

IN THE NAME OF GOD

THE ISM EQUATION OF STATE APPLIED TO REFRIGERANTS

BY

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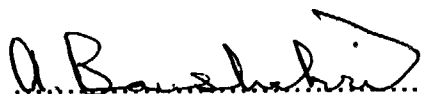
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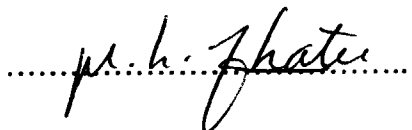
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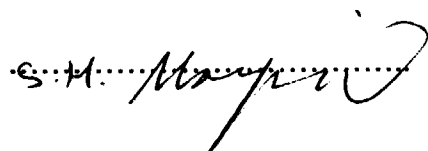
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Dedicated To:

***Those
Who Don't Wait For
The Others***

Y V T F.

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Abstract

The ISM Equation of State Applied to Refrigerants

By

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In this work, we apply an equation of state based on statistical-mechanical perturbation theory to liquid refrigerants and their mixtures. Three temperature-dependent parameters are needed to use the equation of state: 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, ΔH_{vap} , and the liquid density at the freezing point, ρ_{fp} . $\alpha(T)$ and $b(T)$ can also be calculated from the second virial coefficient by a scaling rule. Based on the theory, these two temperature-dependent parameters depend only on the repulsive branch of the potential function, and therefore, by our procedure, can be found from ΔH_{vap} and ρ_{fp} . The theory has a considerable predictive power, since it permits the construction of the p-v-T surface from the heat of vaporization plus the triple-point density. The equation of state is tested for pure, two, and three component liquid refrigerant mixtures.

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The ISM Equation of State Applied to Refrigerants

1.1. Introduction

The study of the P-V-T behavior of gases provides a base from which many practical and penetrating studies stem. Many equation of states, dating back to the work of Scottish mathematician and physicist Peter Guthrie Tait over 100 years ago, have been proposed for practical use [1-3].

The best known example of an equation of state that we can study is the ideal gas equation of state fluids

$$PV=nRT \quad (1)$$

where P is pressure, V is volume, n is mole number, R is gas constant, and T is absolute temperature. The above equation tells us that only two of the three state functions P, V, and T are independent.

Real gases, or vapours, approximate to ideal gas only if the volume is so large that the molecules are, on average, a long way apart from each other. As the gas is compressed this average distance decreases and the effects of the intermolecular forces become apparent. The ideal gas equation of state must then be replaced by an equation, which attempts to allow for these forces.

In 1873, the Dutch chemist J.D. Van der Waals showed that the addition of two parameters to the ideal gases equation of state could account for much of the deviation of real gases from ideal behavior [4]. He attributed the failure of the derived $PV=nRT$ relation to

duplicate the behavior of real gases to the neglect of the volume occupied by the gas molecules and the attractive forces between the molecules. The result of van der Waals' corrections based on these two factors is

$$\left(P + \frac{an^2}{V^2} \right) (V-nb) = nRT \quad (2)$$

where 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. Another form of equation (2) is

$$\frac{P}{\rho kT} = \frac{1}{1-b\rho} - \frac{a\rho}{kT} \quad (3)$$

where, $\rho = n/V$ is the number density and kT is thermal energy per molecule.

The result is an equation that acts much better than the ideal gas equation in describing the P-V-T behavior of real gas. As is well known, this equation shows a critical point and also condensation, when combined with the Maxwell equal-area construction.

A number of other two parameter equation have been developed in attempt over the years to produce modifications of van der Waals equation having a greater accuracy; a few of the better known ones are those of Dieterici [5], Beattie and Bridgeman [6], Benedict, Webb and Rubin [7] and Redlich and kwong [8]. Such equations are widely used in engineering applications [9,10].

The status of van der Waals equation plus the Maxwell construction was considerably enhanced, at least among theoretician, when Kac, Uhlenbeck and Hemmer [11-14] showed in what sense it could be considered an exact result for a model of hard spheres with

weak long-range attractive forces. The main defect is the use of the term $(1-b\rho)^{-1}$ to represent the equation of state of non-attracting hard spheres in three dimensions (the term is exact in one dimension).

The term $a\rho/kT$ for the attractive contribution is exact for the model. This accounts for the great improvement in accuracy for real fluids that Haar and Shenker [15] obtained by replacing the term $(1-b\rho)^{-1}$ by a more accurate Percus-Yevick formula, and by using the correct second virial coefficient instead of the van der Waals result of $B_2=b-a/kT$.

The importance of a hard-sphere model lies in the fact that the structure of simple dense fluid is dominated by the intermolecular repulsive forces [16]. The influence of the attractive forces can then be treated by statistical-mechanical perturbation theory, as can the softness of the repulsions. This approach is very much in the spirit of van der Waals, but the results are far superior, as shown by the pioneering work of Barker and Henderson [17] and of Weeks, Chandler and Andersen [18]. The subject is now highly developed, given the intermolecular potential, it is possible to predict the thermodynamic properties of simple liquids over their stable range of temperature and density. Unfortunately, considerable numerical computation is required, the effective hard-sphere diameter that appears is a function of both temperature and density, and no simple analytical equation of state is forthcoming.

1.2 Literature Review

Several correlation procedures, usually based on principle of corresponding states, exist by which $B(T)$ can be estimated with

reasonable accuracy. The best of these [19,20] require three constants: the critical temperature (T_c), the critical pressure (P_c), and the Pitzer acentric factor (ω). A universal family of curves indexed by the acentric factor is formed by plotting BP_c/RT_c vs. T/T_c . The value of the acentric factor is determined from the vapor pressure at the reduced temperature. Tao and Mason [21] have shown how T_c , P_c and acentric factor can be used to predict the equation of state for normal fluids.

A new method is improved in order to obtain the equation of state of compressed liquids [22] in which we need at least two scaling constants available from simple measurements at ordinary temperatures and pressures. These scaling constants are an energy constant and a volume or density constant.

These parameters would be used to estimate $B(T)$ from corresponding states correlation. The cohesive energy and cohesive energy density can be selected as energy constant and energy density constant, respectively [23-25]. The cohesive energy is defined as "the enthalpy of evaporation plus the change in enthalpy in expanding from the vapor pressure to the ideal gas state minus RT ". Boushehri and Mason [22] has found empirically that the enthalpy of evaporation itself works just as well as the cohesive energy in furnishing a temperature scale for the calculation of $B(T)$. Thus the temperature scale constant is simply $\Delta H_{vap}/R$. The cohesive energy density also furnishes that can be converted to volume scale by choosing the molar volume of the liquid. Boushehri and Mason [22] for ΔH_{vap} and the molar volume used the triple point as a reference point; since the triple point is a unique point on the liquid-vapor coexistence curve other

than critical point. By this method a third constant analogous to acentric factor does not change the final results. A dimensionless plot of $B\rho_{tp}$ as a function of $(RT/\Delta H_{vap})^{-2}$ leads to single curve for a wide variety of nonpolar fluids.

It remains to find the constant λ . For this purpose they used the same data that was used to find ΔH_{vap} - for example, the vapor pressure and liquid density at the triple point or freezing point. Thus parameter λ can be obtained from correlation plot of G^{-1} vs. $b\rho$. This method for determining λ make the whole procedure self-correcting [22]. If the correlation produces values of B that are somewhat in error, or if the input values of ΔH_{vap} and ρ_{tp} are not accurate, the defects will be largely compensated by the determining of λ .

These results show that the equation of state of compressed liquids can be predicted from knowledge of just two constants, ΔH_{vap} and ρ_{tp} , which can be obtained from measurements of the vapor pressures and saturated liquid densities at two temperatures.

Boushehri and Keshavarz [26] have tested the present prediction scheme for compressed liquid mixtures having a variety of structural types. Their survey fluids can be classified into the following groups:

1. Noble gases
2. Diatomics
3. Inorganic polyatomics
4. Alkanes up to octadecane
5. Simple alkenes
6. Simple alkynes
7. Simple aromatic hydrocarbones

Compressed liquid mixtures of the above groups have been tested at different temperatures and compositions. The results show that the density of binary liquid mixtures can be predicted with high accuracy.

Boushehri, Hashemi, and Keshavarzi [27] have showed the first application of a statistical mechanical analytical equation of state to multicomponent liquid mixtures. The agreement with COSTALD, an integrated method for estimating densities of non-polar and slightly polar liquids and liquid mixtures, [28,29] is within 5%.

They have tested the EOS for compressed liquid mixtures, having a variety of structural types (e.g. acentric factor). The test fluids can be classified into the following groups: alkanes up to octane, diatomics, simple aromatic hydrocarbon derivatives (e.g. toluene) and CFCs.

There is a method for predicting an analytical equation of state of liquids from the surface tension which is described in the conclusion part.

The purpose of this work is to present a method for predicting the equation of state of liquid refrigerants and their mixture from properties that are readily available at ordinary pressures and temperatures. In particular, we use the heat of vaporization and the liquid density at the triple point as two quantities that can correlate and predict the behavior of the saturated and compressed liquid. These two quantities, if not directly available, can be obtained with sufficient accuracy from two measured vapor pressures and liquid densities. The equation of state is tested for pure, two, and three component liquid refrigerant mixtures in the temperature range 173-673 K, pressure range 10-100 bar.

1.3 The ISM Equation of State (ISM EOS)

Statistical-mechanical theory for the equation of state of fluids has yielded simple but remarkably accurate results for both spherical [30] and molecular [31] fluids. The equation of state obtained from this work implies a new principle of corresponding states that is much stronger than the traditional principle [32,33]. It is a strong principle in that the entire P-V-T surface is reduced to a single curve, rather than to a whole family of reduced P-V isotherms (the traditional result). This new way of exhibiting P-V-T data amplifies small irregularities and trends in experimental results that would be concealed by the usual representations, and thereby leads to an improved analytical equation of state.

The minimum information needed to reduce the P-V-T surface to a single curve is the second virial coefficient as a function of temperature $B_2(T)$. From this are obtained two other temperature-dependent parameters- an effective van der Waals covolume $b(T)$ and a scaling factor $\alpha(T)$, which is equivalent to the contribution to $B_2(T)$ from just the repulsive branch of the intermolecular forces. The theory then predicts that a suitable combination of P , ρ , T , B_2 , b , and α is a function of the single variable $b\rho$, where ρ is the (molar) density. This combination, according to the statistical-mechanical theory, ought to represent an average pair distribution function at contact for equivalent hard convex bodies, but real data show definite deviations from theoretical expectations. These deviations are caused by many-body forces.

The parameters $B_2(T)$, $b(T)$ and $\alpha(T)$ can all be calculated by integration if the intermolecular potential is accurately known, and a