to find the coefficients L , N , q . The porosity of the reservoir is 0.1, its heat conductivity is 0.16 W/(m·K).

The first column of Table 1 presents the values of the diffusion flowrate $v_d^l = I^l/\rho^l$. It decreases monotonously with saturation, varying from $1.48 \cdot 10^{-10} \text{ m/s}$ at the top of the transition zone ($s = 0$) to 0 at its bottom ($s = 1$). A characteristic value of the diffusion flowrate is of the order of 10^{-10} m/s , or, approximately, one meter per 300 years. Of course, this value is negligibly small compared to flowrates characteristic of the process of development of the reservoir (one meter per day). However, the diffusion flowrate may lead to a significant redistribution of the components on geological time scales.

The last statement is validated by the second column in Table 1 showing the values of the gradient of the reduced chemical potential η^l . This value is of the order of unity, so the total change in the value of the chemical potential can be of the order of several hundred for a large transition zone. An estimate of the order of the value of η^l is $RT/M \sim 10^4$, so that the change may be several percent of its value, leading to significant variation of the composition of the mixture.

The third column of the table shows variation of the geothermal gradient with saturation. This variation is insignificant, it does not exceed 10 %. The largest variations are observed at the bottom of the transition zone ($s \approx 1$). Such an insufficient change in the geothermal gradient is explained by the fact that the heat conductivity of the two-phase mixture in the porous medium is determined by that of the rock, which occupies 90 % of the reservoir space.

CONCLUSIONS

1. The theory of segregation in a thick oil-gas-

condensate reservoir is developed. The action of capillary forces and of the geothermal gradient is taken into account. Analytical solutions for distributions of thermodynamic variables are obtained.

2. Presence or absence of the phenomenon of dynamic thermodiffusion determines, whether there is equilibrium in the transition zone between gas and oil parts of the reservoir (this zone arises due to the action of the capillary forces). If dynamic thermodiffusion is absent or negligible, there is equilibrium in all the three zones of the reservoir: single-phase gas and oil zone, as well as two-phase transition zone.
3. In the presence of dynamic thermodiffusion, neither thermodynamic nor mechanic equilibrium is possible in the transition zone. The segregated state of the two-phase mixture in this zone is characterized by non-zero diffusion fluxes of the components which are equilibrated by the mass exchange between phases.
4. Sample calculations show high thickness of the transition zone (up to several hundred meters) and high intensity of diffusion fluxes in it, compared with geological time scales. The diffusion fluxes may lead to significant redistribution of the components in the reservoir.

NOMENCLATURE

The system of units SI is used.

A	number of components
D	diffusion coefficient
g	acceleration due to gravity
H	bottom of the transition zone
H_{tr}	thickness of the transition zone
h	top of the transition zone
I	diffusion flux
J	capillary pressure function
k	permeability
L	kinetic coefficient of diffusion
M	molar mass of a component
N	kinetic coefficient of dynamic thermodiffusion
P	pressure
q	kinetic coefficient of diffusional heat conductivity
Q	non-convective heat flux
Q_0	heat flux of the Earth
r	kinetic coefficient of heat conductivity
s	saturation of liquid
T	temperature
U	kinetic coefficient of mass exchange
u	component mass exchange between phases
x	molar fraction

z	vertical coordinate
γ	large parameter
ϵ	geothermal gradient
ϕ	porosity
η	reduced chemical potential
μ	chemical potential
ρ	density
σ	surface tension
θ	wetting angle
ψ	difference of chemical potentials
ξ	capillarity factor

Superscripts

i	phase (liquid or vapor)
l	liquid
s	solid
v	vapor

Subscripts

r	residual
α, β	number of a component

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