

การดัดแปลงสมการสภาวะทรงกลมแข็งสำหรับสมบัติเทอร์โมไดนามิกส์ของไฮโดรคาร์บอนเบา



นางสาว อริญญา คชชาญ

ศูนย์วิทยพัทยากร
จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาเทคโนโลยีปิโตรเคมี

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

พ.ศ. 2533

ISBN 974-577-648-3

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

016793

11796095x

MODIFICATION OF HARD-SPHERE EQUATION OF STATE FOR
THERMODYNAMIC PROPERTIES OF LIGHT HYDROCARBONS

Miss Arunya Kotchan

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering
Program of Petrochemical Technology
Graduate School
Chulalongkorn University

1990

ISBN 974-577-648-3



Thesis Title Modification of Hard-Sphere Equation of State for
 Thermodynamic Properties of Light Hydrocarbons
By Miss Arunya Kotchan
Department Petro-Polymer (Inter Program)
Thesis Advisor Associate Professor Pattarapan Prasassarakich, Ph.D.

Accepted by the Graduate School, Chulalongkorn University
in Partial Fullfillment of the Requirements for the Master's Degree.

Thavorn Vajarabhaya
.....Dean of the Graduate School
(Professor Thavorn Vajarabhaya, Ph.D.)

Thesis Committee

Woraphat Arthayukti
.....Chairman
(Associate Professor Woraphat Arthayukti, Dr.Ing.)

Pattarapan Prasassarakich
.....Thesis Advisor
(Associate Professor Patarapan Prasassarakich, Ph.D.)

Shooshat Barame
.....Member
(Associate Professor Shooshat Barame, Dr.Ing.)

L. Mekasut
.....Member
(Assistant Professor Lursuang Mekasut, Dr.Ing.)

สัญญา คชชาดู : การดัดแปลงสมการสภาวะทรงกลมแข็งสำหรับสมบัติเทอร์โมไดนามิกส์ของไฮโดรคาร์บอนเบา (MODIFICATION OF HARD-SPHERE EQUATION OF STATE FOR THERMODYNAMIC PROPERTIES OF LIGHT HYDROCARBONS) อ.ที่ปรึกษา : รศ.ดร. กัทรพรรณ ประศาสน์สารกิจ , 180 หน้า. ISBN 974-577-646-3

สมการสภาวะทรงกลมแข็งได้ดัดแปลงมาจากการรวมพจน์แรงผลักรวมของสมการสภาวะทรงกลมแข็งของอิซีกาวาและพจน์แรงดึงดูดของสมการสภาวะ SRK เพื่อนำมาใช้คำนวณคุณสมบัติของไฮโดรคาร์บอนเบา ($c_1 - c_6$) ได้ถูกต้องแม่นยำยิ่งขึ้น โดยสมการดังกล่าวมีพารามิเตอร์ 2 ตัว ซึ่งขึ้นกับอุณหภูมิ พารามิเตอร์ทั้งสองคำนวณได้จากค่าความดันไอและปริมาตรของของเหลวอิ่มตัว เมื่อเปรียบเทียบความสามารถในการคำนวณความดันไอ ปริมาตรของของเหลวอิ่มตัว และปริมาตรของไออิ่มตัว ระหว่างสมการสภาวะทรงกลมแข็งดัดแปลงกับสมการของ SRK และ PR พบว่าสมการสภาวะทรงกลมแข็งดัดแปลงให้ค่าความแม่นยำในการคำนวณปริมาตรของไอและความดันไอใกล้เคียงกับ SRK และ PR แต่สามารถคำนวณปริมาตรของของเหลวได้ถูกต้องแม่นยำกว่า SRK และ PR มาก



ศูนย์บริการข้อมูลทางวิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา
สาขาวิชา
ปีการศึกษา

ลายมือชื่อนิสิต
ลายมือชื่ออาจารย์ที่ปรึกษา

ARUNYA KOTCHAN : MODIFICATION OF HARD-SPHERE EQUATION OF STATE FOR FOR THERMODYNAMIC PROPERTIES OF LIGHT HYDROCARBONS. THESIS ADVISOR : ASSO.PROF.PATTARAPAN PRASASSARAKICH, Ph.D. 180 PP.

A modified hard-sphere equation which combines the analytical expression of Ishikawa et al. for the hard sphere repulsive term and the empirical attractive term of the Soave-Redlich-Kwong equation has been applied to the calculation of pure component properties of light hydrocarbons ($C_1 - C_6$). The two parameters of the modified hard-sphere equation are treated as temperature functions. Molal volumes and vapor pressures of pure saturated liquids were used for evaluating the two parameters of the equation.

The calculated results obtained for pure component properties, vapor pressure, saturated liquid and vapor volumes indicate that the new equation performs as well as or better than the Soave-Redlich-Kwong equation and Peng-Robinson equation in all cases treated and shows its greatest advantages in the prediction of liquid phase densities.



ภาควิชา
สาขาวิชา
ปีการศึกษา

ลายมือชื่อนิสิต
ลายมือชื่ออาจารย์ที่ปรึกษา
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม



ACKNOWLEDGEMENTS

The author would like to express her sincere gratitude to her advisor, Associate Professor Dr. Pattarapan Prasassarakich, for providing helpful advice and encouragement throughout this study including criticism and for reviewing this thesis.

The financial support for this research from Chulalongkorn University is gratefully acknowledged.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



CONTENTS

	Page
ABSTRACT IN THAI.....	A
ABSTRACT IN ENGLISH.....	B
ACKNOWLEDGEMENTS.....	C
CONTENTS.....	D
LIST OF TABLES.....	F
LIST OF FIGURES.....	J
NOTATION INDEX.....	N
CHAPTER	
1. INTRODUCTION	1
2. LITERATURE REVIEW	4
2.1 Nonideal gases.....	4
2.1.1 Deviation from ideality.....	4
2.1.2 Intermolecular forces.....	7
2.2 Cubic Equations.....	9
2.2.1 The van der Waals Equation.....	9
2.2.2 The Redlich-Kwong Equation.....	11
2.2.3 The Soave Equation.....	14
2.2.4 The Peng Robinson Equation.....	18
2.3 Other Modifications of Redlich-Kwong Equation	21
2.3.1 Modification with one Temperature-Dependent Parameter.....	21
2.3.2 Modification with two Temperature-Dependent Parameters.....	23
2.3.3 Modification of the Attractive Term.....	25
2.3.4 Modification of the Repulsive Term.....	27
2.4 Perturbed Hard-Sphere Equations of State	30

	Page
3. PROPOSED MODIFICATION AND PROCEDURE	38
3.1 Formulation of the Modified Hard-Sphere EOS	38
3.2 Evaluation of Ω_a and Ω_b	42
3.3 Determination of the Temperature Dependence of the Parameters.....	44
3.4 Representation of Pure Component Properties	46
3.5 Application of the Modified Hard-Sphere EOS to Mixtures : Vapor-Liquid Equilibrium.....	48
3.6 Another Modification of Hard-Sphere EOS.....	52
4. RESULTS OF CALCULATIONS	55
4.1 The Temperature-Dependence Parameters.....	55
4.2 Saturated Liquid and Saturated Vapor Densities	61
4.3 Vapor Pressure.....	78
4.4 Compressibility Factor.....	89
4.5 Vapor-Liquid Equilibrium Calculations.....	92
4.6 Another Modified Hard-Sphere EOS.....	97
5. DISCUSSIONS	102
5.1 Representation of Pure Component Properties	102
5.2 Saturated Liquid and Saturated Vapor Densities	102
5.3 Vapor Pressure.....	106
5.4 Compressibility Factor.....	106
5.5 Vapor-Liquid Equilibrium Calculations.....	109
5.5.1 Comparison with experimental data.....	109
5.5.2 Comparison with the PR equation.....	111
6. CONCLUSIONS AND RECOMMENDATIONS	113
REFERENCES.....	115
APPENDIX	
A COMPUTER PROGRAM AND SAMPLE CALCULATION.....	122
B NUMERICAL VALUES OF EXPERIMENTAL DATA AND CALCULATED RESULTS.....	156
VITA.....	180



LIST OF TABLES

Table	Page
2.1 The van der Waals Equation of State	10
2.2 The Redlich-Kwong Equation of State	13
2.3 The Soave Equation of State	15
2.4 Binary interaction Parameters for the Soave Equation	15
2.5 The Peng-Robinson Equation of State	20
2.6 Values of Coefficients a_1 and b_1 of Equations (2.47) and (2.48).	34
2.7 A summary of deviations between calculated and literature values of four saturated properties.	35
3.1 Repulsion and attraction pressure of equation of state	39
3.2 Literature sources of the saturation properties used in this investigation.	41
3.3 Physical properties of pure component.	46
3.4 Cubic equations of state used in this study.	47
4.1 Numerical values of the parameters Ω_a & Ω_b calculated by the modified hard sphere equation.	56
4.2 Values of the coefficients a_1 and b_1 of equations (3.9) & (3.10) determined by the least-square method.	60
4.3 Values of the coefficients a_1 and b_1 of equations (3.38) & (3.39) determined by the least-square method.	98
5.1 Deviations between experimental and calculated saturated liquid volume.	104
5.2 Deviations between experimental and calculated saturated vapor volume.	105
5.3 Deviations between experimental and calculated vapor pressure.	107

LIST OF TABLES (continued)

Table	Page	
5.4	Deviations between experimental and calculated compressibility factor.	108
5.5	Comparison of the calculated and experimental values for four binary systems.	110
5.6	Bubble point deviation for four binary systems, comparison between PR and Modified hard sphere EOS.	112
B.1	Numerical values of experimental and calculated saturated densities for Methane.	156
B.2	Numerical values of experimental and calculated saturated densities for Ethane.	157
B.3	Numerical values of experimental and calculated saturated densities for Propane.	158
B.4	Numerical values of experimental and calculated saturated densities for n-Butane.	159
B.5	Numerical values of experimental and calculated saturated densities for iso-Butane.	160
B.6	Numerical values of experimental and calculated saturated densities for n-Pentane.	161
B.7	Numerical values of experimental and calculated saturated densities for iso-Pentane.	162
B.8	Numerical values of experimental and calculated saturated densities for n-Hexane.	163
B.9	Numerical values of experimental and calculated saturated densities for Ethylene.	164
B.10	Numerical values of experimental and calculated saturated densities for Propylene.	165
B.11	Numerical values of experimental and calculated vapor pressure for Methane, Ethane and Ethylene.	166

LIST OF TABLES (continued)

Table	Page
B.12 Numerical values of experimental and calculated vapor pressure for Propane, Propylene and n-Hexane.	167
B.13 Numerical values of experimental and calculated vapor pressure for n-Butane, iso-Butane, n-Pentane and iso-Pentane.	168
B.14 Numerical values of experimental and calculated compressibility factor for Ethane.	169
B.15 Numerical values of experimental and calculated compressibility factor for Propane.	170
B.16 Numerical values of experimental and calculated compressibility factor for Ethylene.	171
B.17 Numerical values of experimental and calculated compressibility factor for Propylene.	172
B.18 Results of bubble point pressure calculations for Ethane-Propane at 100°F.	173
B.19 Results of bubble point pressure calculations for Ethane-Propane at 140°F.	173
B.20 Results of bubble point pressure calculations for Ethane-Propane at 180°F.	174
B.21 Results of bubble point pressure calculations for Ethane-n-Butane at 150°F.	174
B.22 Results of bubble point pressure calculations for Ethane-n-Butane at 200°F.	174
B.23 Results of bubble point pressure calculations for Ethane-n-Butane at 250°F.	175
B.24 Results of bubble point pressure calculations for Ethane-iso-Butane at 100.6°F.	175
B.25 Results of bubble point pressure calculations for Ethane-iso-Butane at 160.4°F.	176

LIST OF TABLES (continued)

Table	Page
B.26 Results of bubble point pressure calculations for Ethane-iso-Butane at 219.7° F.	176
B.27 Results of bubble point pressure calculations for Propylene-Propane system.	177
B.28 Numerical values of experimental and calculated saturated liquid and vapor volume for Methane and Ethane (calculated by Equation (3.34)).	178
B.29 Numerical values of experimental and calculated saturated liquid and vapor volume for n-Butane and n-Pentane (calculated by Equation (3.34)).	179

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



LIST OF FIGURES

Figure	Page
2.1 Effects of temperature and pressure on the compressibility $Z = PV/RT$, of some gases.	5
2.2 Correlation of compressibilities of common gases.	5
2.3 Phase diagram of isopentane in the two phase and homogeneous regions.	6
2.4 Some Commonly Used Potential Functions.	8
2.5 Saturated curve and 394.2°K isotherm of n-butane, and comparisons with predictions from the ideal, van der Waals and Redlich-Kwong equations of state.	12
2.6 Plots of 250°F isotherms of sulfur dioxide with the Harmens-Knapp, Soave, and van der Waals equations, and comparison with the true saturation curve.	17
2.7 Temperature-dependence of a parameter	22
2.8 Temperature-dependent a and b parameters in Redlich-Kwong equation of state.	25
2.9 Compressibility factor of hard-sphere fluid.	29
2.10 Calculated and experimental VLE values for ethane-propane system.	37
2.11 Calculated and experimental VLE values for n-hexane-benzene system.	37
3.1 Diagram for Evaluation of Ω_a and Ω_b .	45
3.2 Diagram for Bubble Point Pressure Calculations.	51
4.1 Temperature dependent characteristic of Ω_a and Ω_b of C_1 to C_3 .	58
4.2 Temperature dependent characteristic of Ω_a and Ω_b of C_4 to C_6 .	59
4.3 Saturated Liquid and Vapor Densities of Methane.	62

LIST OF FIGURES (continued)

Figure		Page
4.4	Saturated Liquid and Vapor Densities of n-Hexane.	62
4.5	Saturated Liquid and Vapor Densities of Ethane.	63
4.6	Saturated Liquid and Vapor Densities of Ethylene.	63
4.7	Saturated Liquid and Vapor Densities of Propane.	64
4.8	Saturated Liquid and Vapor Densities of Propylene.	64
4.9	Saturated Liquid and Vapor Densities of n-Butane.	65
4.10	Saturated Liquid and Vapor Densities of iso-Butane.	65
4.11	Saturated Liquid and Vapor Densities of n-Pentane.	66
4.12	Saturated Liquid and Vapor Densities of iso-Pentane.	66
4.13	% Deviation in Saturated Liquid Volume for Methane.	68
4.14	% Deviation in Saturated Vapor Volume for Methane.	68
4.15	% Deviation in Saturated Liquid Volume for n-Hexane.	69
4.16	% Deviation in Saturated Vapor Volume for n-Hexane.	69
4.17	% Deviation in Saturated Liquid Volume for Ethane.	70
4.18	% Deviation in Saturated Vapor Volume for Ethane.	70
4.19	% Deviation in Saturated Liquid Volume for Ethylene.	71
4.20	% Deviation in Saturated Vapor Volume for Ethylene.	71
4.21	% Deviation in Saturated Liquid Volume for Propane.	72
4.22	% Deviation in Saturated Vapor Volume for Propane.	72
4.23	% Deviation in Saturated Liquid Volume for Propylene.	73
4.24	% Deviation in Saturated Vapor Volume for Propylene.	73
4.25	% Deviation in Saturated Liquid Volume for n-Butane.	74
4.26	% Deviation in Saturated Vapor Volume for n-Butane.	74
4.27	% Deviation in Saturated Liquid Volume for iso-Butane.	75
4.28	% Deviation in Saturated Vapor Volume for iso-Butane.	75
4.29	% Deviation in Saturated Liquid Volume for n-Pentane.	76
4.30	% Deviation in Saturated Vapor Volume for n-Pentane.	76

LIST OF FIGURES (continued)

Figure	Page
4.31 % Deviation in Saturated Liquid Volume for iso-Pentane.	77
4.32 % Deviation in Saturated Vapor Volume for iso-Pentane.	77
4.33 Vapor Pressure Curve of Methane.	79
4.34 Vapor Pressure Curve of Ethane	80
4.35 Vapor Pressure Curve of Propane	81
4.36 Vapor Pressure Curve of n-Butane	82
4.37 Vapor Pressure Curve of iso-Butane	83
4.38 Vapor Pressure Curve of n-Pentane	84
4.39 Vapor Pressure Curve of iso-Pentane	85
4.40 Vapor Pressure Curve of n-Hexane	86
4.41 Vapor Pressure Curve of Ethylene	87
4.42 Vapor Pressure Curve of Propylene	88
4.43 % Deviation in Vapor Pressure for Methane	79
4.44 % Deviation in Vapor Pressure for Ethane	80
4.45 % Deviation in Vapor Pressure for Propane	81
4.46 % Deviation in Vapor Pressure for n-Butane	82
4.47 % Deviation in Vapor Pressure for iso-Butane	83
4.48 % Deviation in Vapor Pressure for n-Pentane	84
4.49 % Deviation in Vapor Pressure for iso-Pentane	85
4.50 % Deviation in Vapor Pressure for n-Hexane	86
4.51 % Deviation in Vapor Pressure for Ethylene	87
4.52 % Deviation in Vapor Pressure for Propylene	88
4.53 Compressibility factor for Ethane	90
4.54 Compressibility factor for Ethylene	90
4.55 Compressibility factor for Propane	91
4.56 Compressibility factor for Propylene	91
4.57 Calculated and experimental VLE values for Ethane-Propane system.	93

LIST OF FIGURES (continued)

Figure	Page
4.58 Calculated and experimental VLE values for Ethane-n-Butane system.	94
4.59 Calculated and experimental VLE values for Ethane-iso-Butane system.	95
4.60 Calculated and experimental VLE values for Propylene-Propane system.	96
4.61 % Deviation in Saturated Volume for Methane (calculated by Equation (3.34)).	99
4.62 % Deviation in Saturated Volume for Ethane (calculated by Equation (3.34)).	99
4.63 % Deviation in Saturated Volume for Propane (calculated by Equation (3.34)).	100
4.64 % Deviation in Saturated Volume for n-Butane (calculated by Equation (3.34)).	100
4.65 % Deviation in Saturated Volume for n-Pentane (calculated by Equation (3.34)).	101

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



NOTATION INDEX

ACRONYMS

EOS	Equation of State
ICL	Ishikawa-Chung-Lu equation of state
PR	Peng-Robinson equation of state
RK	Redlich-Kwong equation of state
SRK	Soave-Redlich-Kwong equation of state
vdW	van der Waals equation of state
VLE	Vapor-Liquid Equilibrium

LETTERS

a	attraction parameter of the van der Waals, Soave or Peng-Robinson EOS, $(L^6)/M^2$, (liters/gmol) ²
a	attraction parameter of Redlich-Kwong EOS, $(L^6)(T^{0.5})/(M^2)$, (liters) ² (K) ^{0.5} / (gmol) ²
a, b, c	parameters of some cubic equations of state
A	= $aP/R^2 T^{2.5}$, derived parameter of the RK or ICL EOS
A	= $a(T)P/R^2 T^2$, derived parameter of the PR, SRK or this modified hard sphere EOS
b	residual volume parameter of the vdW, RK, SRK, PR, ICL, and some other cubic EOS, $(L^3)/(M)$, liters/gmol
B	= bP/RT , derived parameter of RK, SRK, PR, ICL and this modified hard-sphere EOS
$c_{1,2}$	binary interaction parameter for the cross-attraction parameter of the RK, SRK, PR, ICL and this proposed EOS
f_1	partial fugacity of species i
K_1	= y_1/x_1 , vaporization equilibrium ratio
MW	molecular weight
P	pressure of system
P_c	critical pressure
P_r	= P/P_c , reduced pressure

R	gas constant, (=0.08205 (liter)(atm.)/(gmol)(K)
T	temperature, °K, °R, °C, °F
T_c	critical temperature
T_r	= T/T_c , reduced temperature
V	specific volume, the reciprocal of the density, liters/gmol.
x_i	mol fraction of a species in a liquid phase mixture
y_i	mol fraction of a species in a vapor phase mixture
Z	= PV/RT , compressibility factor
Z_c	= $P_c V_c /RT_c$, critical compressibility

GREEK LETTERS

α	parameter of SRK and PR EOS
ϕ_i	= f_i /P , fugacity coefficient
$\hat{\phi}_i$	= $f_i /y_i P$, partial fugacity coefficient of species i in a mixture
ω	acentric factor

SUBSCRIPTS

A	attraction force
i,j,k,...	identifying a specie in a mixture, as in n_i
c	critical property
r	reduced property
R	Repulsion force