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CAPILLARY — ADSORPTION EFFECTS IN GAS CONDENSATE SYSTEMS IN TIGHT ROCKS — VERTICAL VARIATION OF HYDROCARBON COMPOSITION

ZJAWISKA ADSORPCYJNE I KAPILARNE W UKŁADACH GAZOWO-KONDENSATOWYCH W ZBITYCH SKAŁACH POROWATYCH — PIONOWA ZMIENNOŚĆ SKŁADU WĘGLOWODORÓW

This paper[1] describes the complex phenomena related to mixing and segregation processes occurring during secondary migration and post-filling time of oil and gas-condensate system. The model of segregation of composition using diffusion and convection inside reservoir is analysed entirely: lithology, heterogeneity, and compartmentalized structure. The impact of adsorption, capillarity, thermal, and barodiffusion effects is discussed. The paleo-history of filling and mixing processes is considered as a important factor for present status of reservoir fluid. The paper discusses the non-equilibrium phenomena in the porous medium in presence of thermal gradient. The main governing factor driven composition is gravity, especially in the high asphaltenes content oils and for near-critical oils/gas condensate system. The new term (related to the capillary pressure) in the composition grading equation in the saturated transition region of adsorption-condensation area (for liquid phase) is presented and a new algorithm to find saturated Gas-Oil Contact (GOC) in the adsorption-capillary condensation area is given. The algorithm is based on the Modified Tangent Plane Criterion for Capillary Condensation (MTPCCC) (Nagy 2002). The present paper shows difference driven by capillarity phenomena in the transition region on hypothetical example. The paper discusses the difference between traditional (average) and grade composition of reservoir fluid in estimation OIIP/GIIP.

Key words: hydrocarbon grading composition condensate diffusion gravity capillary condensation porous medium

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[1] The paper is continuation of the paper entitled "Capillary Adsorption Effects In Gas Condensate Systems In Tight Rocks" Archives of Mining and Sciences, Vol. 47, No. 2, p. 205–253, 2002 (by S. Nagy), which content--related scope is extended to the variation of hydrocarbon composition in the vertical profile with the adsorption--capillarity phenomena and with variation driven by gravity segregation in the isothermal conditions and in the presence of thermal gradient.

Niniejszy artykuł jest kontynuacją pracy pt. „Zjawiska adsorpcyjne i kapilarne w układach gazowo-kondensatowych w zbitych skałach porowatych — pionowa zmienność składu węglowodorów" (Nagy 2002), której zakres merytoryczny został poszerzony o aspekt zmienności składu węglowodorowego w profilu pionowym z uwzględnieniem zjawisk adsorpcyjno-kapilarnych i zmienności wywołanej poprzez segregację grawitacyjną w procesach izotermicznych oraz przy istnieniu pionowego gradientu temperatury w złożu. Innym uzupełnieniem pracy jest omówienie warunków koniecznych zmienności składu wywołanych przez proces konwekcji wymuszonej. Niniejsze uzupełnienie pozwala na zunifikowany opis zmian własności *in situ* PVT układów węglowodorowych w skałach zbitych o średnim promieniu porowym mniejszym od 1 μm.

W klasycznym ujęciu termodynamicznym w zakresie własności PVT i równowagi fazowej ciecz--para (VLE) w złożach gazowo-kondensatowych i ropnych pomijany jest efekt segregacji grawitacyjnej, oddziaływań zjawisk kapilarnych czy efekt zmienności temperatury złożowej na ciśnienie nasycenia (ciśnienie rosy — kondensacji, i ciśnienie pęcherzyków — wrzenia), temperaturę krikondentermu czy ciśnienie krikondenbaru. W nowym ujęciu termodynamicznym duże znaczenie — szczególnie w przypadku złóż rozległych — ma poznanie zmienności składu węglowodorowego zarówno w ujęciu poziomym (zmienność lateralna), jak i pionowym. Głównym czynnikiem powodującym zmienność składu jest występowanie siły ciężkości i pionowego (lub/i poziomego) gradientu temperatury. Inne czynniki związane immanentnie z warunkami geologicznymi węglowodorów to: niejednorodność, uskoki tektoniczne, zwilżalność skały. Wpływ warunków genezy odciśnięty jest na składzie płynu złożowego poprzez charakterystykę procesu wtórnej migracji ze skały macierzystej do pułapki złożowej oraz poprzez zmienność paleotemperatur i paleociśnień. Niektóre z wymienionych procesów mogą zachodzić w czasie obecnym, wtedy złoże ropy czy gazu jest złożem o dynamicznej charakterystyce („true dynamic state reservoir"), w którym możliwy jest przepływ metanu z innych stref złożowych („non zero methane flux"). Inne złoża, w których siły grawitacji, kapilarne i termodynamiczne są stałe — nazywane są złożami stacjonarnymi („true steady state reservoir"), zaś złoża, w których występują jedynie siły grawitacji znajdują się w stanie równowagi termodynamicznej („static reservoir"). Ta klasyfikacja jest wynikiem zastosowania kryteriów równowagowych Prigogine'a do złóż naftowych.

Klasyczne terminy przypisane typom złóż węglowodorowych (ropa naftowa „black oil", lekka ropa naftowa „volatile", gaz kondensatowy „condensate gas") tracą swoje identyfikujące atrybuty w związku z możliwością klasyfikacji np. w sposób: gaz kondensatowy na głębokości odniesienia „1". Ten sam układ termodynamiczny może zostać zidentyfikowany jako: lekka ropa naftowa na głębokości odniesienia „2" — kilkadziesiąt lub kilkanaście metrów poniżej głębokości „1". Te zmiany składu płynu złożowego mogą zachodzić w sposób ciągły w profilu złoża, w takim przypadku — w zależności od ciśnienia złożowego — przejście fazowe może być typu nasyconego („saturated Gas Oil Contact") lub nienasyconego („unsaturated Gas Oil Contact"), kiedy brak jest wizualnego przejścia na skutek podwyższonego ciśnienia złożowego. W przypadku skał zbitych dodatkowym zjawiskiem występującym w złożu jest przesunięcie równowagi fazowej w obszarze przejściowym pomiędzy kontaktem gaz-ciecz (w przypadku nasyconych złóż dwufazowych) związane z występowaniem innego ciśnienia w fazie ciekłej — ciśnienia powiększonego o ciśnienie kapilarne. Zjawisko to jest widoczne dla złóż występujących w skałach o średnim promieniu kapilarnym poniżej 10^{-6} m i jest znaczne w przypadku promienia mniejszego niż 10^{-7}–10^{-8} m (Nagy 2002). Przy zaniedbaniu niektórych czynników specyficznych dla charakterystyki geologicznej, omówiono aspekt termodynamiczny zmienności węglowodorów na podstawie teorii nierównowagowej termodynamiki — przy użyciu zasady Onsagera-Casimira i zasady minimalnej produkcji entropii Prigogine'a. Przedstawiono zasadę lokalnej równowagi termodynamicznej w odniesieniu do ośrodka porowatego oraz zasadę minimalnej produkcji entropii Prigogine'a. Pokazano równania opisujące procesy skoniugowane (wywołane poprzez bodźce pierwotne) i sprzężone (poprzez bodźce wtórne) w ośrodku porowatym. Opisano sprzężenia w stanie stacjonarnym, w którym oprócz istnienia sił grawitacji istnieją siły termodynamiczne wynikające z istniejącego gradientu temperatur. Pokazano efekty związane wymianą ciepła i dyfuzją Ficka (procesy koniugowane) i efekty dyfuzji termicznej (efekt Soreta) i przepływu ciepła na skutek gradientu kompozycyjnego (efekt Dufoura) (procesy sprzężone). Pokazano zmienność gradientu temperatury w złożu wynikającą z własności litologicznych skał złożowych i lokalną

zmiennością gęstości powierzchniowej ziemskiego strumienia ciepła. Opisano modele dyfuzyjne zmienności pionowej (1D) węglowodorów:

- bez uwzględnienia procesów sprzężonych (tj. bez termodyfuzji), jako proces izotermiczny;
- bez termodyfuzji, ale z uwzględnieniem wpływu temperatury na potencjał chemiczny i-tego składnika w układzie („pasywny" model);
- model z uwzględnieniem termodyfuzji (według modeli Haase'a, Kempersa i Belery-da Silva/Dougherty-Drickamera);
- modele uwzględniające wpływ efektów kapilarnych w strefie przejściowej w przypadku nasyconego złoża ropy lub/i gazu kondensatowego na głębokości odpowiadającej ciśnieniu nasycenia.

Pokazano zmienność składu w profilu pionowym wygenerowaną na podstawie wzorcowego składu dla danych Montela i Gouela (1985) według zmodyfikowanego równania stanu Penga-Robinsona VTPT (Tai-Chen 1998). Przedstawiono wpływ zmienności ciśnienia nasycenia w obecności sił kapilarnych i przy zaniedbaniu zmienności temperatury dla złoża Ciupaga (dane: Smith et al. 2000). Pokazano warunki konieczne dla istnienia zmienności wywołanej procesem konwekcji naturalnej i wymuszonej w skałach zbitych, a także czas geologiczny konieczny do ustalenia się stanu stacjonarnego w złożu dla skał zbitych dla metanu, składników pośrednich i składników ciężkich. Wskazano na istotny wpływ segregacji termiczno-grawitacyjnej składu płynu złożowego na zasoby geologiczne i wydobywane. Omówiono dodatkowy wpływ kształtu złoża, tj. jego zmienności w profilu pionowym, na szacowanie zasobów geologicznych.

Słowa kluczowe: węglowodory, pionowa zmienność składu, efekt kapilarny, kondensacja kapilarna w ośrodku porowatym

Nomenclature

A_{im}	— coefficient defined by eq. (92),
β	— coefficient of thermal expansion [1/K],
$\dfrac{D}{Dt}$	— operator of substantial time derivative (time Lagrange operator),
∇	— gradient operator,
∇_T	— isothermal part of gradient operator,
c_f	— fluid molar heat capacity [J/(moleK)],
c_i^L	— partial molar liquid i-component isothermal compressibility coefficient [1/Pa],
c_s	— volumetric heat capacity of system [J/(m³K)],
D	— diffusion coefficients in oil/gas condensate medium [m²/s],
D'	— the Soret coefficient,
D''	— the Dufour coefficient,
δ_{im}	— the Kronecker delta,
ds_e	— elementary change of molar entropy of system caused by change of energy with environment [J/(moleK)],
ds_i	— elementary change of molar entropy inside of system in the time dτ [J/(moleK)],

ΔT	— difference temperature between top and bottom layer [K],
E	— empirical dimensionless constant [–],
ε_i	— component Poynting factor ($\varepsilon_i = \dfrac{\bar{V}_i^L}{R \cdot T}$) [1/Pa],
F	— rock compaction exponent [–],
$\vec{F}$	— vector represents the external force (gravity) [N/mole],
F_{Ti}	— term used to account thermal diffusion [J/mole],
ϕ	— porosity coefficient [–],
g	— gravity acceleration constant [m/s^2],
h	— thickness of layer [m],
h_m	— molar enthalpy [J/mole],
h_i	— partial molar enthalpy of i-component [J/mole],
$\vec{J}^S$, $\vec{J}^{S,tot}$	— net influx of entropy [W/(m^{2}K)],
$\vec{J}'_q$, $\vec{J}_q$	— net influx of heat [W/m^2],
$\vec{J}_k$	— mole diffusion flux of k-component [mole/(m^{2}s)],
J_1, J_2, J_3	— heat or diffusion fluxes,
$L_{11}, L_{12}, ..., L_{22}, L_{21}$	— phenomenological coefficients,
$L'_{k1}, L'_{1i}, ..., L'_{ki}, L'_{i1}$	— phenomenological coefficients,
L	— length scale over which mixing takes place [m],
λ_e	— effective conductivity [W/(m K)],
λ	— dimensionless acceleration exponent [–],
K_i, K_i^∞	— equilibrium constant of i-component: capillary condensation and bulk phase [–],
M_i	— molecular mass of i-component [kg/mole],
m, M_m	— molar mass [kg/mole],
μ_i	— chemical potential of i-component [J/mole],
$\bar{\mu}_k$, $\tilde{\mu}_k$	— chemical potential of i-component in the presence of gravity [J/mole],
μ_{vis}	— dynamic viscosity coefficient [Pa s],
n_i	— mole number of i-component [–],
N_V	— mole fraction of vapour phase [–],
v_f	— coefficient of kinematics' viscosity [m^2/s],
p	— pressure [Pa],
p_c	— capillary pressure [Pa],
p_V, p_L	— vapor and liquid phase pressure [Pa],
p_V^∞	— bulk gas phase pressure [Pa],
π_i	— parachor of i-component [–],
q	— geothermal heat density flow [W/m^2],
r, r_e	— capillary radius [m],
r_i	— dimensionless function defined by eq. (74),

$\bar{\rho}$ — mass density [kg/m^3] (eq. (18)–(24)),

$\rho_f,\ \rho_L,\ \rho_V$ — fluid, liquid and vapour density [kg/m^3],

$\bar{\rho}_i$ — molar density of i-component [mole/m^3],

s — specific entropy [J/(moleK)],

S_k — partial molar entropy of k-component [J/(moleK)],

S_{LHC} — saturation of liquid hydrocarbons [–],

S_{wi} — connate water saturation [–],

σ — volume density of entropy production in the time [W/(Km^3)],

σ_{IFT} — interfacial surface tension (IFT) coefficient [N/m],

t — film thickness of wetting fluid inside capillary [m],

T — temperature [K],

T_{eq} — time needed to diffusion mixing [s],

θ — factor that accounts tortuosity of rock pore system [–],

u — internal molar energy [J/mole],

Δu_i^* — partial molar energy of activation eq. (105),

Δu_m^* — function defined as viscosity to density ratio (eq. 106),

$\bar{v}$ — velocity vector [m/s],

$\bar{v}_i$ — partial molar volume of i-component [m^3/mole],

$v,\ v_L,\ v_V,\ v_m$ — specific molar volume [m^3/mole],

V — volume of system [m^3],

$x_i,\ x_m,\ x_{nc}$ — mole fraction of $i,\ m,\ nc$-component,

$X_1,\ X_2,\ X_3$ — thermodynamic forces,

Y_i — mole fraction of tested-origin phase of i-component [–],

Y_i — dimensionless function defined by eq. (74),

z — vertical coordinate [m],

$Z^L,\ Z^V$ — vapour and liquid phase compressibility factor [–],

Ω — surface area of system [m^2],

abbr.

CCE   — Constant Composition Expansion,

CVD   — Constant Volume Depletion,

PNA   — Paraffin's -Naphtenes- Aromatics ratio.

1. Introduction

The variation of composition in the reservoir is known for many years (e.g. Muskat 1930; Sage, Lacey 1938; Schulte 1980; Holt et al. 1983; Montel, Gouel 1985). The common known examples of grading reservoir are described in detail in papers: Kaufman et al. 2000; Aplin et al. 2000; Smalley, England 1992, 1994; di Primio et al. 1998;

Khavari-Khorasani et al. 1998). The observed spatial variation concern heavy oils with high asphaltene content (Hirschberg 1988; Firoozabadi 1998) as well as black oil, near critical oil and gas-condensate systems in Gulf of Mexico, North Sea, Gulf Of Persia, Brazil shelf. The phenomenon is very important in exploitation of giant fields with high thickness (Creek, Schrader 1985; Wheaton 1988; Hamodi, Abel 1994; Padua 1998). The summary of grading phenomena may be found in papers: Hoeier, Whitson (2001); Padua (1998); Ghorayeb, Firoozabadi (1999). The fully thermodynamic analysis of reservoir hydrocarbon system is impossible because of large influence of environmental factors.

The environmental factors may be divided into following classes, according to their features (Lee 1989; Nagy 2002):

I. Thermodynamic factors:
   a) local temperature,
   b) local pressure,
   c) local composition,
   d) slope of reservoir bottom and top layers (gravity forces),
   e) curvature of porous media (capillary forces).
II. The factors connected to the thermodynamic phenomena:
   a) thermal gradients (induced thermal convection — natural or forced),
   b) molecular diffusion.
III. The factors connected immediately to the porous media:
   a) heterogeneity,
   b) faults (slowing down of equilibrium process),
   c) wettability.
IV. The factors connected with the hydrocarbon accumulation and generation processes:
   a) genesis,
   b) migration,
   c) reservoir traps.

Including all above presented factors it is not possible in the reservoir simulation model. The factors classified into the III and IV group are not almost useful because of specific features of individual hydrocarbon accumulation. The building of thermo-dynamic reservoir model with features of I–II group and with some selected features from III group may be possible for the "virgin" (i.e. before exploitation) and exploitation status.

2. Factors governing spatial composition variation

When we consider all mentioned above factors, we might classify aerial and vertical variation of composition as a single or composite impact of various present- and paleo-factors. Some of them may act in the present time; some of them had influenced in the past: several thousand and million years ago. We have to recognize the geochemical and geological data in the individual case (Fig.1, 2). The hydrocarbon reservoirs may be
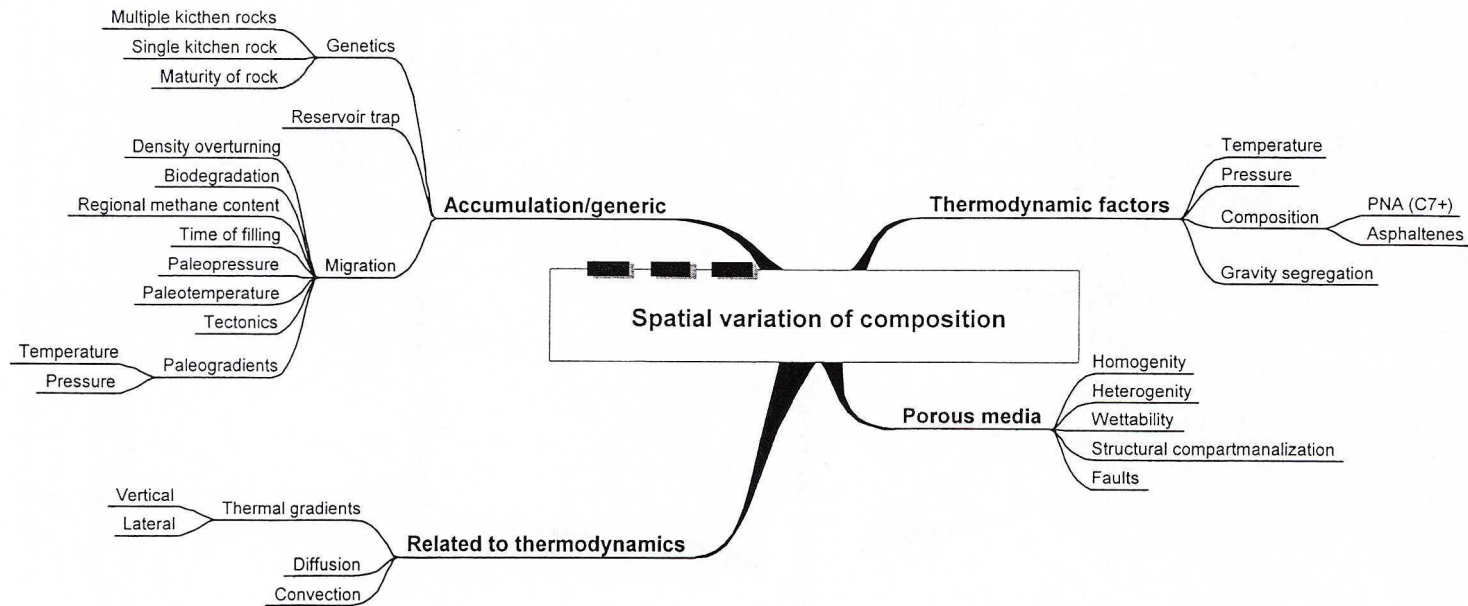
Spatial variation of composition

Accumulation/generic

Genetics
- Multiple kicthen rocks
- Single kitchen rock
- Maturity of rock

Reservoir trap

Migration
- Density overturning
- Biodegradation
- Regional methane content
- Time of filling
- Paleopressure
- Paleotemperature
- Tectonics

Paleogradients
- Temperature
- Pressure

Thermodynamic factors
- Temperature
- Pressure
- Composition
  - PNA (C7+)
  - Asphaltenes
- Gravity segregation

Porous media
- Homogenity
- Heterogenity
- Wettability
- Structural compartmanalization
- Faults

Related to thermodynamics

Thermal gradients
- Vertical
- Lateral

Diffusion

Convection

Fig. 1. The paleo- and present-factors influenced on spatial variation of composition of reservoir fluid

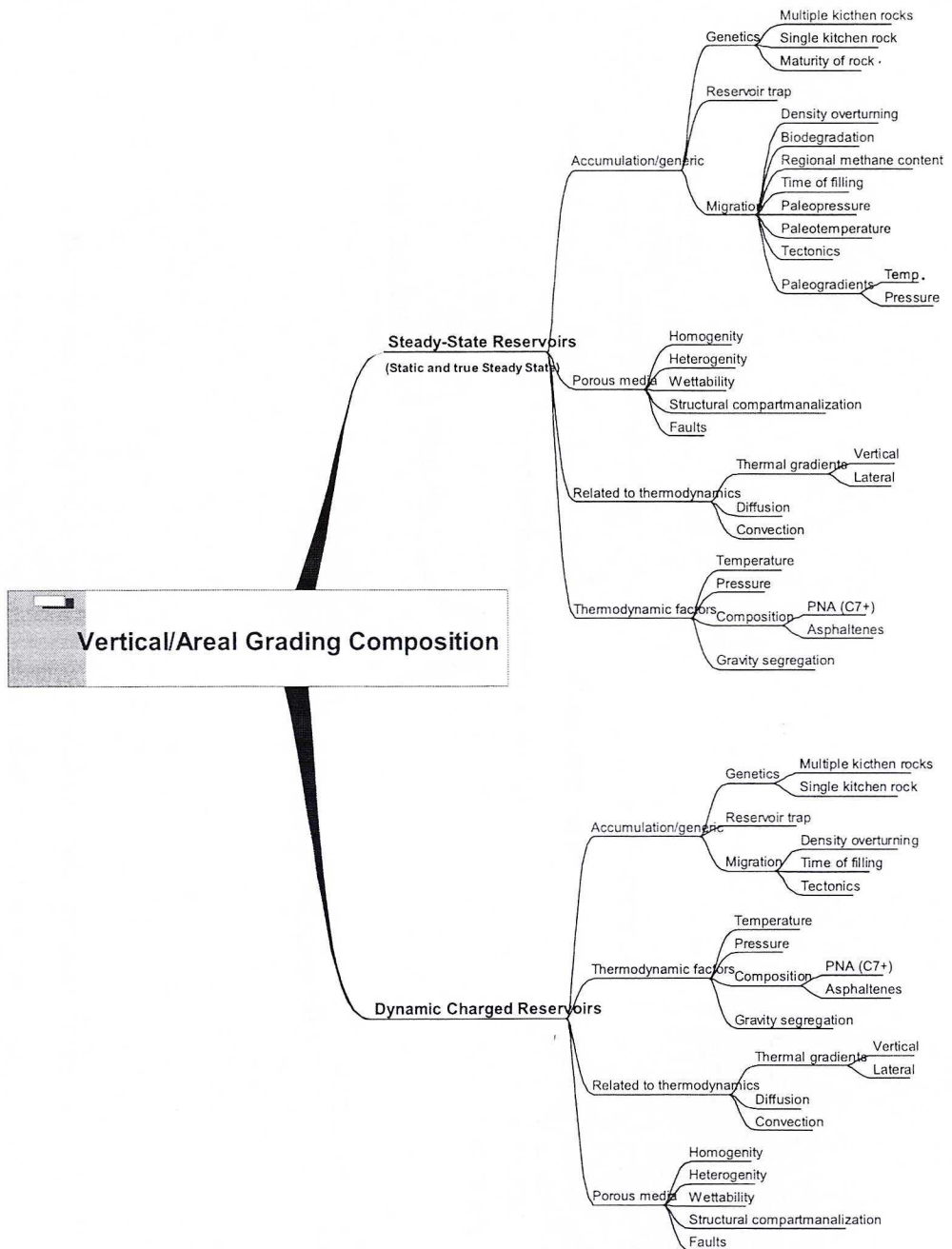Rys. 1. Czynniki paleo i aktualnie wpływające na przestrzenną zmienność składu płynu złożowego

Fig. 2. The Dynamic Charged and Steady State (Static and "True" Steady State) Reservoirs.
Paleo and present factors governing the spatial composition of fluids

Rys. 2. Złoża węglowodorów w procesie niezakończonego mieszania wtórnej migracji i złoża w stanie
ustalonym (bez przepływów dyfuzyjnych). Czynniki wpływające na zmienność składu płynu

divided into the two groups depending on thermodynamic equilibrium factors and dynamics of fluid movement in the present day (Table 1). When the process of secondary migration and post migration mixing is not finished — the reservoir may be "dynamic charged" (Siddiqui, Lake 1997, Siddiqui 1999). When exchange of mass between reservoir and surroundings is not observed ("zero mass flux") two groups of reservoir may be marked. The first group may be "static", where insignificant thermal gradient exists, and "true-steady state", where more evident thermal gradient is motor of mixing phenomena. The "dynamic charged" reservoirs are distinguish by not finished secondary migration and not finished filling of the trap. The main types of reservoirs based on criterion of thermodynamic equilibrium and dynamics of fluid movement (Siddiqui 1999; Montel et al. 2002) are summarized by author in the Table 1.

TABLE 1

Type of reservoirs based on criterion of thermodynamic equilibrium (author)

TABLICA 1

Klasyfikacja złóż z uwagi na równowagę termodynamiczną

Item	Type		Description
1	Steady State and Equilibrium ("Zero Mass flux")	"static"	Reservoir with no measurable thermodynamic gradients; secondary migration finished; no measurable composition gradients — e.g. "thin" gas reservoirs
		"true" steady state	Reservoir with significant composition variation in vertical and lateral directions with steady local thermal gradients; secondary migration finished
2	Dynamic Charged Reservoirs or/and Methane External Flux ("Non-zero mass flux")		Evidence of changing the geochemical markers in various parts of system; secondary migration in progress; post secondary migration mixing

2.1. Factors pertained to accumulation and generation of hydrocarbons

The formation of petroleum and natural gas is still subject of research. Based on accepted organic theory of origin (Tissot, Welte 1978) one may find that most important process, which is responsible for spatial variation of composition, is secondary migration (e.g. movement in carrier rocks or reservoir rock outside source rock or movement through fractures within the source rocks) or tertiary migration (e.g. movement of previously formed oil and condensate accumulation). The primary migration by diffusion is negligible in comparison with the second and tertiary (Tissot, Welte

Types of spatial variation of composition (author)

Klasyfikacja zmienności przestrzennej zmienności składu węglowodorów

Item	Variation		Comments
	Laterally	Vertically	
1	static	stable	Full diffusion time for mixing laterally; lack of vertical gradient
2	stable	grade	Full diffusion/convection mixing laterally with vertical gradient
3	hetero/grade	stable	Various source rocks or insufficient time for mixing; lack of vertical gradient
4	hetero/grade	grade	Various source rocks or insufficient time for mixing with vertical gradient
5	stable/non stable	non stable	Underground Gas Storage

1978). The types of spatial variation of composition of oils and gases are summarized in the Table 2.

2.1.1. Secondary migration distances

About 2/3 of known reservoirs appear to have accumulated due to vertical migration and about 1/3 due to lateral migration from the source bed. There are many known reservoirs built using both: lateral and vertical migration. Vertical migration is generally more efficient than lateral, but less petroleum is collected because of lack of traps. Lateral migration can drain a larger volume of source rock.

2.1.2. Time of accumulation

The relative time of migration and the time of formation of traps are the most important for oil and gas accumulation to occur. Time of formation of traps dates the earliest time of any accumulation. The age of structure rather than the age of the reservoir rocks limits the time of accumulation. Structures affected by tectonic deformation may be formed much later. Time of formation of traps does not indicate date the exact time of accumulation, but it fixes the time before accumulation.

1.1.2.1. Accumulation time based on capacity of trap to hold gas and oil

Capacity of trap is proportional to pressure and inversely to temperature. Both are function of depth. Changing depth by deposition or erosion of surface has a marked

influence on gas capacity of trap. By comparing, the volume of gas may be estimated the paleo-pressure and paleo-temperature and paleo-depth occurring formation of trap and accumulation process (Gussow 1968)

2.1.2.2. Accumulation time based on bubble point pressure

The most exact methods for determination the time of migration and accumulation of oil and condensate. The idea is based upon saturation pressure related to paleo-hydro-static pressure of migration time. This may be erroneous when compare with other geologic factors (e.g. time of trap).

2.2. Factors pertained to present porous media properties
(heterogeneity, faults, wettability)

There are some factors immanently connected with porous media properties. When we consider classical attitude to the reservoir properties we assume homogenous horizontal radial layer usually with the well in the centre. The describing real porous model systems are much more complicated. The layer is usually non-horizontal (slope) with anisotropy and heterogeneity; discontinuity may change shape of reservoir. The properties of rock may spatially vary: vertically or laterally.

2.3. Thermodynamic factors (temperature, pressure, capillary pressure)

The thermodynamic features together with the "accumulation/generation" factors are the most important for fixing the present fluid configuration. The gravity force is the most important factor in the vertical segregation of fluid. The capillary-adsorption phenomena are significantly in the tight rocks, where the average phase permeability is about 0.5 md ($0.5 \cdot 10^{-3}$ μm^2) or less (Nagy 2002). Additionally, the capillary pressure has a great influence on the range of transition zone of oil-water and gas-oil/condensate interfaces. The present temperature and pressure as well as paleo-pressure and paleo--temperature have a great impact on thermodynamic status of fluid.

2.4. The factors pertinent to thermodynamics
(thermal gradient, diffusion)

The group of factors related to thermodynamic conditions is responsible for addi-tional phenomena occurring in presence of thermal field. The existing thermal gradients in the world are shown in the Table 3, based upon Haenel et al. (1988) data. According to the non-equilibrium thermodynamics theory (Kondepudi, Prigogine 1998), the thermal gradient may minimize the gravity segregation by Soret effect (thermal diffusion effect, it is characterised by setting up of concentration gradient as a result of a temperature gradient). Unfortunately, the phenomenon of thermodiffusion is not well recognized in case of multicomponent hydrocarbon system mixture. It is observed that the lightest and heaviest components are moving into the deepest and shallowest place in the reservoir in

Thermal gradients in the hydrocarbon reservoirs (after Haenel et al. 1988)

Charakterystyka gradientów geotermicznych w złożach węglowodorowych (Haenel et al. 1988)

Type of gradient	Min. gradient	Average gradient	Max. gradient
Vertical	1.00 K/km	3.0 K/km	7.0 K/km
Lateral	0.35 K/km	1.0 K/km	2.0 K/km

Diffusion time of mixing for typical rocks (Smalley, England 1994)

Czas potrzebny na zakończenie procesu mieszania dyfuzyjnego dla typowych złóż węglowodorowych (Smalley, England 1994)

Distance [m]		C_1 (10^6 years)	C_{12}(10^6 years)	C_{200}(10^6 years)	Water(10^6 years)
Vertical	100	0.1	0.2	1.0	0.1
Lateral	2000	40.0	80.0	400.0	20.0

lack of gravity field. The diffusion time needed to finish equilibrium process in the tack of thermal gradient is given in the Table 4. In presence of gravity, field segregation processes are slowed down by thermodiffusion. The thermodiffusion may be considered as a secondary order phenomenon – opposite to gravity segregation process. The present status of theory (Ghorayeb, Firoozabadi 1999; Hoeier, Whitson 2001) not allow to definitive describe the mechanism of moving the intermediate components as well as direction of moving – up or down. The mechanism of thermal diffusion in critical region is not good recognized, esp. for intermediate component in the condensate system (Hoeier, Wilson 2001).

3. Dynamics of mixing and segregation process

Characteristics of reservoir may be done using dynamics of mixing phenomena. A Dynamic Charged Reservoir is one that has active source rock feeding fresh hydrocarbon into it of the present time (Table 1). This is in contrary that is assumed that in geologic time complete gravity-capillary-adsorption equilibrium has been achieved. The reservoir which have mentioned equilibrium (steady state) is known as "static" reservoir (Table 1).

The status of fluid mixing can be verified using: Pressure-Volume-Temperature (PVT) sampling and laboratory test or using geochemistry sampling. The first is done using standard DST (Drill-Steam Test) or RTF (Repeat Formation Test) tools in the appraised stage of reservoir life. Alternatively, it is done using surface sampling during first production test. The second method consists of several geochemical tools. The geochemical tools available for reservoir compartmentalization has been shown in the Fig. 3
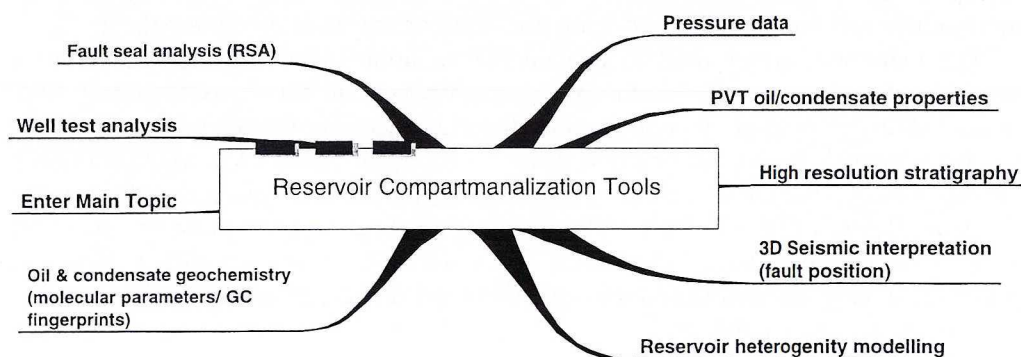

Fig. 3. Tools for analysis of integrity /compartmentalization of reservoir

Rys. 3. Narzędzia do analizy integralności i segmentacji złóż węglowodorowych

4. Simplified approach to modelling of grading phenomena

It is impossible to include in the model all factors described above — in synergistic way. It is a common practice to use the geochemistry, reservoir engineering models and thermodynamic description of reservoir (by use of equation of state).

The equation of state (EOS) method is very useful in the analysis of variation of heavy (C_{7+}) components. Some of compositional simulators include the influence of gravity and thermal gradient for fixing the steady state. The geochemistry analysis of extraction of reservoir fluid taken from cores by gas chromatography and mass spectro-photometer make possible to determine the biomarkers of oil/condensate and estimate fingerprints of specific components of fluid, which are very useful for understanding genesis and migration processes.

The use of PVT analysis in geochemical exploration is now a standard procedure (di Primio et al. 1998). It is possible (using geochemistry) to characterize oil, estimate relative oil maturity, evaluate complex reservoir filling history and recognize of mixing of oils and condensates. The detection of spatial reservoir compartmentalization using geochemistry method is separate task — not discussed here.

5. Thermodynamic models of stationary state of hydrocarbon reservoirs

The phenomenon of vertical composition variation has been first described by Gibbs (Gibbs 1961). The first analysis of phenomenon in petroleum has been done by Muskat (1930) and Sage, Lacey (1938, 1949). The next step — new approach to the problem was done in early 80's — using data taken from the North Sea oil reservoir, which confirmed variation of vertical composition in porous media. In 1983 Holt et al. proposed new methodology to include into traditional — classical solution of thermodynamic — thermodiffusion into model based upon non-equilibrium thermodynamic theory.

The mentioned paper tried to explain the variation of composition of complex multicomponent system by means pseudo-binary system with gravity segregation, thermodiffusion. Various thermodynamic theories based on Onsager-Casimir theory has been publish by several authors: Riley, Firoozabadi (1998), Firoozabadi (1999), Montel, Gouel (1985), Riemans, Jong (1985), Wheaton (1988), Belery, da Silva (1990), Whitson, Belery (1995), Padua (1999). Some of cited papers have more advanced 1D vertical model, some have 2D models, and some of them are simplified. Below is presented a short discussion about assumptions and models presented in the literature and novel view on the theory.

5.1. Phenomenological aspect of non-equilibrium thermodynamics

In this paper only phenomenal attitude to the continuous medium (macroscopic) are considered. The non-equilibrium processes are considered on measurable parameters (distinct from statistical thermodynamics). The main difference between classical and non-equilibrium thermodynamics lies in the fact that the first consider only series of equilibrium states. The additional parameter that is important in the second theory is time. With reference to thermodynamics of porous media may be formulated main task: description of mass and heat change in hydrocarbon and geothermal reservoirs. The main reasons that caused non-equilibrium processes in porous media are the lateral and vertical temperature gradients and pressure gradients in system.

5.2. Selected problems to the non-equilibrium thermodynamics in porous media

5.2.1. Local thermodynamic equilibrium concept in the porous media

The most important assumption (which allows developing and utilizing of non--equilibrium thermodynamic theory) is the concept of local equilibrium in the porous media. Using this concept one may attribute thermodynamic variables (temperature and pressure) to the elementary volume of porous media. Based on this concept one may define intensive parameters in function of position (x, y, z), time (t) and composition function:

$$T = T(x, y, z, t) \tag{1}$$

$$p = p(x, y, z, t) \tag{2}$$

$$\mu_i = \mu_i(x, y, z, t, n_1, n_2, \ldots, n_{nc-1}) \tag{3}$$

The other system variables — volume specific entropy, volume specific internal energy, and mole number per unit volume of component — are depended on position and time.

The concept of locally equilibrium theory assumes that in presence of gravity field in porous media the fundamental Gibbs relation (4) of n-component system is valid for elementary volume:

$$du = Tds - pdv + mgdz + \sum_{i=1}^{n} (\mu_i + M_i zg) dn_i \tag{4}$$

where:

u — molar internal energy [J/mole],

T — temperature [K],

s — specific molar entropy [J/moleK],

p — pressure [Pa],

v — molar volume [m³/mole],

m — mass of mole [kg/mole],

z — vertical coordinate [m],

μ_i — chemical molar of i-component [J/mole],

M_i — molecular mass of i-component [kg/mole],

g — gravity acceleration constant [m/s²],

n_i — mole number of i-component [–].

The intensive parameters in the elementary volume of phase and in the time are these that may be obtained by isolation of volume element in this time and fixing the equilibrium in this element.

5.2.2. The local form of the Second Thermodynamic Law in the porous media

The elementary change of entropy of composed system during τ and $\tau + d\tau$ time is ds:

$$ds = d_i s + d_e s \tag{5}$$

where:

$d_i s$ — elementary change of specific entropy inside of system in the time $d\tau$ [J/(moleK)],

$d_e s$ — elementary change of specific entropy of system caused by change of energy with environment [J/(moleK)].

The elementary increase of entropy inside of system according to Second Thermodynamic Principle $d_i s$ in the time $d\tau$ is:

$$d_i s = 0 \text{ for reversible process}$$

$$d_i s > 0 \text{ for irreversible process.}$$

The elementary change of entropy $d_e s$, which is exchanged with the environment, may be positive, negative or zero. The classical thermodynamics assumes possibility to vanish entropy in one place and possibility to produce the entropy in the other place of system, on condition that total change of produced entropy is nonnegative. The Local Concept of Second Thermodynamics Law demands that change of entropy $d_i s$ in the every elementary volume of system is non-negative. The non-equilibrium thermodynamics does not exclude possibility of existing a several processes, some of them may cause lowering the entropy, and some other may increase entropy. The total changes of entropy in the elementary volume of system must not be no negative. The possibility of co-existing of various processes in the system is connected with the concept of coupling processes to the one — fundamental. The existence of coupling processes is verified experimentally and has been basic for the Onsager theory of linear non-equilibrium thermodynamics (Onsager 1931a, b). The co-existence of conduction of heat and coupled process of thermal diffusion is a good example of phenomena.

5.3. Prigogine minimum production entropy principle in the porous media

The phase equilibrium modelling uses fundamental assumption of quasi-state (reversible) process and equilibrium concept. Because of reversible process: constant temperature, pressure and composition are required for equilibrium. In presence of external field (e.g. gravitational field), the constancy of pressure may be reduced, but requirement of constant temperature is still valid.

Under non-isothermal conditions, all mass and heat exchange processes are irreversible. This situation does not allow to achieve the equilibrium process; the classic Gibbs criterions of equilibrium are not satisfied. In the real hydrocarbon system, we have vertical and lateral local thermal gradient of range presented in the Table 3. During the irreversible process of change of mass and heat in the porous media, all properties (density, pressure, temperature, composition, specific entropy, specific enthalpy etc.) are function of time and position (see eq. 1–3). We assume that processes running in the porous media are close to equilibrium state, so have low "turbulences". The Gibbs criterion of equilibrium must be replaced by the concept of local thermodynamic equilibrium, the Onsager theory and the Prigogine minimum entropy production principle (de Groot, Mazur 1962; Haase 1969).

5.3.1. The fundamental coupling and coupled processes of mass and energy transfer in porous media

The confirmation that mass and heat transfer are coupling processes may be found in many reference textbooks (e.g. De Groot, Mazur 1962; Haase 1969, and Kondepudi, Prigogine 1998). The thermal diffusion process is coupled with the heat conduction process and may run (in some conditions) in opposite direction to the ordinary diffusion (opposite process to the Fick diffusion). The thermal diffusion process is forced by the thermal gradient and follows from connection of energy flow with particle motion. The energy flow consists of the kinetic transport of particles. With the heat flow there is associated the motion of particles in the mixture. The energy is transported in the translational motion. Parallel to the movement of particles with energy the phenomenon of concentration gradient is created. The thermal diffusion is the conjugated process with the non-equilibrium heat conduction process. The non-equilibrium heat conduction process creates entropy in the system and the thermal diffusion process diminishes the entropy in the some time and elementary volume.

Because of coupling of both processes: heat conduction and diffusion, two secondary orders processes are invoked (assuming no chemical reactions in the system):
- Soret effect (thermal diffusion, compositional gradient driven by thermal gradient),
- Dufour effect (heat flow driven by the compositional gradient).

The secondary phenomena related to the fundamental coupling processes are described by including additional terms to the First Law equation for single processes:
- by adding to the right side of Fick equation the proportional to the pressure and temperature gradient term one may find the diffusion flow of substance is driven by ordinary diffusion, pressure gradient (baro-diffusion) and thermal gradient (thermal diffusion),
- by adding to the right side of Fourier equation the term related to the concentration gradient, one may find that the heat conduction is result not only temperature gradient (conduction) but also concentration gradient (effect of Dufour).

The equations of coupled processes for binary system may be written:

$$J_1 = L_{11}X_1 + L_{12}X_2 \tag{6}$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \tag{7}$$

or may be written in matrix form:

$$\begin{bmatrix} J_1 \\ J_2 \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} \tag{8}$$

where:

X_1, X_2 — thermodynamic force,
J_1, J_2 — heat and mass flow,

L_{11}, L_{22}, L_{21}, L_{22} — phenomenological coefficients:

L_{12} — the coupling coefficient showing the effect of mass transfer (diffusion) on energy transfer (related to Dufour effect), for binary system:

$$D'' = \frac{L_{12}}{\rho \cdot c_1 \cdot c_2 \cdot T^2}$$ — Dufour coefficient;

c_1, c_2 — concentration of component 1 and component 2,

ρ — density of fluid,

L_{21} — the coupling coefficient showing the effect of energy transfer on mass transfer (diffusion) (related to the Soret effect — the estimation of thermal diffusion coefficient in oil/gas condensate system is very difficult (Seoris et al. 1998)) (from Onsager relation $L_{12} = L_{21}$), for binary system:

$$D' = \frac{L_{21}}{\rho \cdot c_1 \cdot c_2 \cdot T^2}$$ — Soret coefficient;

L_{11} — the thermal transfer coefficient (in absence of diffusion flow, eg. single component system) (Fourier's Law), for binary system:

$$\lambda = \frac{L_{11}}{T^2}$$ — thermal conductivity of fluid;

L_{22} — diffusion (mass transfer coefficient) (e.g. in absence of thermal field) (Fick's Law), for binary system:

$$D = \frac{L_{22} \cdot \mu_{22}}{\rho \cdot c_2 \cdot T^2}$$ — isothermal (Fick's) diffusion coefficient,

μ_{22} — chemical potential of component "2".

The basic processes are defined by the diagonal coefficients in matrix, the secondary processes are defined by the off-diagonal terms.

Because the processes of diffusion of matter and transfer of energy are coupled, thermal conduction will have an effect on diffusion. Diffusion process has the effect of redistribution of mass throughout whole system, in an attempt to achieve the equilibrium state (maximum entropy, minimum potential). The diffusion process achieves by mass transfer — each molecule of mater carries some entropy with it.

Let assume only a single process (diffusion or conduction):

$$J_1 = L_{11} X_1 \qquad (9)$$

• simple conduction process without diffusion or

$$J_2 = L_{22} X_2 \qquad (10)$$

simple diffusion without heat conduction process.

When we add secondary coupling process, we can show that:

$$J_1 = L_{11} X_1 + L_{12} X_2 \qquad (11)$$

where:

L_{12}— coupling coefficient of effect of mass transfer on energy transfer (thermal diffusion)

and for mass transfer:

$$J_2 = L_{21}X_1 + L_{22}X_2 \tag{12}$$

where:

L_{21}— coupling coefficient of effect of energy transfer on diffusion (Dufour effect).

When we consider ternary mixture, we could write two additional terms to the eq. (11)–(12) and additional equation related to diffusion flux of second component:

$$J_1 = L_{11}X_1 + L_{12}X_2 + L_{13}X_3 \tag{13}$$

$$J_2 = L_{21}X_1 + L_{22}X_2 + L_{23}X_3 \tag{14}$$

$$J_3 = L_{31}X_1 + L_{32}X_2 + L_{33}X_3 \tag{14a}$$

The first equation is related to the heat flux, the next two to the diffusion flow of the component No. 1 and No. 2. The diffusion flow of component No. 3 is equal $J_3 = -(J_1 + J_2)$. The thermodynamic forces X_3 has origin in a compositional gradient of second component. According to the Onsager principle (1931a, b) the coefficients must satisfy equations (symmetry principle):

$$L_{12} = L_{21}, \qquad L_{13} = L_{31}, \qquad L_{23} = L_{32} \tag{15}$$

Additionally, the production of entropy must be non-negative, so we have:

$$L_{11} \geq 0, \qquad L_{22} \geq 0, \qquad L_{33} \geq 0 \tag{16}$$

$$\left. \begin{array}{l} L_{11}L_{22} - L_{12}L_{21} \geq 0 \\ L_{11}L_{33} - L_{13}L_{31} \geq 0 \\ L_{33}L_{22} - L_{32}L_{23} \geq 0 \end{array} \right\} \tag{17}$$

Some of cross coefficients have to be zero because of restriction of Curie principle (De Groot, Mazur 1962; Haase 1969; Wiśniewski et al. 1974; Gumiński 1984; Kondepudi, Prigogine 1998).

5.3.2. The entropy balance in the presence of thermal gradient in the porous media

The change of entropy inside the system may be found by balance equation:

$$\frac{\partial S}{\partial t} = \frac{\partial S_e}{\partial t} + \frac{\partial S_i}{\partial t} \tag{18}$$

where

$$\frac{\partial S}{\partial t} = \int_V \frac{\partial(\overline{\rho}s)}{\partial t} dV$$

$$\frac{\partial S_e}{\partial t} = -\int_\Omega J^{S,tot} d\Omega$$

$$\frac{\partial S_t}{\partial t} = \int_V \sigma dV$$

where:

$J^{S,tot}$ — the total flux density of entropy [W/(K·m²)],

Ω — surface area of system [m²],

σ — volume density of entropy production in the time [W/(K·m³)].

The eq. (18) may be written in different form:

$$\int_V \frac{\partial(\overline{\rho}s)}{\partial t} dV = -\int_\Omega J^{S,tot} d\Omega + \int_V \sigma dV \tag{18a}$$

The reversible processes are running by zero production of entropy inside the system. In case of no existence of thermodynamic equilibrium the production of entropy inside the system is positive, because it is related to the non-equilibrium thermodynamic process (or processes) passed in the system. The product of entropy production rate (σ) and temperature (T) is called dissipative function (Wiśniewski et al. 1974):

$$\psi \equiv T \cdot \sigma \geq 0 \tag{19}$$

In the case of separation of phase surface — the entropy quantity has to be related to the elementary surface, instead of the total volume. The entropy production rate productivity is defined using the equation of entropy balance in the elementary volume of porous media Δv (Δx, Δy, Δz). The entropy flux $\vec{J}^{S,tot}(\vec{J}_x^{S,tot}, \vec{J}_y^{S,tot}, \vec{J}_z^{S,tot})$ during Δt through the cross-section — in direction x, y, z, may be written:

$$\frac{\partial}{\partial t}(\overline{\rho} \cdot s \cdot \Delta x \Delta y) = \tag{20}$$

$$= -\left(J_x^{S,tot} \Delta y \Delta x \Big|_x^{x+\Delta x} + J_y^{S,tot} \Delta x \Delta z \Big|_y^{y+\Delta y} + J_z^{S,tot} \Delta x \Delta y \Big|_z^{z+\Delta z} \right) + \sigma \cdot \Delta x \Delta y \Delta z$$

The left side in the eq. (20) describes the rate of entropy change; the first term in the right side is the net influx of entropy. The last term on the right side is the rate of entropy production for elementary volume.

By dividing the entropy balance equation (20) by $\Delta x \Delta y \Delta z$ and by taking the time and $\Delta x \Delta y \Delta z$ going to zero and apply the Gauss theorem — the equation may be written in the vector form:

$$\frac{\partial(\overline{\rho}s)}{\partial t} = -\mathrm{div}(\vec{J}^{S,tot}) + \sigma \tag{21}$$

Equation (21) together with equation (20) formulates the local mathematical expression for the Second Law of Thermodynamics:

$$\sigma \geq 0 \tag{22}$$

The eq. (21) is formally a balance equation for entropy density ρs with a source term σ, which satisfies the important inequality (22) (de Groot, Mazur 1962, eq. III.10–11). The eq. (21) can be rewritten in the form (by apply of mass continuity equation):

$$\overline{\rho}\frac{Ds}{Dt} = -\mathrm{div}(\vec{J}^{S}) + \sigma \tag{23}$$

where entropy flux $\vec{J}^{S}$ is difference between the total entropy flux $\vec{J}^{S,tot}$ and the convective term $\rho \cdot s \cdot \vec{v}$:

$$\vec{J}^{S} = \vec{J}^{S,tot} - \overline{\rho} \cdot s \cdot \vec{v} \tag{24}$$

where:

$\vec{v}$ — velocity vector [m/s].

The first term in the right side of eq. (23) is responsible for entropy fluxes, and the last term is "production of entropy". The simplified (without chemical reaction, for non-elastic fluids) form of entropy production equation has form (de Groot, Mazur 1962):

$$T \cdot \sigma = -\vec{J}^{S} \cdot \nabla T - \sum_{k=1}^{nc} \vec{J}_{k} \cdot (\nabla \mu_{k} + \vec{F}_{k}) \tag{25}$$

or

$$T \cdot \sigma = -\vec{J}^{S} \cdot \nabla T - \sum_{k=1}^{nc} \vec{J}_{k} \cdot (\nabla \widetilde{\mu}_{k}) \tag{25a}$$

where:

$\vec{F}_{k}$ — vector represents the external force (gravity) [N/mole],

$\widetilde{\mu}_{k}$ — chemical potential of i-component in the presence of gravity [J/mole],

and $\vec{J}_{k}$ is "diffusion flow" of substance k defined with respect to the barycentric motion velocity according to the formula:

$$\vec{J}_{k} = \rho_{k}(\vec{v}_{k} - \vec{v}) \tag{26}$$

The other equation of entropy production may be written, when heat flow term is defined by

$$\frac{\vec{J'}_q}{T} = \vec{J}^S - \sum_{k=1}^{nc} \bar{s}_k \vec{J}_k \qquad (27)$$

where:

$\bar{s}_k$ — partial molar entropy of k-component [J/moleK].

The production entropy equation with heat flux density (with irreversible heat flow) is written by (de Groot, Mazur 1962):

$$\sigma = -\frac{1}{T^2} \vec{J'}_q \cdot \nabla T - \frac{1}{T} \sum_{k=1}^{nc} \vec{J}_k \cdot \nabla_T \tilde{\mu}_k \qquad (28)$$

where:

∇_T — isothermal part of gradient operator.

The form used in the eq. (28) is the most convenient to use in the describing diffusion phenomena in multicomponent mixtures.

5.3.3. The equilibrium conditions and stationary state of system in the porous medium and free/forced convection in the reservoir

In the porous medium may exist thermodynamic equilibrium as well as stationary state of first, second kind. During isothermal condition in reservoir, in case of end of secondary migration processes only gravitational force, interact on the reservoir fluid. Presence of this force allows fix mechanical equilibrium (de Groot, Mazur 1962; Kondepudi, Prigogine 1998). The existence of other thermodynamic forces like thermal gradient, composition gradient, external interaction with aquifer or additional hydrocarbon reservoir may make impossible to fulfil equilibrium conditions. The existence of external forces manifests itself in e.g. existence of free and forced convection is described in many papers (Jacqmin 1990; Riley, Firoozabadi 1998; Firoozabadi 1999; Ghorayeb, Firoozabadi 1999). In the second case, non-stationary and stationary states may be allowed in the reservoir. The type of stationary state depends on the number of forces interacted on the system. In the stationary state, the Prigogine principle "Minimum Entropy Production" is valid (de Groot, Mazur 1962; Haase 1969; Faissat 1994; Kondepudi, Prigogine 1998). In the stationary state, the rate of entropy production is zero, because of compensation of production entropy by outflow flux through boundary of system (Kondepudi, Prigogine 1998). The system discards the entropy generated by irreversible processes. The necessary condition to existence of stationary state is disappearing of all fluxes in the system. *"The stationary irreversible states ... may be described by the extreme principle, according to which the entropy increment per every second has a minimum value, being the state stationary. It is impossible to mix up such stationary irreversible states with the equilibrium states, where the entropy enlargement per every second is zero"* (Prigogine 1955).

5.4. Temperature field in the porous medium

Let us discuss the process of heat and mass flow in porous medium. Entropy production per unit volume (as effect of single process — heat conduction) is defined by formula:

$$\sigma = \vec{J}_q \cdot \mathrm{grad}\left(\frac{1}{T}\right) \tag{29}$$

where:

$\vec{J}_q$ — heat flux density [W/m^2].

If we assume that thermal gradient is in vertical direction, we may write:

$$\sigma(z) = \vec{J}_{q,z}\frac{\partial}{\partial z}\frac{1}{T(z)} = -\vec{J}_{q,z}\frac{1}{T^2}\frac{\partial T(z)}{\partial z} \tag{30}$$

If we analyse the heat balance equation in the porous medium (restricted to the conduction and single component), we can see that in stationary state the heat flow is uniform, otherwise there will be an accumulation or depletion of heat, resulting in a time dependent temperature:

$$c_s\frac{\partial T}{\partial t} = -\nabla J_q \tag{31}$$

where:

c_s — volumetric heat capacity of system [J/K·m^3],
λ — heat conduction coefficient [W/m·K].

$$J_q = -\lambda \cdot \mathrm{grad}T \tag{32}$$

By combining equations (31) and (32) for one dimension (vertical direction) it may be obtained:

$$c_s\frac{\partial T}{\partial t} = -\lambda\frac{\partial^2 T}{\partial z^2} \tag{33}$$

In the stationary state it is obvious that $T(z)$ is linear function of z and heat flux is constant. The heat conduction coefficient is generally function of material property. It is evident that based upon first Fourier Law eq. the vertical/lateral gradient may be constant only for small space: say 0–0.5 m. This is visible during comparing the vertical profile in the sand (or quartz) content as well as tortuosity, porosity, free/connate water and liquid hydrocarbon saturation. Assuming that system is convection free, the local thermal gradient may be expressed not only as a function of local vertical heat flux density but also as a function of type rock and fluid properties, because of function (34):

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$$\lambda = \lambda(q, \phi, S_{wi}, S_{LHC}, F, T) \tag{34}$$

where:

q — geothermal heat flow density [W/m^2],

ϕ — porosity coefficient [–],

S_{wi} — connate water saturation [–],

S_{LHC} — saturation of liquid hydrocarbons [–],

F — rock compaction exponent [–].

In the near of vapour/liquid interface one may observe additional effect of increase of vertical thermal conductivity (e. i. local thermal gradient). The phenomenon Vaporizing Capillary Condensing effect (VCC) (Somerton 1992) may accelerate the heat transfer in this case. The VCC effect is observed in the steam flooding of oil reservoir, but is not very important in the typical oil/condensate systems.

In case of several lithological layers, $(n - 1)$ Fourier's equations may be rewritten as (Fig. 4a and 4b):

$$q \equiv -\lambda_1 \left(\frac{dT}{dz} \right)_1 = -\lambda_2 \left(\frac{dT}{dz} \right)_2 = \ldots = -\lambda_n \left(\frac{dT}{dz} \right)_n \tag{35}$$

The additional phenomena, which can affect the change of vertical heat flux density, may be:

1. Generation of heat (in case of natural radioactivity or radioactive waste deposition).
2. Natural convection in the slopes layers.
3. Regional flow of groundwater's (e.g. in the shallow layers).
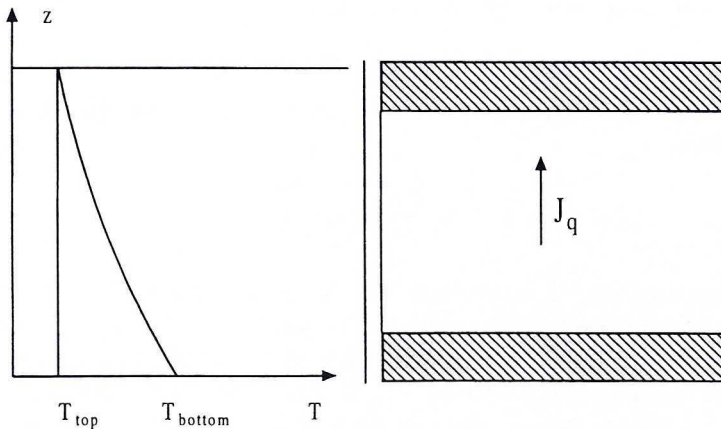4. Diapers phenomena.

Fig. 4a. The thermal gradient and heat flow in the quasi-homogenous reservoir with quasi-linear thermal gradient

Rys. 4a. Gradient geotermiczny i przepływ ciepła w prawie jednorodnym złożu dla prawie liniowego gradientu termicznego
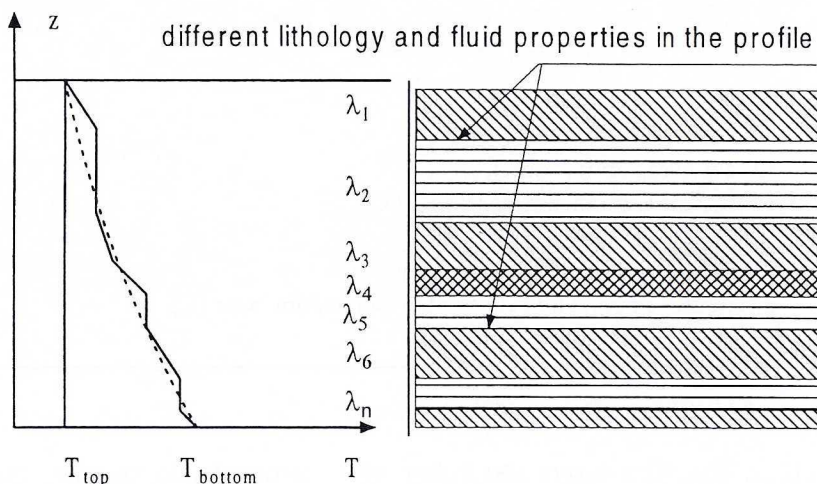
Fig. 4b. The thermal gradient and heat flow in the heterogonous reservoir with complicated lithology and different fluid properties and saturation (the dot line in the left side is average geothermal gradient; the layers with the zero thermal gradient (e.g. layer 2, layer 5) probably caused by free convection)

Rys. 4b. Gradient geotermiczny i przepływ ciepła w niejednorodnym złożu o skomplikowanej litologii oraz różnych własnościach płynu i nasycenia płynem złożowym i wodą złożową (linią kropkowaną oznaczono średni gradient geotermiczny; w warstwach złożowych z zerowym gradientem geotermicznym (warstwa 2 i 5) występuje prawdopodobnie proces konwekcji naturalnej

5. Local endothermic or/and exothermic chemical reaction in the sedimentary package.

Instead of solving of set of energy equation together with the component mass flux equation, the function of temperature is assumed, interpolated or extrapolated. It is very difficult to accurate solve energy equation in the reservoir based upon limited petrophysical and thermal data. Usually the temperature gradients are evaluated using existing temperature measurements in the appraisal/production well. The data are usually extrapolated using griding techniques or assumed as the linear function with depth.

6. Diffusion model of vertical grading of hydrocarbon system in presence of various thermodynamic forces (zero mass flux)

Assuming zero mass flux into and inside of reservoir following two classes of reservoir may be separated (Table 1):
1) static — full equilibrium field with zero or negligible geothermal gradient,
2) stationary state — with non-vanishing geothermal gradient.

We assume additionally, that conditions to ongoing free multicomponent convection in these types of reservoir are not fulfilled. It means that Rayleigh dimensionless number (Nield 1991) defined by equation (36):

$$Ra = g \frac{\beta \cdot \rho_f \cdot c_f \cdot \Delta T \cdot h \cdot k}{v_f \cdot \lambda_e} \qquad (36)$$

where:

c_f — fluid heat capacity [J/kgK],

β — coefficient of thermal expansion [1/K],

ρ_f — fluid density [kg/m^3],

v_f — coefficient of kinematic viscosity [m^2/s],

ΔT — difference temperature between top and bottom layer [K],

λ_e — effective conductivity [W/m·K],

h — thickness of layer [m],

g — gravity acceleration constant [m/s^2].

is below 32 in the slope layers and below 40 in horizontal layers. The necessary condition to account non-diffusion flow is discussed below.

6.1. The isothermal diffusion model of gravitational compositional grading with/without capillary condensation effect

6.1.1. The typical rock case

The equation describing the equilibrium conditions in hydrocarbon column has been derived first by Muskat (1930) and later by Sage, Lacey (1938). Unfortunately, the simplification of formulas describing the chemical potential made it impossible to define the real scale of gravity segregation. The conclusion from these earlier works caused adoption of uniform composition in the virgin state of hydrocarbon reservoirs for many years. The modern sampling techniques and enhanced frequency of downhole sampling (e.g. RFT) as well as more detailed chromatography analysis and PVT tests (Constant Composition Expansion, Constant Volume Depletion) indicate that variation of composition is high in the thick hydrocarbon reservoir (Schulte 1985)

The derivation of equilibrium conditions of isothermal compositional grading may be done using classical thermodynamics. The conditions of multicomponent equilibrium in the presence of gravity and in the isothermal conditions are following:

$$\text{grad } \mu_i + \vec{F}_i = 0 \qquad i = 1, ..., nc \qquad (37)$$

$$dT = 0 \qquad (38)$$

where:

μ_i — chemical (mole) potential of i-component [J/mole],

$\vec{F}_i = M_i g$ — gravity force having effect on every i-component [N/mole],

g — gravity acceleration constant [m/s²],

M_i — molecular mass of i-component [kg/mole],

or for one dimension (vertical) (isothermal):

$$\frac{d\mu_i}{dz} + M_i g = 0 \qquad i = 1, ..., nc \tag{39}$$

The eq. (40) allows to formulate the change of partial molar fugacity, in isothermal conditions and in presence of gravity force, in following form:

$$f_i(T, p(z), x_1, ..., x_{nc-1}) = f_i(T, p(z_0), x_{01}, ..., x_{0nc-1}) \exp\left(\frac{-M_i g(z - z_0)}{RT}\right) \tag{40}$$

where:

x_0 $(x_{01}, x_{02}, ..., x_{0nc-1})$ — composition of fluid on the z_0 level,

x $(x_1, x_2, ..., x_{nc-1})$ — composition of fluid on the z level,

In the isothermal conditions, the chemical potential is function of pressure and composition:

$$(\text{grad } \mu_i)_T = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,x} \text{grad } p + \sum_{j=1}^{nc-1}\left[\frac{\partial \mu_i}{\partial x_j}\right]_{T,P,x_{j\neq i}} \text{grad } x_j \tag{41}$$

and for vertical (one) direction:

$$\left(\frac{\partial \mu_i}{\partial z}\right)_T = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,x} \frac{dp}{dz} + \sum_{j=1}^{nc-1}\left[\frac{\partial \mu_i}{\partial x_j}\right]_{T,P,x_{j\neq i}} \frac{dx_j}{dz} \tag{42}$$

By substitution of isothermal hydrostatic gradient by:

$$\frac{dp}{dz} = -\rho(z)g \tag{43}$$

and using relation $\left(\dfrac{\partial \mu_i}{\partial p}\right)_T = \bar{v}_i$, (where $\bar{v}_i$ — partial molar volume of i-component), one may write for one dimension:

$$-M_i g = -\bar{v}_i \cdot \rho \cdot g + \sum_{j=1}^{nc-1}\left[\frac{\partial \mu_i}{\partial x_j}\right]_{T,P,x_{j\neq i}} \frac{dx_j}{dz} \tag{44}$$

The eqs. (37), (38) and (43) create the set of equilibrium conditions of multi-component system in the presence of gravity force with absence of capillarity forces and

adsorption for isothermal conditions of the whole system. This assumes that vertical thermal gradient in the reservoir is negligible.

Rearranging above equation (44) one may see:

$$\sum_{j=1}^{nc-1} \left(\frac{\partial \mu_i}{\partial x_j} \right)_{T,P,x_j} \frac{dx_j}{dz} = g(\rho \bar{v}_i - M_i) \tag{45}$$

The eq. (45) is valid for multicomponent isothermal case in presence of hydrostatic gradient. The eq. (45) may be written in the convenient matrix notation:

$$\mathbf{A} \cdot \mathbf{X} = \mathbf{C} \tag{46}$$

where:

$$\mathbf{A} = \frac{\partial \mu_i}{\partial x_j}$$

$$\mathbf{X} = \frac{dx_j}{dz}$$

$$\mathbf{C} = g(\rho \bar{v}_i - M_i)$$

The solution of system in the critical point is impossible because of singularity of matrix **A**. Based upon (46) relation, it is evident that two real cases may be important for detection and evaluation of isothermal compositional grading phenomena in multi-component system in presence of hydrostatic fluid equilibrium:

1. When gradient of mole fraction of *i*-component is very high in case of high value of vector **C** — it is equivalent when of high molecular mass of *i*-component of order 1000 (typically occurrence of asphaltenes (Hirschberg 1988; Firoozabadi 1998).
2. When determinant has low value **A** — it is typically in the near-critical volatile oils and gas condensate systems. The determinant **A** is going to zero in the near critical point and reaching zero in the critical point (Modell, Reid 1974; Lira--Galena 1992; Firoozabadi 1998).

The use of continuous thermodynamics (related to the semicontinuous mixtures) has been applied to calculation of compositional isothermal gradient in typical rocks by Lira-Galena (1994).

6.1.2. The tight rock case (the isothermal case for transition zone in the tight rock)

The previous case has been valid for presence of one phase in porous medium: gas or liquid. Whether the fluid changes state — going into second phase — it is very important to know position of transition called Gas-Oil Contact (GOC). In the grading system, the GOC may be saturated or unsaturated depending on the present temperature and pressure of rock and composition of fluid.

In the presence of transition region (gas/oil) in the very tight rock (where average capillary radius is below 1 μm — see Nagy 2002) we should include the additional term to the eq. (39) or (40) in the liquid phase. The eq. (39) or (40) for gas phase are invariable). The presented below modification is valid only in the transition two-phase region. Because of relatively short column of transition region (typically below 50 m), the transition zone may be treated as isothermal case.

In case of capillary condensation phenomena for liquid phase, we have eq. (47) (assuming δp_c very small, expanding chemical potential to the Taylor series, and restrict to the first term) (Nagy 2002):

$$\left(d\mu_i^L(p_L)\right)_T = \left(d\mu_i^L(p_v)\right)_T \frac{\partial \mu_i^L}{\partial (p_v - p_c)} p_c \tag{47}$$

or

$$f_i(p_v) = f_i(p_v)\exp\left(\frac{\bar{v}_{Li}}{RT} p_c\right) \tag{48}$$

The chemical potential pressure gradient in the transition zone may be evaluated from eq. (47):

$$\left(\frac{\partial \mu_i^L(p_L)}{\partial p}\right)_T = \left(\frac{\partial \mu_i^L(p_v)}{\partial p}\right)_T + \bar{v}_i^v(1 - c_i^L p_c) \tag{49}$$

where:

$$c_i^L = -\frac{1}{\bar{v}_i^L}\left(\frac{\partial \bar{v}_i^L}{\partial p}\right)_T$$

Rewriting the eq. (45) and/or (46) for pronounced compositional variation of liquid phase in the transition (GOC), we may obtain:

$$-Mg = -\bar{v}_i^L(1 - c_i^L p_c)\rho_L g + \sum_{j=1}^{nc-1}\left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,P,x_j\neq i} \frac{dx_j}{dz} \tag{50}$$

or after rearrangement:

$$\sum_{j=1}^{nc-1}\left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,P,x_j\neq i} \frac{dx_j}{dz} = [\bar{v}_i^L(1 - c_i^L p_c)\rho_L - M_i]\cdot g \tag{51}$$

where term $(1 - c_i^L p_c)$ has form inside the transition region (for liquid composition only, e.i for saturated volatile oils); for vapour phase eq. (51) has simplified form:

$$\sum_{j=1}^{nc-1}\left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,P,x_j\neq i} \frac{dx_j}{dz} = [\bar{v}_i^v\rho_v - M_i]\cdot g \tag{52}$$

The chemical potential of i-component in the liquid phase is evaluated at the pressure $p_L = p_v - p_c$ using eg. (51), and the chemical potential of i-component in the gas phase is evaluated at the reservoir pressure p_v using eq. (52). The term $(c_i^L p_c)$ in the right side of eq. (51) is vanishing in the vicinity of critical point. In the real situation in porous medium, where exist zone with high/moderate and low permeability, capillary pressure can change the vertical gradient of composition in the reservoir on the GOC. The similar capillarity effect may be evaluated in the presence of additional thermal gradient in the field.

6.1.3. Saturated Gas-Oil Contact (sGOC) and saturated pressure in presence of capillary condensation phenomenon in uns table thermodynamic conditions

6.1.3.1. Thermodynamics of capillary condensation vapour — liquid system (Nagy 2002)

A capillary condensation phenomena (for the pore radius below 10^{-6} m) at saturation point of reservoir fluid occurs three type of chemical potential (or fugacity):

$$\mu_i^L = \mu_i^V = \mu_i^{Vad}, \qquad i = 1, ..., n_c \tag{53}$$

or

$$f_i^L(p_v - p_c, T, x_1, x_2, ..., x_{nc}) - f_i^V(p_v, T, y_1, y_2, ..., y_{nc}) = 0, \tag{54}$$
$$i = 1, ..., n_c$$

material balance equation group:

$$\sum_{i=1}^{nc} x_i - 1 = 0 \tag{55}$$

$$\sum_{i=1}^{nc} y_i - 1 = 0 \tag{56}$$

The Laplace equation:

$$p_v - p_L - \frac{2 \cdot \sigma_{IFT}}{r_e} = 0 \tag{57}$$

the modified Kelvin equation (based on FHH equation (see Nagy 2002)):

$$\ln\left(\frac{p_v}{p_v^\infty}\right) = -\frac{2 \cdot \sigma_{IFT} \cdot v_L}{R \cdot T \cdot (r - t)} \tag{58}$$

where:
  r — capillary radius [m],
  t — film thickness of wetting fluid inside capillary [m];

interfacial multicomponent surface tension:

$$\sigma_{\text{IFT}}^{1/E} = \frac{p_v}{Z^v \cdot R \cdot T} \sum_{i=1}^{nc} \left[\left(\frac{Z_v}{Z_L} \right) \cdot x_i - y_i \right] \cdot \pi_i \tag{59}$$

where:

σ_{IFT} — interfacial surface tension (IFT) [N/m],

Z^v, Z^L — vapour and liquid phase compressibility factor [–],

E — empirical dimensionless constant [–],

π_i — parachor of i-component [–].

6.1.3.2. Bulk and capillary dew/bubble point (Nagy 2002)

Based upon above derivation difference between bulk and capillary condensate dew point ($N_v = 1$, where N_v — vapour phase mole fraction) following equations may be formulate:

$$F(N_v = 1, p_c(r,t) = 0) \equiv 1 - \sum_{i=1}^{nc} \frac{y_i}{K_i} = 0 \tag{60}$$

$$F(N_v = 1, p_c(r,t) \neq 0) \equiv 1 - \sum_{i=1}^{nc} \frac{y_i}{K_i} \exp(-\varepsilon_i p_c(r,t)) = 0 \tag{61}$$

where:

$$\varepsilon_i = \frac{\overline{V}_i^L}{R \cdot T} \text{ — component Poynting factor,}$$

Similar equation may be written for bubble point:

$$F(N_v = 0, p_c(r,t) \neq 0) \equiv \left[\sum_{i=1}^{nc} x_i K_i \exp(\varepsilon_i p_c(r,t)) \right] - 1 = 0 \tag{62}$$

6.1.3.3. Equilibrium constant modification for account capillary effects (Nagy 2002)

The equation the new capillary condensation equilibrium (assuming constant partial molar volume) has form:

$$K_i = K_i^\infty \cdot \exp(\varepsilon_i p_c(r,t)) \tag{63}$$

6.1.3.4. The Modified Tangent Plane Criterion for Capillary Condensation (MTPCCC) (Nagy 2002)

Thermodynamic stability of phase $\underline{x}_0(x_{01},...,x_{0nc})$ is equivalent of reaching absolute minimum of Gibbs free energy of system (Michelsen 1982a, b). This condition may be expressed as inequality:

$$F(\underline{y}) = \sum_{i=1}^{nc} y_i [\mu_i(\underline{y}) - \mu_i(\underline{x}_0)] \geq 0 \tag{64}$$

for all composition data of origin phase $\underline{y}(y_1, y_2,...,y_{nc})$

Stability requires that tangent plane at no point lies above the surface of Gibbs free energy of initial phase $\underline{x}_0(x_{01},...,x_{0nc})$. Stability condition of equation (64) is tested in stationary points:

$$\left(\frac{\partial F}{\partial y_i}\right)_N \equiv \mu_i(\underline{y}) - \mu_i(\underline{x}_0) - F(\underline{y}) = 0 \tag{65}$$

or using fugacity coefficients for bulk liquid phase:

$$\ln Y_i - \ln \phi_i(\underline{y}^\infty) - \ln x_{0i} - \ln \phi_i(\underline{x}_0^\infty) = 0, \qquad i = 1, ..., n_c \tag{66}$$

or for capillary condensation liquid phase using equation (67):

$$\ln Y_i - \ln \phi_i(\underline{y}^\infty) - \ln x_{0i} - \ln \phi_i(\underline{x}_0^\infty) + \frac{\bar{v}_{Li}}{RT} p_c = 0, \qquad i = 1, ..., n_c \tag{67}$$

where:

$$Y_i = y_i \exp(-K), \qquad K \text{— non negative number} \tag{68}$$

and mole fraction of origin phase:

$$y_i = \frac{Y_i}{\sum_{i=1}^{nc} Y_i} \tag{69}$$

For instability of initial phase $\underline{x}_0(x_{01},...,x_{0nc})$ one may test using the verification of inequality:

$$\sum_{i=1}^{nc} Y_j \leq 1 \qquad \text{for stable system}$$

$$\sum_{i=1}^{nc} Y_j > 1 \qquad \text{for unstable system} \tag{70}$$

in all stationary points.

6.1.3.5. The algorithm to estimate of the saturated capillary condensation gas-oil contact (sGOC)

The algorithm for estimation of saturation pressure in the tight rocks for isothermal case is presented in the Fig. 5. In this scheme two solution method are preferable,
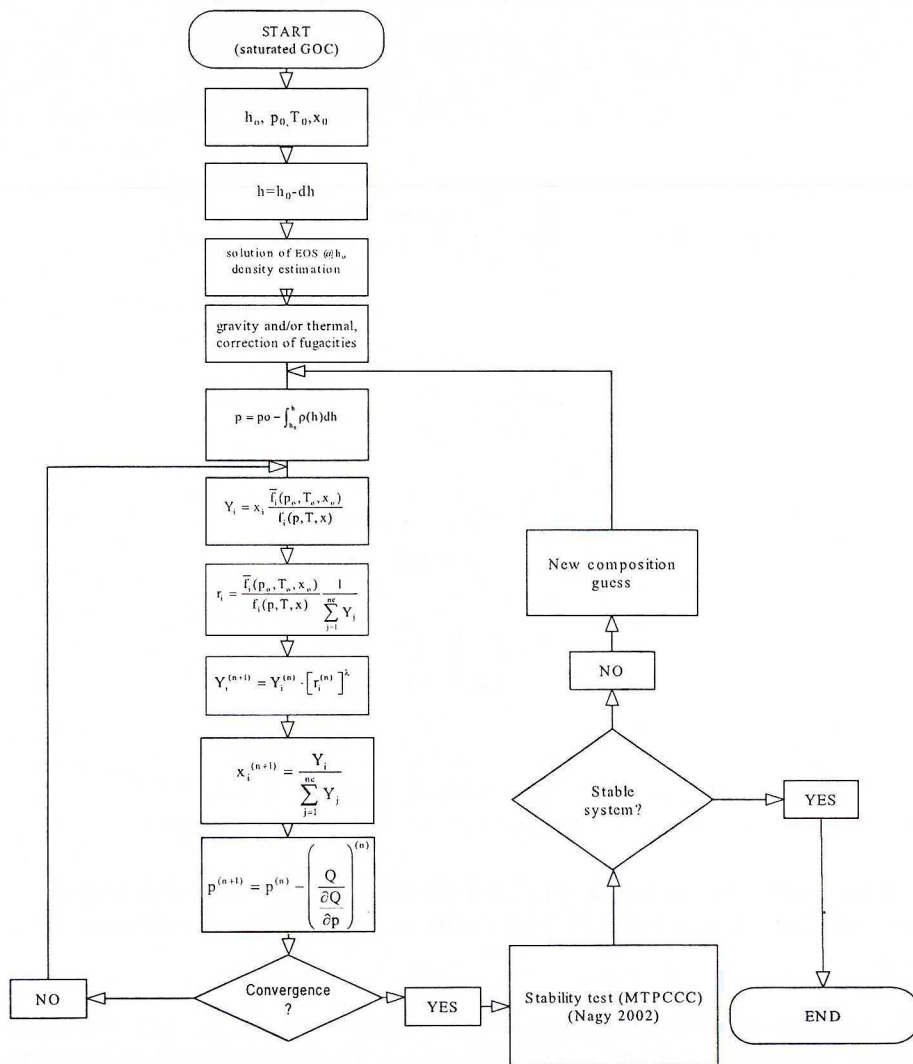

Fig. 5. The algorithm for estimation of grading composition and saturation pressure in the tight rocks (isothermal case) [modified from proposed by Whitson, Belery for bulk phase based on saturation pressure algorithm of Michelsen (1995)]

Rys. 5. Algorytm wyznaczający zmianę składu w profilu i ciśnienie nasycenia w skałach zbitych (przypadek izotermiczny) [zmodyfikowany algorytm Whitsona i Belery'ego (1995) na podstawie algorytmu Michelsen (1985) dla wyznaczania ciśnienia nasycenia]

simple successive substitution ($\lambda = 1$) or GDEM (General Dominant Eigenvalue Method) where λ-acceleration exponent (Crowe, Nishio 1975). The method has been tested in several papers (e.g. Nagy 1992a, b, 1996, 2002; Siemek, Nagy 2001; Kolenda et al. 2003).

For convergence of scheme, following criteria were selected:

$$|Q| \leq 10^{-13} \tag{71}$$

and

$$\left| \sum_{i=1}^{nc} \frac{\ln(r_i)}{\ln \dfrac{Y_i}{x_i}} \right| \leq 10^{-8} \tag{72}$$

where

$$Q = 1 - \sum_{i=1}^{nc} Y_i \tag{73}$$

$$Y_i = x_i \frac{\bar{f}_i(p_0, T_0, x_0)}{f_i(p, T, x)} \tag{74}$$

$$r_i = \frac{\bar{f}_i(p_0, T_0, x_0)}{f_i(p, T, x)} \frac{1}{\sum_{j=1}^{nc} Y_j} \tag{75}$$

$x_0(x_{01}, x_{02}, ..., x_{0nc-1})$ — composition of fluid on the z_0 level,
$x(x_1, x_2, ..., x_{nc-1})$ — composition of fluid on the z level.

6.2. The non-isothermal diffusion model of gravitational compositional grading with/without capillary condensation effect

The full extension of model described in the previous point 6.1 into non-isothermal conditions in porous medium is possible only with theory of non-equilibrium thermodynamics as described in the point 5.

6.2.1. The complete non-equilibrium model of grading phenomena

The full non-equilibrium model is based on the stationary state concept (Prigogine) using formulas described in point 5.

Because the chemical potential is function pressure, composition and temperature:

$$d\mu_k = \left(\frac{\partial\mu_k}{\partial p}\right)_{T,x} dp + \sum_{i=1}^{nc-1}\left(\frac{\partial\mu_k}{\partial x_i}\right)_{T,x_{i\neq k}} dx_i + \left(\frac{\partial\mu_k}{\partial T}\right)_{p,x} dT \qquad (76)$$

where first term derivative in the right side is called partial volume of k-component (for vapour phase and for unsaturated liquid phase):

$$\left(\frac{\partial\mu_k}{\partial p}\right)_{T,x} = \bar{v}_k \qquad (77)$$

and for transition zone (for liquid saturated composition):

$$\left(\frac{\partial\mu_k}{\partial p}\right)_{T,x} = \bar{v}_k^L \cdot (1 - c_k^L p_c) \qquad (78)$$

and the last term partial derivative is partial molar entropy of k-component:

$$\left(\frac{\partial\mu_k}{\partial T}\right)_{p,x} = -\bar{s}_k \qquad (79)$$

following relation may be written:

$$d\mu_k = \bar{v}_k dp + \sum_{i=1}^{nc-1}\left(\frac{\partial\mu_k}{\partial x_i}\right)_{T,x_{i\neq j}} dx_i - \bar{s}_k dT \qquad (80)$$

and in presence of mechanical (hydrostatic equilibrium), where $\nabla p = -\rho g$:

$$d\mu_k = \bar{v}_k \rho g + \sum_{i=1}^{nc-1}\left(\frac{\partial\mu_k}{\partial x_i}\right)_{T,x_{i\neq j}} dx_i - \bar{s}_k dT \qquad (81)$$

For the isothermal condition, using Gibbs-Duhem equation following relation is valid:

$$-v \cdot dp + \sum_{i=1}^{nc} x_i d_T\mu_i = 0 \qquad (82)$$

and additionally in the mechanical equilibrium state Gibbs-Duhem equation may be written:

$$\sum_{i=1}^{nc} \bar{\rho}_i \cdot (\mathrm{grad}\,\mu_i)_T = \mathrm{grad}\,p \qquad (83)$$

and

$$\sum_{i=1}^{nc} \bar{\rho}_i \cdot (\mathrm{grad}\,\tilde{\mu}_i)_T = \mathrm{grad}\,p \qquad (84)$$

or

$$\sum_{i=1}^{nc} x_i (\mathrm{grad}\, \widetilde{\mu}_i)_T = 0 \tag{85}$$

where

$\widetilde{\mu}_i = \mu_i + \psi_i$ — molar chemical potential of i component in the gravity field and $\nabla\psi_i = +M_i g,\ \psi = M_i g \cdot 2$

$\overline{\rho}_i$ — molar density of i component.

The eq. (85) which is valid in the mechanical equilibrium and in the constant temperature. Because only $(nc-1)$ diffusion fluxes are independent one may write:

$$\sum_{j=1}^{nc} \vec{J}_k \nabla_T \widetilde{\mu}_j = \sum_{j=1}^{nc-1} \vec{J}_j \nabla_T (\widetilde{\mu}_j - \widetilde{\mu}_{nc}) \tag{86}$$

The eq. (86) let to simplify the formula for entropy production:

$$\sigma = -\frac{1}{T^2} \vec{J'}_q \cdot \nabla T - \frac{1}{T} \sum_{k=1}^{nc-1} \vec{J}_k \nabla_T (\widetilde{\mu}_k - \widetilde{\mu}_{nc}) \tag{87}$$

The heat density flux $\vec{J'}_q$ is equal:

$$\vec{J'}_q = -\frac{1}{T^2} L'_{11} \nabla T - \frac{1}{T} \sum_{i=1}^{nc-1} L'_{1i} \nabla_T (\widetilde{\mu}_j - \widetilde{\mu}_{nc}), \qquad k = 1, ..., nc-1 \tag{88}$$

and diffusion flux for k-component $\vec{J}_k$

$$\vec{J}_k = -\frac{1}{T^2} L'_{k1} \nabla T - \frac{1}{T} \sum_{i=1}^{nc-1} L'_{ki} \nabla_T (\widetilde{\mu}_j - \widetilde{\mu}_{nc}), \qquad k = 1, ..., nc-1 \tag{89}$$

and finally in case of hydrodynamic (mechanical) equilibrium (using eq. (85) and using arbitrary chosen reference velocity (based upon Prigogine theory) (taken as molar fraction x_i):

$$\vec{J'}_q = -\frac{1}{T^2} L'_{11} \nabla T - \frac{1}{T} \sum_{m=1}^{nc-1} \sum_{i=1}^{nc-1} L'_{1i} A_{im} \nabla_T \widetilde{\mu}_m, \qquad k = 1, ..., nc-1 \tag{90}$$

$$\vec{J}_k = -\frac{1}{T^2} L'_{k1} \nabla T - \frac{1}{T} \sum_{m=1}^{nc-1} \sum_{i=1}^{nc-1} L'_{ki} A_{im} \nabla_T \widetilde{\mu}_m, \qquad k = 1, ..., nc-1 \tag{91}$$

where:

$$A_{im} = \delta_{im} + \frac{x_m}{x_{nc}} \tag{92}$$

δ_{im} — the Kronecker delta,

where phenomenological coefficients are following:

L'_{11} — phenomenological coefficient related to the heat transfer by conduction and by diffusion heat transport) (Fourier's Law),

L'_{1i} — phenomenological coefficient related to the heat transfer by diffusion of "k" and "i" components (not by conduction heat flow) (Dufour effect),

L'_{k1} — phenomenological coefficient related to the diffusion of k component driven by heat flow (Soret effect),

L'_{ki} — phenomenological coefficient related to the diffusion caused by isothermal compositional gradient (ordinary Fick's diffusion)

and

$$\left. \begin{array}{l} L_{i1} = L_{1i} \\ L_{ik} = L_{ki} \end{array} \right\} \tag{93}$$

and additional conditions which follows from Second Law Thermodynamics:

$$\left. \begin{array}{l} L_{11} \geq 0 \\ L_{ii} \geq 0 \\ L_{11}L_{ii} - L_{1i}^2 \geq 0 \\ L_{ii}L_{kk} - L_{ki}^2 \geq 0 \end{array} \right\} \tag{94}$$

The equation (91) may be rewritten in following way:

$$\vec{J}_k = -\frac{1}{T^2} L'_{k1} \nabla T - \frac{1}{T} \sum_{m=1}^{nc-1} \sum_{i=1}^{nc-1} L'_{ki} A_{im} \left\{ \vec{F}_i - \left(\frac{\partial \mu_i}{\partial p} \right)_{T,x} \cdot \rho \cdot g + \sum_{j=1}^{nc-1} \left(\frac{\partial \mu_i}{\partial x_j} \right)_{P,T,x_j \neq i} \nabla_T x_j \right\}, \tag{95}$$

$$k = 1, ..., nc - 1$$

If we assume stationary state in the reservoir, then the mass flux for every k-component has to be zero:

$$\vec{J}_k = 0, \qquad k = 1, ..., nc - 1 \tag{96}$$

Additionally local temperature gradient is steady $\left(\dfrac{\partial T}{\partial t} = 0 \right)$ and system is in the mechanical equilibrium. The eq. (96) formulates the necessary conditions for stationary state, when the right side of eq. (95) is equal zero. The condition zero mass diffusion fluxes in the mixture, eq. (96) may be written in the form:

$$-\frac{1}{T}\sum_{m=1}^{nc-1}\sum_{i=1}^{nc-1}L'_{ki}A_{im}\left\{(M_i-\bar{v}_i\rho)\cdot g+\sum_{j=1}^{nc-1}\left(\frac{\partial\mu_i}{\partial x_j}\right)_{T,p,x_j\neq i}\nabla_T x_j\right\}=-\frac{1}{T^2}L'_{k1}\nabla T, \tag{97}$$

$$k = 1, ..., nc - 1$$

The equation (97) formulates stationary state condition in existing hydrocarbon equilibrium of typical rocks with hydrodynamic equilibrium and thermal gradient.

6.2.2. Vertical variation models of hydrocarbon grading with thermal diffusion phenomenon

In the stationary state (assuming zero mass flux) in the presence of gravity and thermal field we have following set of equation, for all but one component (see eq. (51)):

$$\sum_{j=1}^{nc-1}\left(\frac{\partial\mu_i}{\partial x_j}\right)_{p,T,x_{i\neq j}}\nabla x_j=-(M_i-\rho\bar{v}_i)g-F_{Ti}\nabla\ln T \tag{98}$$

where:

μ_i — chemical potential of i-component [J/mole],

x_i — mole fraction of i-component [–],

M_i — molecular mass of i-component [kg/mole],

ρ — mass density [kg/m^3],

g — gravity acceleration constant [m/s^2],

$\bar{v}_i$ — partial molar volume of i component [m^3/mole],

F_{Ti} — term used to account the thermal diffusion [J/mole].

The term F_{Ti} may be evaluated using following models:

$$F_{Ti}=\frac{1}{M_m}(M_i h_m - M_m \bar{h}_i) \tag{99}$$

$$F_{Ti}=\frac{1}{v_m}(\bar{v}_i h_m - v_m \bar{h}_i) \tag{100}$$

$$F_{Ti}=\frac{1}{2v^*}(\bar{v}_i\Delta u_m^* - v_m\Delta u_i^*) \tag{101}$$

where

$$v_m=\sum_{i=1}^{nc}x_i\bar{v}_i \tag{102}$$

$$M_m = \sum_{i=1}^{nc} x_i M_i \tag{103}$$

$$h_m = \sum_{i=1}^{nc} x_i \overline{h_i} \tag{104}$$

$$\Delta u_i^* = \left(\frac{\partial \Delta u_m^*}{\partial n_i} \right)_{p,T,n_k} \quad \text{— partial molar energy of activation,} \tag{105}$$

n — number of moles,

Δu_m^* — function defined as viscosity to density ratio:

$$\Delta u_m^* = R \left(\frac{\partial \ln \frac{\mu_{vis}}{\rho}}{\partial \left(\frac{1}{T} \right) n_i} \right)_{p,x_i} - p \cdot T \left(\frac{\partial \ln \frac{\mu_{vis}}{\rho}}{\partial p} \right)_{T,x_i} \tag{106}$$

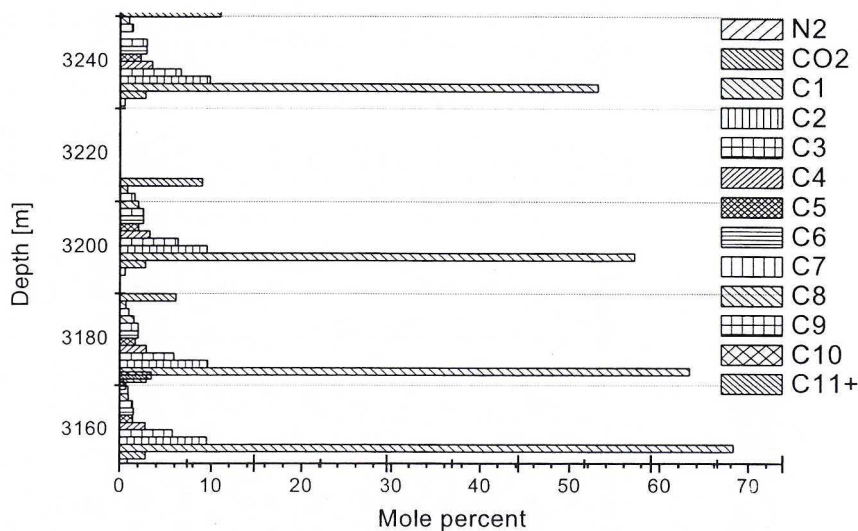μ_{vis} — dynamic viscosity coefficient of mixture.

Fig. 6. The vertical profile of composition of gas-condensate reservoir
(after data Montel, Gouel 1985, see Table 5 and Fig.7)

Rys. 6. Pionowy profil zmienności składu układu gazowo-kondensacyjnego
(na podstawie danych Montel, Gouel 1985, patrz także tablica 5 i rys. 7)

The comparison of isothermal grading data of Montel, Gouel (1985) with present work calculation using translated-modified Peng-Robinson EOS (Tsai, Chen 1998; Nagy 2002) at three depths [reference level — TVD (True Vertical Depth) 3174.5 m]

a — 3162.5 m, b — 3204.4 m, c — 3241 m

Porównanie danych Montela i Gouela (1985) z obliczeniami zmienności izotermicznej przy użyciu zmodyfikowanego równania Penga-Robinsona (VTPR-Tsai, Chen 1998 oraz Nagy 2002) na trzech głębokościach w odniesieniu do rzeczywistej głębokości TVD: 3174,5 m)

a — 3162,5 m, b — 3204,4 m, c — 3241m

| a				b				c			
Depth (TVD) 3162.50 m — Composition [mole%]				Depth (TVD) 3204.50 m — Composition [mole%]				Depth (TVD) 3241 m — Composition [mole%]			
	Calc	Exp	%Error		Calc	Exp	%Error		Calc	Exp	%Error
C1	66.48	68.31	−2.69	C1	57.41	57.20	0.37	C1	53.21	53.06	0.29
C2	9.62	9.52	1.09	C2	9.43	9.53	−1.08	C2	9.16	9.84	−6.94
C3	5.72	5.77	−0.80	C3	6.09	6.33	−3.85	C3	6.09	6.65	−8.43
C4	2.70	2.75	−1.88	C4	3.05	3.24	−5.94	C4	3.12	3.49	−10.63
C5	1.52	1.45	5.12	C5	1.87	2.01	−7.08	C5	1.97	2.25	−12.42
C6	1.76	1.50	17.49	C6	2.38	2.51	−4.98	C6	2.61	2.88	−9.27
C7	1.70	1.36	24.77	C7	2.46	2.50	−1.67	C7	2.76	2.93	−5.71
C8	1.30	0.94	38.37	C8	1.99	1.98	0.44	C8	2.28	2.31	−1.35
C9	0.77	0.88	−11.95	C9	1.25	1.61	−22.43	C9	1.46	1.39	4.90
C10	0.52	0.45	14.94	C10	0.85	0.78	9.11	C10	1.00	0.95	5.30
C11+	4.32	3.44	25.71	C11+	9.88	9.02	9.48	C11+	13.12	11.00	19.26
CO2	2.88	2.77	4.00	CO2	2.80	2.75	1.85	CO2	2.72	2.75	−1.01
N2	0.70	0.87	−19.87	N2	0.55	0.54	2.45	N2	0.50	0.51	−2.39
AAD(%)			12.48	AAD(%)			4.58	AAD (%)			4.74
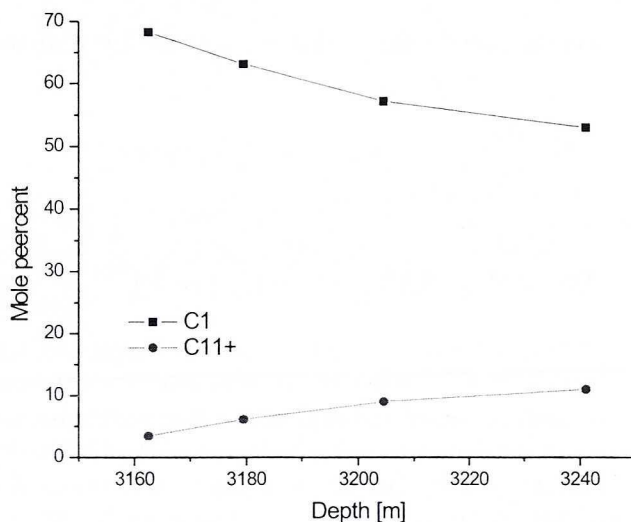
Fig. 7. The change of methane (C_1) and heavy fraction (C_{11+}) in the depth using eq. (45) and VTTP EOS (Tsai, Chen 1998 and Nagy 2002) for Montel, Gouel (1985) system

Rys. 7. Zmiana składu metanu (C1) i frakcji (C_{11+}) w funkcji głębokości według równania (45) i równania stanu Penga-Robinsona (VTPR-Tsai, Chen 1998 oraz Nagy 2002) na podstawie danych Montel, Gouel (1985)

The appropriate models (99)–(101) are given respectively by Haase (1969) (eq. (99)) Kempers (1989) (eq. (100)) and Belery-da Silva/Dougherty-Drickamer (1990) (eq. (101)). The model of Belery-da Silva is not recommended (Hoeier, Whitson 2000).

In case of tight rocks and transition region in the capillary-adsorption area, following modification in the eq. (98) [similar to isothermal model (51)] may be written for liquid saturated composition only (for the vapour composition unchanged model is preferred):

$$\sum_{j=1}^{nc-1} \frac{\partial \mu_i}{\partial x_j} \frac{dx_j}{dz} = \left[\bar{v}_i^L (1 - c_i^L p_c) \rho_L - M_i \right] \cdot g - F_{Ti} \nabla \ln T \tag{107}$$

6.2.3. The simplified non-isothermal model ("passive" thermal diffusion)

The 1D model described by eq. (98) — may be simplified after making some assumptions regarding the impact of secondary order processes in the vertical profile. The simplified attitude is possible only in some cases, when the impact of thermal diffusion is small (e.g. when the thermal gradient is small and below moderate

and the fluid is far from critical conditions). When we omit the last term in the eq. (98), we may write:

$$\sum_{j=1}^{nc-1}\left(\frac{\partial\mu_i}{\partial x_j}\right)_{p,T,x_{i\neq j}}\nabla x_j = -(M_i - \rho\bar{v}_i)g \tag{108}$$

$$\nabla x_i = M_i g - \bar{s}_i\nabla T, \qquad i = 1, ..., nc - 1 \tag{109}$$

We may see that eq. (108) is the same as in the isothermal case, and additional term compare to isothermal model in the compositional gradient of *i*-component is on the right side of eq. (45). This may be considered as slightly better isothermal case, known in the literature as "passive" thermal model — first proposed by Bedrikovetsky (1993) and later Padua (1999). Analysis done by Hoeier, Whitson (2000) shows that difference between isothermal and "passive" thermal is so small, that this substitutive model is not recommended.

7. Impact of capillary condensation-adsorption forces on the composition of oils and gas condensates

Capillary-adsorption forces can cause significant difference in case of two-phase reservoirs (gas-condensate, volatile oil) inside classical and capillary-condensation phase envelopes (Nagy 2002).

7.1. Saturated pressure in the presence of capillary condensation and compositional vertical gradient phenomena

In presence of capillary and adsorption forces the position of saturated Gas Oil Contact may be moved. It is because of existence of additional term related to the capillary pressure. The equilibrium constant is defined by the gas phase pressure (for gas component fugacity) and for liquid phase pressure (for liquid component fugacity). The saturation pressure in the absence/presence of capillary condensation phenomenon in the tight rock (reference data from Smith et al. 2000) in the vertical profile using capillary condensation model described by Nagy (2002) is presented in the Fig. 10. The movement of pressure in the profile is caused by introducing into equilibrium constant the correction term related to capillary pressure and possible thickness of liquid film in the narrow capillaries (10^{-8} m).
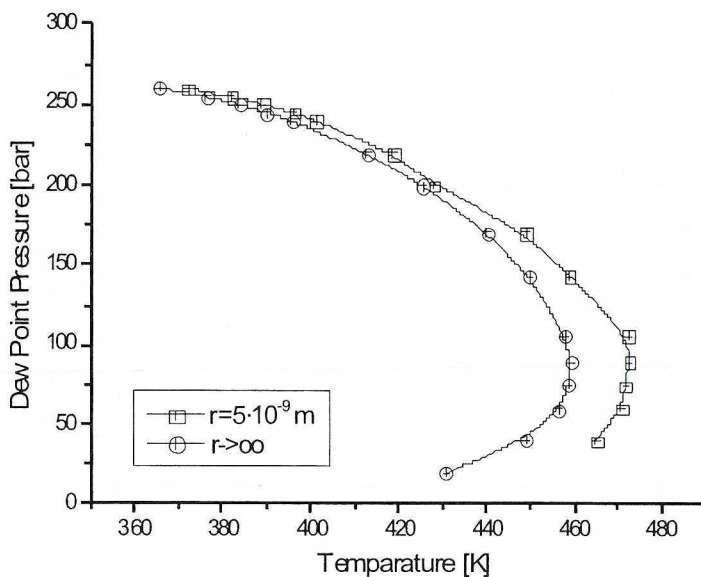
Fig. 8. Impact of pore radius of porous media on phase boundary movement (Nagy 2002)

Rys. 8. Wpływ wielkości promienia porowego na przesunięcie krzywej nasycenia w złożach gazowo-kondensacyjnych (Nagy 2002)
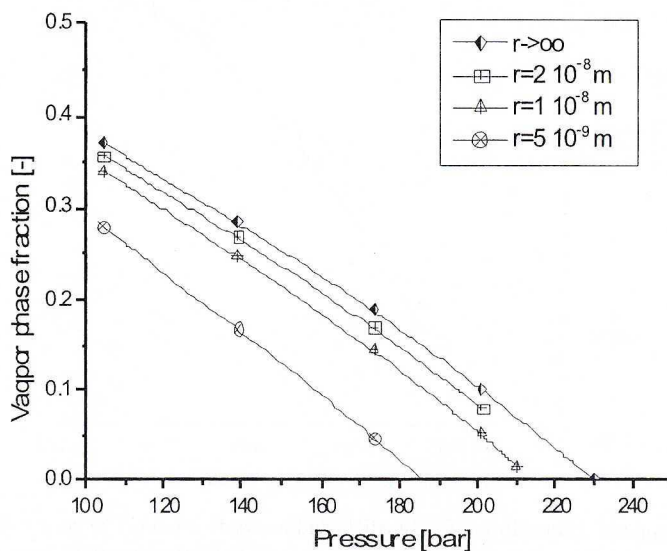

Fig. 9. The change of saturation curve in presence of curvature of porous media in volatile oil systems (Nagy 2002)

Rys. 9. Przesunięcie krzywej nasycenia w ośrodku porowatym z uwzględnieniem zmienności porów w złożu lekkiej ropy naftowej (Nagy 2002)
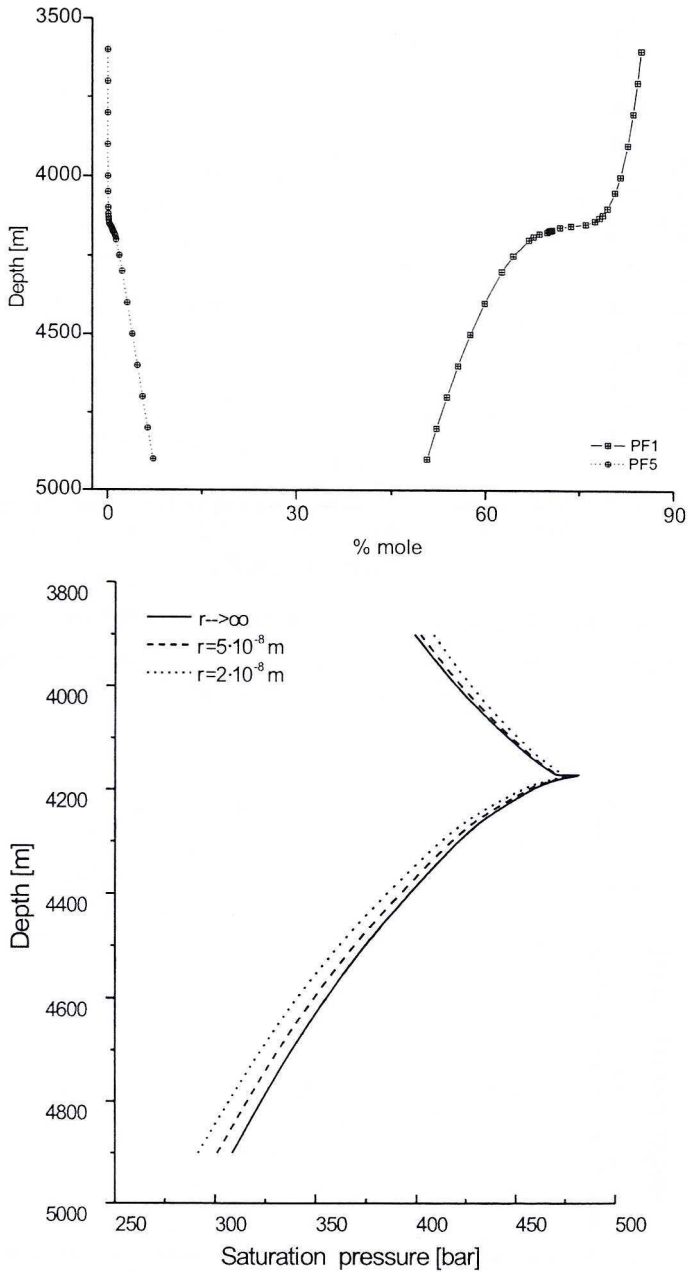
Fig. 10. The change of composition of light (PF1) and heavy fraction (PF5) versus depth (upper) and change of saturation pressure in the absence/presence of capillary condensation phenomenon in the tight rock ($r = 5\cdot10^{-8}$ m, $r = 2\cdot10^{-8}$ m) in vertical profile — reference data from Smith et al. (2000) (below)

Rys. 10. Zmiana składu lekkiej (PF1) i najcięższej frakcji (PF5) w funkcji głębokości (powyżej) oraz zmiana ciśnienia nasycenia dla typowych i zbitych skał w profilu pionowym — dla danych: Smith et al. (2000) (poniżej)

8. Diffusion-Convection model (non-zero flux model). Free and forced convection

The diffusion and convection processes in porous medium are possible, but it is very hard to find in the literature their simulation results. The attempts of Jacqmin (1990) and Firoozabadi et al. (1998 and 2000) are rather theoretical attitude than real. The most complicated boundary conditions as well as complication with accurate description of thermal lateral and vertical gradients are responsible for difficulties of real solutions. The separate question is correctness of model of multicomponent thermal diffusion in hydrocarbon mixture.

When we consider the free and forced convection in the reservoir, we may check the structure of rocks. It is very low probability that in the sub- and mesopores (Everett 1972) (below 1 μm, where capillary-adsorption forces are active) may be started free convection.

The minimum permeability for thick reservoir (e.g. 300 m) with high temperature gradient (difference in temperature 15°C) and with average of other rock and fluid parameters may be estimated in extreme case (horizontal layer) for $Ra = 40$ (see Elder 1965; Combarnou, Boria 1975):

$$k = \frac{Ra \cdot v_f \cdot \lambda_e}{\beta \cdot g \cdot \rho_f \cdot c_f \cdot \Delta T \cdot h} = \sim 10^{13} \text{ m}^2 = \sim 100 \text{ mD} \tag{110}$$

where:

c_f — fluid heat capacity [kg/m^3],

β — coefficient of thermal expansion [1/K],

ρ_f — fluid density [kg/m^3],

v_f — coefficient of viscosity [m^2/s],

ΔT — difference temperature between top and bottom layer [K],

λ_e — effective conductivity [W/m·K],

h — thickness of layer [m],

g — gravity acceleration constant [m/s^2].

This value is equivalent to the average porous radius greater than 2 μm (Nagy 2002) and is not classifying as a tight rock. The existence of forced convection in presence of external forces is possible — the Darcy flow is during normal exploitation of reservoir is example of forced convection in the field. Because of considering only "virgin" state — the forced convection is not analysed in the typical systems, yet in some of fields, then post secondary migration mixing may occur, the forced convection may be driving force of non-steady state segregation process.

It is probably impossible to start ongoing convection in the tight rocks, where permeability is below 1 mD. The minimal vertical temperature difference necessary to start of convection (for 500 m thick layer) is:

$$\Delta T = \frac{Ra \cdot v_f \cdot \lambda_e}{\beta \cdot g \cdot \rho_f \cdot c_f \cdot h \cdot k} = \sim 700 \text{ K} \tag{111}$$

This is 20 times higher, when compared with max gradient in the hydrocarbon reservoirs (see Table 6). The numerical attempts of analysis of convection of hydrocarbons in the low permeability system $(0.01–1 10^{-15} \text{ m}^2)$ are presented in the Ghorayeb, Firoozabadi (2000). The results of computation show that the difference of compositional gradient without and with convection is small — compare with the sampling error. The other case of — double porosity reservoir (or naturally fracture reservoir — NFR) is not discussed here, because this type of reservoir contain primary porosity (matrix porosity) of capillary radius below 1 μm and secondary porosity (fractures, with aperture above 10^{-4} m) where convection — instead diffusion process — is dominant
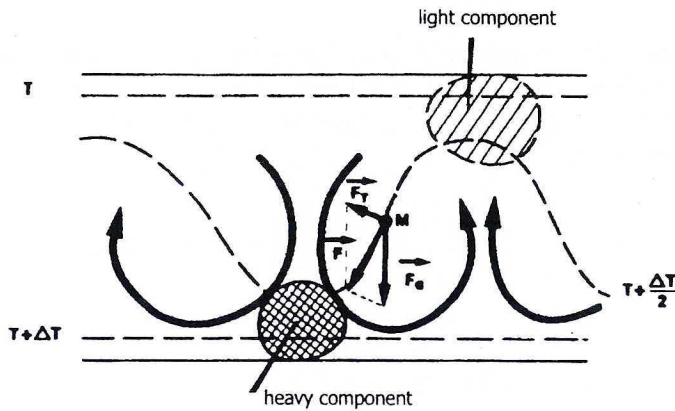

Fig. 11. The mechanism of segregation of components in presence of thermal and gravity forces for stable convection-diffusion processes (for high permeability system, Ra > 40)
(after Montel and Gouel 1985)
Rys. 11. Mechanizm segregacji składników węglowodorowych w obecności gradientu termicznego i sił grawitacji dla stabilnego procesu dyfuzyjno-konwekcyjnego (dla złóż o dużej przepuszczalności, Ra > 40) (na podst. Montel, Gouel 1985)

TABLE 6

Maximal geothermal gradient in the hydrocarbon reservoirs (Haenel et al. 1988)

TABLICA 6

Maksymalne gradienty geotermiczne zaobserwowane w złożach węglowodorowych (Haenel i in. 1988)

Type of gradient	Max gradient
Vertical	7.0 K/km
Lateral	2.0 K/km

way of transport, because of high permeability of fractures (often tens Darcy). The mass transport in case of NFR is different task (Ghorayeb, Firoozabadi 2000) and not discussed here.

It seems that the geothermal gradient may exist only in the hypergeothermal area, where the change of temperature of rock is 300°C in the profile 50 m, with high fracture structure, which allows to start convection. The existence of hydrocarbon reservoir in these areas is not known (Haenel et al. 1988). However, the influence of convection in the high permeability reservoirs may be significant in the near critical oils (Hoeier, Whitson 2001; Ghorayeb, Firoozabadi 2001).

The recent paper of Montel et al. (2002) is the one of rarely work scarified to the non-zero mass flux. He analyses the impact of methane flux in the reservoir caused by post secondary migration mixing. In case of methane flux, the new model can estimate methane gradient in the uppermost part of reservoirs, where post secondary mixing processes are not finished. However, this model may be solved only for assumed methane flux inside reservoir. The numerical estimation of methane flux density are not available from the geochemistry and multiple sampling methods.

9. The necessary time to fix steady state condition in the tight rocks

The geologic time needed to diffusion mixing of petroleum may be estimate-using equation (Bird et al. 1960; DeGroot, Mazur 1962; Smalley, England 1994):

$$T_{eq} = 0.1 \cdot \left(\frac{L^2 \theta^2}{D} \right) \tag{112}$$

where:
T_{eq} — time needed to diffusion mixing [s],
L — length scale over which mixing takes place [m],
θ — factor that accounts for tortuosity of rock pore system (typical hydrocarbon reservoir case $\theta^2 = 3$),
D — diffusion coefficients in oil medium [m²/s].

The full geochemistry/reservoir engineering simulation make possible to observe dynamic effects (secondary migration, trap forming) filling, accumulation, mixing of different oils) on composition of oils and condensates. It seems that such analysis will be only partly accurate, because lot of unknown factors (e.g. time of every phase forming of reservoir), although it makes possible verification of the geologic models. The raw simulations may suggest if geologic structure, variety of permeability, porosity, and capillary are important for spatial variation of composition in specific case. Based upon estimation of time of diffusion for tight rocks (Table 7 and 8) one may conclude that stationary state in the presence of heavy asphaltene fraction may not be achieved up to now in some young geologic structures.

Diffusion time of vertical mixing (100 m) for tight rocks (in million years) (θ = 4)

Czas potrzebny na zakończenie mieszania pionowego (w milionach lat) dla zbitych skał (θ = 4)

	Tortuosity factor		
	2	3	4 (tight rocks)
C_1	0.1	2.6	8.1
C_{12}	0.3	5.1	16.2
C_{200}	1.3	25.7	81.1

Diffusion time of lateral mixing (2000 m) for tight rocks (in million years) (θ = 4)

Czas potrzebny na zakończenie mieszania poziomego (w milionach lat) dla zbitych skał (θ = 4)

	Tortuosity factor		
	2	3	4 (tight rocks)
C_1	50	114	202
C_{12}	101	228	405
C_{200}	506	1140	2027

9.1. The impact of grading phenomena on the geologic and recoverable reserves

Estimation of vertical variation of geological reserves (Gas in Place/Oil in Place) in the grading hydrocarbon reservoirs in comparison with classical methods may be done in following manner: Instead of traditional attitude based on uniform total fluid volume coefficients, a new method should be used. The new method will take into account vertically changes of hydrocarbon fraction of each component. Instead of average volume thermodynamic properties, the component density of hydrocarbon has been proposed to following equation:

$$G = f_{ST} \sum_{i=1}^{nc} \int_{h_{bottom}}^{h_{top}} \{\rho_i(h) \cdot A(h) \mathrm{NTG}(h) \cdot \phi(h)[1 - S_w(h)]\} \cdot dh \qquad (113)$$

where:

$$f_{ST} = \frac{RT_{ST}}{p_{ST}}$$ — standard condition coefficient,

$A(h)$ — vertical function of reservoir area,

NTG(h) — "net to gross" function of depth (related to non-productive layers: e.g. shale's),

$F(h)$ — effective porosity function of depth,

$S_w(h)$ — water saturation function of depth.

Reserves in the grading system depend not only on vertical profile of PVT and other parameters, but also on the shape of trap ($A(h)$). The relation between shape and reserves is much stronger than in the classical (non grading) system. Assuming simplification of shape of reservoir (e.g. hemisphere, cutting cone) and comparing impact of the classical fluid (non grading) and grading fluid and grading with capillary effect on reserves, we may observe the importance of detailed thermodynamic description of fluid in evaluation of possible/proved GIIP/OIIP in reference to classical (Craft, Hawkins 1959) approach.

10. Examples

The impact of capillarity — adsorption effects on the composition and location of saturated Gas Oil Contact has been done for the mixture taken from paper Montel, Gouel (1985). The isothermal case without/with capillary effects in the depth range (TVD) 3162–3241 m has been examined first. The computation has been done using modified and translated Peng-Robinson Equation of State (VTTP — Tsai-Chen 1998; Nagy 2002). The constants and formulas needed to calculation may be found in the original work (Tsai-Chen 1998) except for formula for fugacity which may be taken from Nagy (2002). In the Fig. 10 there is shown vertical variation of ligjht (PF1) and heavy (PF5) hydrocarbon fraction using sampling data taken from Smith et al. (2000) and influence of capillarity effect on saturated Gas-Oil-Contact GOC (based on sampling data from Smith et al. (2000).

The change of composition shown in the Fig. 10 (upper) is high: the concentration of methane droping from 82% at the top of reservoir to the 48% at the bottom (PF1 fraction) and concentration of heavy fraction (PF5) increase from trace percent at the top to the 12% at the bottom at the vertical distance 1200 m.

Three curves of saturation envelopes are given in the Fig. 10 (lower fig.) — for bulk phase and for $r = 5 \cdot 10^{-8}$ m and $r = 2 \cdot 10^{-8}$ m. The vertical profile of saturated pressure is skewed in the GOC point — capillary dew curves lie outside of bulk saturation envelope and bubble curves are moved into bulk bubble curve. The influence of capillarity effect is high (about 10 bars) in the top and bottom of layer, at the GOC the effect is below 2 bar. This is caused by low interfacial tension (IFT) at this example. In the areas where IFT increases the capilary effect is higher (top and bottom of reservoir).

11. Conclusions

1. The mechanism of grading phenomena depends on several factors; some of them are not recognized at appraisal stage or later. The sampling technique which is used in petroleum industry does not allow to fix reference depth of sampling point and composition of fluid. This may cause additional uncertainties.

2. Capillary-adsorption forces can cause significant difference in the case of two--phase reservoirs (gas-condensate, volatile oil) inside classical and capillary-condensation phase envelopes (Nagy 2002);

   Thermal field is responsible for several dynamic processes inside of reservoirs (Hoeier, Whitson 2001; Firoozabadi 1998). It seems that none of these models in the satisfactory way can describe the secondary effects related to the thermodiffusion.

3. The presented extensions of grading model in the transition region (between oil and gas) allow to estimate influence of adsorption and capillarity on the saturation pressure Gas-Oil Contact (Fig. 10). The effects of capillarity exist only for saturated oil/gas condensate contact (for oil wettability rocks and for tight rocks). The change of composition shown in the Fig. 10 (upper) is high: the concentration of methane dropping from 82% at the top of reservoir to the 48% at the bottom (PF1 fraction) and concentration of heavy fraction (PF5) increase from trace percent at the top to the 12% at the bottom. The vertical profile of saturated pressure is skewed in the GOC point — capillary dew curves lie outside of bulk saturation envelope and bubble curves are moved into bulk bubble curve (Fig. 10). The influence of capillarity effect is high (about 10 bars) in the top and bottom of layer, at the GOC the effect is below 2 bar. This is caused by low interfacial tension (IFT) at this example. In the areas where IFT increases, the capilary effect is higher (top and bottom of reservoir).

4. Evaluation of uncertainties in the estimation of geological reserves based upon vertical compositional grading may be done bye use of "interval" griding technique. Impact of grading phenomena and grading/capillarity-adsorption on positioning of GOC and GIIP/OIIP may be significant (Fig. 10). Other uncertainties in estimation of hydrocarbon liquid reserves (for grading reservoirs) using reservoir simulation may be caused by:
   a) data inaccuracies,
   b) data coverage,
   c) data smoothing/interpolating,
   d) numerical solution limits.

5. For specific situation in estimation of the composition grading in the reservoir, following recommendation may given:
   a) isothermal case — for negligible temperature gradient: simple model (45) and for tight rocks case (in the capillary-adsorption area in the saturated transition region for liquid composition — presented model (51),
   b) non-isothermal case — for non vanishing temperature gradient: full model (98) and for tight rocks case (in the capillary-adsorption area in the saturated transition region for liquid composition — presented model.

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