

Physicochemical Fluid Dynamics in Porous Media

Applications in Geosciences and Petroleum Engineering

Mikhail Panfilov

WILEY-VCH

Contents

Preface *xv*

Introduction *xvii*

1	Thermodynamics of Pure Fluids	1
1.1	Equilibrium of Single-phase Fluids – Equation of State	2
1.1.1	Admissible Classes of EOS	2
1.1.2	van der Waals EOS	3
1.1.3	Soave-Redlich-Kwong EOS	3
1.1.4	Peng–Robinson EOS	5
1.1.5	Mixing Rules for Multicomponent Fluids	5
1.2	Two-phase Equilibrium of Pure Fluids	5
1.2.1	Pseudo-liquid/Pseudo-gas and True Liquid/Gas	6
1.2.2	Equilibrium Conditions in Terms of Chemical Potentials	6
1.2.3	Explicit Relationship for Chemical Potential	7
1.2.4	Equilibrium Conditions in Terms of Pressure and Volumes	8
1.2.5	Solvability of the Equilibrium Equation – Maxwell’s Rule	9
1.2.6	Calculation of Gas–Liquid Coexistence	10
1.2.7	Logarithmic Representation for Chemical Potential – Fugacity	11
2	Thermodynamics of Mixtures	13
2.1	Chemical Potential of an Ideal Gas Mixture	13
2.1.1	Notations	13
2.1.2	Definition and Properties of an Ideal Gas Mixture	14
2.1.3	Entropy and Enthalpy of Ideal Mixing	15
2.1.4	Chemical Potential of Ideal Gas Mixtures	16
2.2	Chemical Potential of Nonideal Mixtures	17
2.2.1	General Model for Chemical Potential of Mixtures	17
2.2.2	Chemical Potential of Mixtures Through Intensive Parameters	19
2.3	Two-phase Equilibrium Equations for a Multicomponent Mixture	20
2.3.1	General Form of Two-phase Equilibrium Equations	20
2.3.2	Equilibrium Equations in the Case of Peng–Robinson EOS	21
2.3.3	<i>K</i> -values	23
2.3.4	Calculation of the Phase Composition (“flash”)	24
2.3.5	Expected Phase Diagrams for Binary Mixtures	24

2.4	Equilibrium in Dilute Mixtures	26
2.4.1	Ideal Solution	26
2.4.2	Chemical Potential for an Ideal Solution	27
2.4.3	Equilibrium of Ideal Gas and Ideal Solution: Raoult's Law	27
2.4.4	Equilibrium of Dilute Solutions: Henry's Law	28
2.4.5	K -values for Ideal Mixtures	28
2.4.6	Calculation of the Phase Composition	29
3	Chemistry of Mixtures	31
3.1	Adsorption	31
3.1.1	Mechanisms of Adsorption	31
3.1.2	Langmuir's Model of Adsorption	32
3.1.3	Types of Adsorption Isotherms	34
3.1.4	Multicomponent Adsorption	35
3.2	Chemical Reactions: Mathematical Description	36
3.2.1	Elementary Stoichiometric System	36
3.2.2	Reaction Rate	37
3.2.3	Particle Balance Through the Reaction Rate in a Homogeneous Reaction	37
3.2.4	Particle Balance in a Heterogeneous Reaction	38
3.2.5	Example	39
3.3	Chemical Reaction: Kinetics	39
3.3.1	Kinetic Law of Mass Action: Guldberg–Waage Law	39
3.3.2	Kinetics of Heterogeneous Reactions	40
3.3.3	Reaction Constant	41
3.4	Other Nonconservative Effects with Particles	42
3.4.1	Degradation of Particles	42
3.4.2	Trapping of Particles	42
3.5	Diffusion	42
3.5.1	Fick's Law	43
3.5.2	Properties of the Diffusion Parameter	44
3.5.3	Calculation of the Diffusion Coefficient in Gases and Liquids	45
3.5.3.1	Diffusion in Gases	45
3.5.3.2	Diffusion in Liquids	46
3.5.4	Characteristic Values of the Diffusion Parameter	46
3.5.5	About a Misuse of Diffusion Parameters	47
3.5.5.1	A Misuse of Nondimensionless Concentrations	47
3.5.5.2	Diffusion as the Effect of Mole Fraction Anomaly but not the Number of Moles	47
3.5.6	Stefan–Maxwell Equations for Diffusion Fluxes	48
4	Reactive Transport with a Single Reaction	51
4.1	Equations of Multicomponent Single-Phase Transport	51
4.1.1	Material Balance of Each Component	51
4.1.2	Closure Relationships	52
4.1.2.1	Chemical Terms	52
4.1.2.2	Total Flow Velocity – Darcy's Law	53

4.1.2.3	Diffusion Flux – Fick’s Law	53
4.1.3	Transport Equation	53
4.1.4	Transport Equation for Dilute Solutions	55
4.1.5	Example of Transport Equation for a Binary Mixture	55
4.1.6	Separation of Flow and Transport	56
4.2	Elementary Fundamental Solutions of 1D Transport Problems	56
4.2.1	Convective Transport – Traveling Waves	57
4.2.2	Transport with Diffusion	58
4.2.3	Length of the Diffusion Zone	59
4.2.4	Peclet Number	59
4.2.5	Transport with Linear Adsorption – Delay Effect	60
4.2.6	Transport with Nonlinear Adsorption: Diffusive Traveling Waves	60
4.2.7	Origin of Diffusive Traveling Waves	62
4.2.8	Transport with a Simplest Reaction (or Degradation/Trapping)	62
4.2.9	Macrokinetic Effect: Reactive Acceleration of the Transport	63
4.3	Reactive Transport in Underground Storage of CO ₂	64
4.3.1	Problem Formulation and Solution	65
4.3.2	Evolution of CO ₂ Concentration	66
4.3.3	Evolution of the Concentration of Solid Reactant	67
4.3.4	Evolution of the Concentration of the Reaction Product	67
4.3.5	Mass of Carbon Transformed to Solid	68
5	Reactive Transport with Multiple Reactions (Application to In Situ Leaching)	71
	ISL Technology	71
5.1	Coarse Monoreaction Model of ISL	73
5.1.1	Formulation of the Problem	73
5.1.2	Analytical Solution	74
5.2	Multireaction Model of ISL	75
5.2.1	Main Chemical Reactions in the Leaching Zone	75
5.2.2	Transport Equations	77
5.2.3	Kinetics of Gypsum Precipitation	78
5.2.4	Definite Form of the Mathematical Model	79
5.3	Method of Splitting Hydrodynamics and Chemistry	80
5.3.1	Principle of the Method	80
5.3.2	Model Problem of In Situ Leaching	81
5.3.3	Analytical Asymptotic Expansion: Zero-Order Terms	82
5.3.4	First-Order Terms	83
5.3.5	Solution in Definite Form	84
5.3.6	Case Without Gypsum Deposition	84
5.3.7	Analysis of the Process: Comparison with Numerical Data	85
5.3.8	Experimental Results: Comparison with Theory	86
5.3.9	Recovery Factor	88
6	Surface and Capillary Phenomena	91
6.1	Properties of an Interface	91
6.1.1	Curvature of a Surface	91

6.1.2	Signed Curvature	92
6.1.3	Surface Tension	94
6.1.4	Tangential Elasticity of an Interface	95
6.2	Capillary Pressure and Interface Curvature	96
6.2.1	Laplace's Capillary Pressure	96
6.2.2	Young–Laplace Equation for Static Interface	97
6.2.3	Soap Films and Minimal Surfaces	99
6.2.4	Catenoid as a Minimal Surface of Revolution	101
6.2.5	Plateau's Configurations for Intercrossed Soap Films	102
6.3	Wetting	103
6.3.1	Fluid–Solid Interaction: Complete and Partial Wetting	103
6.3.2	Necessary Condition of Young for Partial Wetting	104
6.3.3	Hysteresis of the Contact Angle	106
6.3.4	Complete Wetting – Impossibility of Meniscus Existence	106
6.3.5	Shape of Liquid Drops on Solid Surface	107
6.3.6	Surfactants – Significance of Wetting for Oil Recovery	109
6.4	Capillary Phenomena in a Pore	110
6.4.1	Capillary Pressure in a Pore	110
6.4.2	Capillary Rise	112
6.4.3	Capillary Movement – Spontaneous Imbibition	113
6.4.4	Menisci in Nonuniform Pores – Principle of Pore Occupancy	114
6.4.5	Capillary Trapping – Principle of Phase Immobilization	115
6.4.6	Effective Capillary Pressure	116
6.5	Augmented Meniscus and Disjoining Pressure	118
6.5.1	Multiscale Structure of Meniscus	118
6.5.2	Disjoining Pressure in Liquid Films	119
6.5.3	Augmented Young–Laplace Equation	120
7	Meniscus Movement in a Single Pore	123
7.1	Asymptotic Model for Meniscus near the Triple Line	123
7.1.1	Paradox of the Triple Line	123
7.1.2	Flow Model in the Intermediate Zone (Lubrication Approximation)	124
7.1.3	Tanner's Differential Equation for Meniscus	125
7.1.4	Shape of the Meniscus in the Intermediate Zone	127
7.1.5	Particular Case of Small θ : Cox–Voinov Law	128
7.1.6	Scenarios of Meniscus Spreading	128
7.2	Movement of the Augmented Meniscus	130
7.2.1	Lubrication Approximation for Augmented Meniscus	130
7.2.2	Adiabatic Precursor Films	132
7.2.3	Diffusive Film	132
7.3	Method of Diffuse Interface	133
7.3.1	Principle Idea of the Method	133
7.3.2	Capillary Force	134
7.3.3	Free Energy and Chemical Potential	135
7.3.4	Reduction to Cahn–Hilliard Equation	137

8	Stochastic Properties of Phase Cluster in Pore Networks	139
8.1	Connectivity of Phase Clusters	139
8.1.1	Connectivity as a Measure of Mobility	139
8.1.2	Triple Structure of Phase Cluster	140
8.1.3	Network Models of Porous Media	140
8.1.4	Effective Coordination Number	142
8.1.5	Coordination Number and Medium Porosity	143
8.2	Markov Branching Model for Phase Cluster	144
8.2.1	Phase Cluster as a Branching Process	144
8.2.2	Definition of a Branching Process	145
8.2.3	Method of Generating Functions	147
8.2.4	Probability of Creating a Finite Phase Cluster	148
8.2.5	Length of the Phase Cluster	149
8.2.6	Probability of an Infinite Phase Cluster	150
8.2.7	Length-Radius Ratio Υ : Fitting with Experimental Data	151
8.2.8	Cluster of Mobile Phase	153
8.2.9	Saturation of the Mobile Cluster	154
8.3	Stochastic Markov Model for Relative Permeability	155
8.3.1	Geometrical Model of a Porous Medium	155
8.3.2	Probability of Realizations	156
8.3.3	Definition of Effective Permeability	156
8.3.4	Recurrent Relationship for Space-Averaged Permeability	157
8.3.5	Method of Generating Functions	158
8.3.6	Recurrent Relationship for the Generating Function	159
8.3.7	Stinchcombe's Integral Equation for Function $F(x)$	160
8.3.8	Case of Binary Distribution of Permeabilities	161
8.3.9	Large Coordination Number	162
9	Macroscale Theory of Immiscible Two-Phase Flow	165
9.1	General Equations of Two-Phase Immiscible Flow	165
9.1.1	Mass and Momentum Conservation	165
9.1.2	Fractional Flow and Total Velocity	167
9.1.3	Reduction to the Model of Kinematic Waves	167
9.2	Canonical Theory of Two-Phase Displacement	168
9.2.1	1D Model of Kinematic Waves (the Buckley–Leverett Model)	168
9.2.2	Principle of Maximum	169
9.2.3	Nonexistence of Continuous Solutions	170
9.2.4	Hugoniot–Rankine Conditions at a Shock	171
9.2.5	Entropy Conditions at a Shock	172
9.2.6	Entropy Condition for Particular Cases	174
9.2.7	Solution Pathway	175
9.2.8	Piston-Like Shocks	176
9.3	Oil Recovery	177
9.3.1	Recovery Factor and Average Saturation	177
9.3.2	Breakthrough Recovery	178

9.3.3	Another Method of Deriving the Relationship for the Recovery Factor	179
9.3.4	Graphical Determination of Breakthrough Recovery	179
9.3.5	Physical Structure of Solution. Structure of Nondisplaced Oil	180
9.3.6	Efficiency of Displacement	181
9.4	Displacement with Gravity	182
9.4.1	1D-model of Kinematic Waves with Gravity	182
9.4.2	Additional Condition at Shocks: Continuity w.r.t. Initial Data	183
9.4.3	Descending Flow	185
9.4.4	Ascending Flow	186
9.5	Stability of Displacement	187
9.5.1	Saffman–Taylor and Raleigh–Taylor Instability and Fingering	187
9.5.2	Stability Criterion	188
9.6	Displacement by Immiscible Slugs	189
9.6.1	Setting of the Problem	190
9.6.2	Solution of the Problem	191
9.6.3	Solution for the Back Part	192
9.6.4	Matching Two Solutions	192
9.6.5	Three Stages of the Evolution in Time	192
9.7	Segregation and Immiscible Gas Rising	196
9.7.1	Canonical 1D Model	196
9.7.2	Description of Gas Rising	197
9.7.3	First Stage of the Evolution: Division of the Forward Bubble Boundary	198
9.7.4	Second Stage: Movement of the Back Boundary	199
9.7.5	Third Stage: Monotonic Elongation of the Bubble	200
10	Nonlinear Waves in Miscible Two-phase Flow (Application to Enhanced Oil Recovery)	203
	Expected Scenarios of Miscible Gas–Liquid Displacement	203
10.1	Equations of Two-Phase Miscible Flow	205
10.1.1	General System of Equations	205
10.1.2	Formulation Through the Total Velocity and Fractional Flow	206
10.1.3	Ideal Mixtures; Volume Fractions	207
10.1.4	Conversion to the Model of Kinematic Waves	208
10.1.5	Particular Case of a Binary Mixture	209
10.1.5.1	Conclusion	209
10.2	Characterization of Species Dissolution by Phase Diagrams	209
10.2.1	Thermodynamic Variance and Gibbs' Phase Rule	209
	Example	210
10.2.2	Ternary Phase Diagrams	211
10.2.3	Tie Lines	213
10.2.4	Tie-Line Parametrization of Phase Diagrams (Parameter α)	214
10.2.5	Saturation of Gas	216
10.2.6	Phase Diagrams for Constant K -Values	216
10.2.7	Phase Diagrams for Linear Repartition Function: $\beta = -\gamma\alpha$	219
10.3	Canonical Model of Miscible EOR	221

10.3.1	Problem Setting	221
10.3.2	Fractional Flow of a Chemical Component	222
10.4	Shocks	224
10.4.1	Hugoniot–Rankine and Entropy Conditions at a Shock. Admissible Shocks	225
10.4.2	Mechanical Shock (C -shock) and Its Graphical Image	226
10.4.3	Chemical Shock ($C\alpha$ -shock) and Its Graphical Image	227
10.4.4	Shocks of Phase Transition	228
10.4.5	Weakly Chemical Shock	230
10.4.6	Three Methods of Changing the Phase Composition	231
10.4.7	Solution Pathway	231
10.5	Oil Displacement by Dry Gas	232
10.5.1	Description of Fluids and Initial Data	232
10.5.2	Algorithm of Selecting the Pathway	233
10.5.3	Behavior of Liquid and Gas Composition	235
10.5.4	Behavior of Liquid Saturation	236
10.5.5	Physical Behavior of the Process	237
10.5.6	EOR Efficiency	239
10.6	Oil Displacement by Wet Gas	239
10.6.1	Formulation of the Problem and the Pathway	239
10.6.2	Solution to the Problem. Physical Explanation	240
10.6.3	Comparison with Immiscible Gas Injection	242
10.6.4	Injection of Overcritical Gas	243
10.6.5	Injection of Overcritical Gas in Undersaturated Single-Phase Oil	245
10.7	Gas Recycling in Gas-Condensate Reservoirs	246
10.7.1	Techniques of Enhanced Condensate Recovery	246
10.7.2	Case I: Dry Gas Recycling: Mathematical Formulation	247
10.7.3	Solution to the Problem of Dry Gas Recycling	247
10.7.4	Case II: Injection of Enriched Gas	249
10.7.4.1	Conclusion	251
10.8	Chemical Flooding	251
10.8.1	Conservation Equations	251
10.8.2	Reduction to the Model of Kinematic Waves	252
10.8.3	Diagrams of Fractional Flow of Water $F(s, c)$	253
10.8.4	Shocks and Hugoniot–Rankine Conditions	253
10.8.5	Solution of the Riemann Problem	255
10.8.6	Impact of the Adsorption	256
11	Counter Waves in Miscible Two-phase Flow with Gravity (Application to CO_2 & H_2 Storage)	257
	Introducing Notes	257
11.1	Two-component Two-phase Flow in Gravity Field	258
11.1.1	Formulation	259
11.1.2	Solution Before Reaching the Barrier	261
11.1.3	Reverse Wave Reflected from Barrier	261
11.1.4	Calculation of the Concentrations at the Shocks	263
11.1.5	Rate of Gas Rising and Bubble Growth Under the Barriers	264

11.1.6	Comparison with Immiscible Two-phase Flow	264
11.2	Three-component Flow in Gravity Field	265
11.2.1	Problem Setting	265
11.2.2	Solution of the Riemann Problem	266
11.2.3	Propagation of the Reverse Wave Under the Barrier	268
12	Flow with Variable Number of Phases: Method of Negative Saturations	271
12.1	Method NegSat for Two-phase Fluids	271
12.1.1	Interface of Phase Transition and Nonequilibrium States	271
12.1.2	Essence of the Method Negsat	273
12.1.3	Principle of Equivalence	275
12.1.4	Proof of the Equivalence Principle	276
12.1.5	Density and Viscosity of Fictitious Phases	277
12.1.6	Extended Saturation – Detection of the Number of Phases	277
12.1.7	Equivalence Principle for Flow with Gravity	279
12.1.8	Equivalence Principle for Flow with Gravity and Diffusion	279
12.1.9	Principle of Equivalence for Ideal Mixing	281
12.1.10	Physical and Mathematical Consistency of the Equivalent Fluids	282
12.2	Hyperbolic-parabolic Transition	282
12.2.1	Phenomenon of Hyperbolic-parabolic Transition (HP Transition)	282
12.2.2	Derivation of the Model (12.23)	284
12.2.3	Purely Hyperbolic Case	284
12.2.4	Case of Hyperbolic-parabolic Transition	285
12.2.5	Generalization of Hugoniot–Rankine Conditions for a Shock of HP-transition	287
12.2.6	Regularization by the Capillarity	288
12.2.7	Reduction to VOF or Level-set Method for Immiscible Fluids	290
13	Biochemical Fluid Dynamics of Porous Media	291
13.1	Microbiological Chemistry	291
13.1.1	Forms of Existence of Microorganisms	291
13.1.2	Bacterial Metabolism	292
13.1.3	Bacterial Movement	293
13.1.4	Chemotaxis	294
13.1.5	Population Dynamics	295
13.1.6	Kinetics of Population Growth and Decay: Experiment	295
13.1.6.1	Population Decay	295
13.1.6.2	Population Growth	296
13.1.7	Kinetics of Population Growth: Mathematical Models	297
13.1.8	Coupling Between Nutrient Consumption and Bacterial Growth	298
13.1.9	Experimental Data on Bacterial Kinetics	300
13.2	Bioreactive Waves in Microbiological Enhanced Oil Recovery	300
13.2.1	The Essence of the Process	300
13.2.2	Metabolic Process	302

13.2.3	Assumptions	303
13.2.4	Mass Balance Equations	303
13.2.5	Description of the Impact of the Surfactant	304
13.2.6	Reduction to the Model of Kinematic Waves	304
13.2.7	1D MEOR Problem	305
13.2.8	Solution and Analysis of the MEOR Problem	305
13.3	Nonlinear Waves in Microbiological Underground Methanation Reactors	308
13.3.1	Underground Methanation and Hydrogen Storage	308
13.3.2	Biochemical Processes in an Underground Methanation Reactor	309
13.3.3	Composition of the Injected Gas	311
13.3.4	Mathematical Model of Underground Methanation	311
13.3.5	Kinematic Wave Model	313
13.3.6	Asymptotic Model for Biochemical Equilibrium	314
13.3.7	Particular Case of Biochemical Equilibrium	315
13.3.8	Solution of the Riemann Problem	315
13.3.9	Comparison with the Case Without Bacteria. Impact of Bacteria	317
13.4	Self-organization in Biochemical Dynamical Systems (Application to Underground Methanation)	318
13.4.1	Integral Material Balance in the Underground Reactor	318
13.4.2	Reduction to a Dynamical System	319
13.4.3	Singular Point Analysis – Oscillatory Regimes	320
13.4.4	Existence of a Limit Cycle – Auto-oscillations	321
13.4.5	Phase Portrait of Auto-oscillations	323
13.5	Self-organization in Reaction–Diffusion Systems	325
13.5.1	Equations of Underground Methanation with Diffusion	325
13.5.2	Turing’s Instability	327
13.5.3	Limit Space Oscillatory Waves at $\epsilon = 0$	328
13.5.4	Three Types of Limit Patterns at Large Times	329
13.5.5	Exact Analytical Solution of Problem (13.52). Estimation of Parameters	330
13.5.6	Limit Two-scale Spatial Oscillatory Patterns at $\epsilon > 0$	331
13.5.7	Two-scale Asymptotic Expansion of Problem (13.59)	333
13.5.7.1	Two-scale Formulation	333
13.5.7.2	Two-scale Expansion	334
13.5.7.3	Zero-order Terms c_0 and n_0	334
13.5.7.4	First-order Term n_1	335
13.5.7.5	Second-order Term c_2	336
13.5.8	2D Two-scale Spatial Patterns	336
A	Chemical Potential of a Pure Component from the Homogeneity of Gibbs Energy	339
B	Chemical Potential for Cubic EOS	341
C	Chemical Potential of Mixtures from the Homogeneity of Gibbs Energy	343

D	Calculation of the Integral in (2.25a)	<i>347</i>
E	Hugoniot–Rankine Conditions	<i>349</i>
F	Numerical Code (Matlab) for Calculating Phase Diagrams of a Pure Fluid	<i>351</i>
	Bibliography	<i>355</i>
	Index	<i>363</i>