بسم ا... الرحمن الرحيم

به نام خدا

# یک معادله حالت تحلیلی برای مبردهای مایع در حالت خالص و مخلوط

کاربرد معادله حالت اصلاح شده اختلال یافته زنجیرکره سخت برای مخلوط مبردها

محاسبه خواص ترمودینامیکی مبردهای مایع با استفاده از معادله حالت
GMA

به وسیله:

زهرا شرفی

پایان نامه

ارایه شده به تحصیلات تکمیلی دانشگاه به عنوان بخشی

از فعالیت های تحصیلی لازم برای اخذ درجه دکتری (پی. اچ. دی)

در رشته:

شیمی ( شیمی فیزیک)

از دانشگاه شیراز

شیراز

جمهوری اسلامی ایران

**IN THE NAME OF GOD**

# An Analytical Equation of State Applied to Pure Refrigerants and Refrigerant Mixtures

# A Modified Perturbed Hard-Sphere-Chain Equation of State for Refrigerant Mixtures

# Thermodynamic Properties of Refrigerants using GMA Equation of State

**BY**

## ZAHRA SHARAFI

**THESIS**

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUREMENTS FOR THE DEGRRE OF DOCTOR OF PHILOSOPHY (Ph.D.)

**IN**

CHEMISTRY (PHYSICAL CHEMISTRY)

SHIRAZ UNIVERSITY

SHIRAZ

ISLAMIC REPUBLIC OF IRAN

**EVALUATED AND APPROVED BY THE THESIS COMMITTEE AS:** *Excellent*

A. BOUSHEHRI, Ph.D., Prof. Of Chemistry (CHAIRMAN)

J. MOGHADASI, Ph.D., Assoc. Prof. Of Chemistry

S. H. MOUSAVIPOUR, Ph.D., Assoc. Prof. Of Chemistry

H. ESLAMI, Ph.D., Assoc. Prof. Of Chemistry
(Persian Gulf University, Boushehr)

A. MOHAJERI., Ph.D., Assist. Prof. Of Chemistry

JUNE 2007

# Dedicated to

*All of My Teachers*

*&*

*My Parents*

*&*

*My Dear Husband*

# Acknowledgment

I am most grateful to express my deep gratitude and appreciations to Professor Ali Boushehri, my supervisor for his constructive guidance and helpful suggestions.

I would like to thank Dr. J. Moghadasi, my advisor, who read the thesis very carefully and for useful suggestions.

Also I like to express my appreciations to Dr. H. Eslami for his making valuable suggestions and useful advice.

Thanks should be made of the members of the thesis committee, Dr. S. H. Mousavi pour and Dr. A. Mohajeri.

Also I like to thank the chemistry department of Shiraz University for their useful helps.

I give my deepest thanks to all of my colleagues, especially my dear friend Miss. F. Mousavi for her valuable helps.

My special appreciations are due to my dear husband and my family for their supports during the years.

# ABSTRACT

An Analytical Equation of State Applied to Pure Refrigerants and
Refrigerant Mixtures

A Modified Perturbed Hard-Sphere-Chain Equation of State for
Refrigerant Mixtures

Thermodynamic Properties of Refrigerants Using GMA Equation of
State

**By**

**Zahra Sharafi**

**Chapter I**: In this chapter, the ISM equation of state based on statistical mechanical perturbation theory, using correlations of Boushehri and Mason has been applied to pure and refrigerant mixtures. Three temperature-dependent parameters exist in the EOS; the second virial coefficient, $B_2(T)$, an effective van der Waals covolume, $b(T)$, and a scaling factor, $\alpha(T)$. The second virial coefficients are calculated from a correlation based on the heat of vaporization, $\Delta H_{vap}$, and the liquid density at the normal boiling point, $\rho_{nb}$. $\alpha(T)$ and $b(T)$ can also be calculated from second virial coefficients by scaling rules. The theory has considerable predictive power, since it permits the construction of the $P$-$V$-$T$ surface from the heat of vaporization and the liquid density at the normal boiling point. The equation of state is tested on some pure and refrigerant mixtures to calculate liquid densities, and the results are compared with experiment.

**Chapter II**: A new equation of state is proposed to calculate liquid densities of refrigerant mixtures. Two temperature-dependent parameters; an effective hard sphere diameter and a parameter for the strength of the attractive forces between two non-bonded segments, and a third parameter representing the number of chains per molecule appear in the existing perturbed hard-sphere-chain equation of state. Knowing the critical constants of fluids as input data is sufficient to calculate the temperature-dependent parameters. Our proposed equation of state is applied to a variety of refrigerant mixtures over a wide temperature, pressure, and concentration range. A comparison with the experimental data and ISM EOS for refrigerant mixtures shows that the predicting ability of the present equation of state is quite good.

**Chapter III**: In this study, the thermodynamic properties such as density, $\rho$, isobaric expansion coefficient, $\alpha$, isothermal compressibility, $\kappa$, and internal pressure, $P_i$, for some refrigerants based on GMA equation of state have been calculated and a wide comparison with experimental data was made. The accuracy of the equation of state is determined by a statistical parameter; absolute average deviation (AAD). The results show that the GMA EOS reproduces the experimental volumetric properties within experimental errors throughout the liquid phase. Also there are many comparisons of isobaric expansion coefficient, $\alpha$, isothermal compressibility, $\kappa$, and internal pressure, $P_i$, with the corresponding experimental results for the fluids. The generally excellent agreement with experimental data indicates that this EOS can be used to calculate the thermodynamic properties of liquid refrigerants with a high degree of certainty.

# TABLE OF CONTENT

| CONTENT | PAGE |
|---|---|

# LIST of TABLES

# LIST of FIGURES

## Nomenclature

| | |
|---|---|
| $A_0$ | constant of GMA EOS ($L^3$ mol$^{-3}$) |
| $A_1$ | constant of GMA EOS ($L^4$ atm mol$^{-4}$) |
| $A_2$ | constant of GMA EOS ($L^4$ atm mol$^{-4}$ K$^{-1}$) |
| AAD | Average Absolute Deviation |
| $B$ | second virial coefficient |
| $B_0$ | constant of GMA EOS ($L^4$ mol$^{-4}$) |
| $B_1$ | constant of GMA EOS ($L^5$ atm mol$^{-5}$) |
| $B_2$ | constant of GMA EOS ($L^5$ atm mol$^{-5}$ K$^{-1}$) |
| $a$ | a temperature-dependent parameter (L mol$^{-1}$) |
| $a_1$-$a_4$ | coefficients in Eq. (2.13) |
| $b$ | van der Waals covolume per segment (L mol$^{-1}$) |
| $b_1$-$b_4$ | coefficients in Eq. (2.14) |
| $d$ | the hard-sphere diameter |
| Dev | Deviation |
| $\Delta H_{vap}$ | heat of vaporization |
| $g(d^+)$ | pair distribution function for hard spheres at contact |
| $k$ | Boltzmann's constant (J K$^{-1}$) |
| $P$ | pressure (atm) |
| $P_i$ | internal pressure (atm) |
| $q_a$ | a coefficient defined in Eq. (2.10) |
| $q_b$ | a coefficient defined in Eq. (2.10) |
| $q_{1a}$-$q_{3a}$ | coefficients in Eq. (2.15) |
| $q_{1b}$-$q_{3b}$ | coefficients in Eq. (2.16) |
| $r$ | the number of segments per chain |
| $R$ | gas constant |
| $T$ | temperature (K) |
| $V_m$ | molar volume |
| $x$ | mole fraction |

## Greek letters

| | |
|---|---|
| $\alpha$ | isobaric expansion coefficient (K$^{-1}$) |
| $\beta$ | isothermal compressibility (atm$^{-1}$) |
| $\lambda$ | the magnitude of $G^{-1}$ vs. $b\rho$ |
| $\xi$ | defined in Eq. (2.19) |
| $\eta$ | packing fraction |
| $\rho$ | molar density (mol L$^{-1}$) |

## Subscripts

| | |
|---|---|
| $C$ | critical point |
| m | molar |
| nb | normal boiling point |
| ij | components i and j |
| ref | reference system |
| pert | perturbed system |
| vap | vaporization |

# CHAPER I

An Analytical Equation of State Applied to
Pure Refrigerants and Refrigerant Mixtures

## 1.1 Introduction

Halogenated hydrocarbons are the generic base of most refrigerants. There are different kinds of halocarbon refrigerants such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs). The ozone-depleting and global warming properties of CFCs and HCFCs encouraged the international community to replace these materials by HFCs and their mixtures.

Hydroflourocarbons (HFCs) contain no chlorine and are thus given ozone depletion potentials of essentially zero. So HFCs are most promising candidates to substitute the CFCs and HCFCs.

Accurate knowledge and prediction of the thermophysical properties of refrigerants, is of great importance to evaluate the performance of refrigeration cycles and to determine the optimum composition of new working fluids in pure and mixture states. The development of models for representation and prediction of physical properties and phase equilibria as well as the improvement of current equations of state (EOS) is of particular interest for the refrigeration industry. Thermodynamic properties of the long-known refrigerants and the new refrigerants are the key data needed for the calculation of refrigeration cycles and for designing refrigeration and air-conditioning equipment.

In addition to experimental measurements, the common procedure to determine the thermodynamic properties of refrigerants is by means of equation of state (EOS). Equations of state are powerful tools in chemical engineering practice since they can be used to correlate and/or predict the

2

thermodynamic properties and phase behavior of pure fluids and mixtures over large ranges of temperatures and pressures.

The quest for a simple analytical equation of state for fluids is very old. The first real success was the van der Waals equation [1], which can be written as

$$\frac{P}{\rho kT} = \frac{1}{1 - b\rho} - \frac{a\rho}{kT} \tag{1.1}$$

where $P$ is the pressure, $\rho = N / V$ is the number density, $kT$ is the thermal energy per one molecule, and $a$ and $b$ are constants for a given fluid. Another form of equation (1.1) is

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^{\,2}} \tag{1.2}$$

and $V_m$ is molar volume. This was the first equation capable of reasonably representing both gas and liquid phases. Also it has two features that make it very convenient for calculations. First, it can be rewritten as a cubic polynomial with respect to volume and so can be solved numerically for volume or density. This property has been retained by contemporary cubic equations of state. Second, the two van der Waals parameters $a$ and $b$ can be determined from critical-point coordinates:

$$\frac{\partial P}{\partial V_m} = \frac{\partial^2 P}{\partial^2 V_m} = 0 \quad \text{at T=T}_c \tag{1.3}$$

The values of parameters "$a$ and $b$" as functions of the critical temperature $T_c$, and critical pressure $P_c$, then will be:

$$a = 27 / 64 \frac{R^2 T_c^{\,2}}{P_c} \tag{1.4}$$

$$b = 1 / 8 \frac{R T_c}{P_c} \tag{1.5}.$$

The parameter $a$ and $b$ remain reasonable, although not accurate, in other regions of the *PVT* space. Actually, parameter $a$ is a constant which is a measure of the strength of the attractive force between a pair of molecules and $b$ is the excluded volume. Much of our knowledge of the law of force between molecules comes from the study of gases under conditions where they depart only slightly from ideal behavior. Under these conditions one may express the equation of state in the form of a simple power series such as

$$\frac{p}{\rho kT} = 1 + \sum_{i=2}^{\infty} B_i(T)\rho^{i-1} \qquad (1.6).$$

This is the virial expansion, and the temperature-dependent coefficients $B_i$ $(T)$ are called $i_{th}$ virial coefficients.

## 1.1.1 Some Modifications of the van der Waals Equation of State

Many modifications have been proposed to the van der Waals equation of state to improve the prediction of volumetric, thermodynamic and the phase equilibrium properties. Two of them, which can be regarded as precursors of modern cubic equations of state, are the works of Clausius [2] and Berthelot [3]. In 1881, Clausius replaced the volume in the van der Waals attraction term, by $(V_m + c)$ and creating a three-parameter equation of state:

$$P = \frac{RT}{V_m - b} - \frac{a}{(V_m + c)^2} \qquad (1.7)$$

This approach resembles the volume-translation technique, which became popular almost a century later [4,5]. In 1899, Berthelot introduced an equation with a temperature-dependent attractive parameter, that is, $a$ $(T) = a / T$.

$$P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2} \qquad (1.8)$$

This concept several decades later proved to be essential for practical success of cubic equations of state for phase-equilibrium calculations.

Although virial-type equations like the Benedict-Webb-Rubin EOS [6] have the statistical-mechanical foundation, which is important from the theoretical viewpoint, but the need for simple analytical tools for the calculation of fugacities for process design made a revival of interest in cubic equations of state. Redlich and Kwong [7] proposed the first cubic EOS that became widely accepted as a tool for routine engineering calculations of the fugacity. The equation has the following form:

$$P = \frac{RT}{V_m - b} - \frac{a}{T^{1/2} V_m (V_m + b)} \qquad (1.9)$$

$$a = 0.42747 \frac{R^2 T_c^{2.5}}{P_c} \qquad (1.10)$$

$$b = 0.0867 \frac{RT_c}{P_c} \qquad (1.11)$$

The Redlich-Kwong equation is very successful for the calculation of the properties of gas mixtures. However, it was not adequate for modeling of both gas and liquid phases. The simple temperature-dependence of the attractive parameter was insufficient for the representation of vapor pressures and liquid volumes were not predicted with acceptable accuracy. Therefore, further research in this area focused on two branches:

1) Improving the temperature dependence of the attractive parameter to control the vapor pressure predictions.

2) Improving the functional form of $P(V_m)$ to optimize the prediction of volumetric properties.

For the case (1) we can example Soave modification to the Redlich-Kwong EOS which frequently referred to as SRK EOS [8], which assumed $a = a_c . \alpha$ $(T_r)$ and $\alpha$ has the form:

$$\alpha = [1 + m(1 - T_r^{1/2})]^2 \tag{1.12}$$

where $a_c$ is the value of "$a$" parameter at critical point, $T_r = (T / T_c)$ and $m$ is a function of acentric factor, $\omega$, as:

$$m = 0.48 + 1.574\,\omega - 0.175\,\omega^2 \tag{1.13}.$$

For the second case, we can mention the Peng-Robinson EOS [9] that is:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \tag{1.14}.$$

The trends in research on cubic EOS's after the contributions of Soave and Peng-Robinson have followed three main groups:

a) Modifications to $\alpha$ ($T_r$) in the SRK and PR equations of state to obtain more accurate predictions of vapor pressure and vapor-liquid equilibrium.

b) Modifications to the volume-dependence of the attractive pressure term, which has given rise to the volume-translation concept.

c) Use of a third (or more) substance-dependent parameter(s) which constitutes the so-called group of three (or more)-parameter equations of state.

## 1.2 Literature Review

The equation of state plays a central role in the treatment of the thermodynamic properties of fluids, particularly of mixtures. For this purpose, an analytical equation having a statistical-mechanical basis in molecular theory is very desirable. The most fundamental tool in providing a basis to predict the thermophysical properties of matter is the equation of state. Equations of state attempt to describe the relationship between temperature, pressure and volume for fluids or mixtures of substances. Once the EOS of a system is established, all thermodynamic behavior of the system can be calculated by means of statistical mechanical tools. Unfortunately, among the available equations of state, only a few are on a sound analytical basis and are proper for this purpose.

6

Regarding the vast applicability of different refrigerants, a precise knowledge of the pressure-density relation of these refrigerants over an extended range of temperature and pressure is extremely useful in predicting thermophysical properties. Theories of liquids have been developed over the past years based on the recognition that the structure of a liquid is determined primarily by repulsive forces, so that fluids of hard bodies can serve as a useful reference state for perturbation theories.

An analytical EOS, which has a sound basis in statistical-mechanical perturbation theory, was proposed by Song and Mason [10] for pure fluids. This equation of state produces very accurate results for fluids up to the critical temperature. One of the most powerful features of this equation of state is the presence of only one adjustable parameter related to the structure of the substance. The only initial information needed for this equation of state is the intermolecular potential function of the systems. But there are no exact intermolecular potential energies (except for some simple compounds) for real fluids. Ihm, Song and Mason [11] presented a new strong principle of corresponding states method that reduces the entire pressure-volume-temperature (PVT) surface of a pure nonpolar fluid to a single curve. This reduction of a surface to a curve is based on statistical-mechanical theory, which also furnishes the algorithms for calculating, from the intermolecular pair potential, the three temperature-dependent parameters are needed for the reduction. If the pair potential is not known, data on the second virial coefficient as a function of temperature can be used instead. The ISM equation of state is not accurate enough in the critical and two-phase regions, but otherwise describes the volumetric behavior of real fluids well over the entire range from the dilute gas to the dense liquid. It has considerable predictive power, since it permits the construction of the entire PVT surface from just the second virial coefficient plus a few liquid densities.