

# Calculation of Density for Refrigerant Mixtures in Sub Critical Regions for Use in the Buildings

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**Abstract**—Accurate and comprehensive thermodynamic properties of pure and mixture of refrigerants are in demand by both producers and users of these materials. Information about thermodynamic properties is important initially to qualify potential candidates for working fluids in refrigeration machinery. From practical point of view, Refrigerants and refrigerant mixtures are widely used as working fluids in many industrial applications, such as refrigerators, heat pumps, and power plants. The present work is devoted to evaluating seven cubic equations of state (EOS) in predicting gas and liquid phase volumetric properties of nine ozone-safe refrigerants both in super and sub-critical regions. The evaluations, in sub-critical region, show that TWU and PR EOS are capable of predicting PVT properties of refrigerants R32 within 2%, R22, R134a, R152a and R143a within 1% and R123, R124, R125, TWU and PR EOS's, from literature data are 0.5% for R22, R32, R152a, R143a, and R125, 1% for R123, R134a, and R141b, and 2% for R124. Moreover, SRK EOS predicts PVT properties of R22, R125, and R123 to within aforementioned errors. The remaining EOS's predicts volumetric properties of this class of fluids with higher errors than those above mentioned which are at most 8%. In general, the results are in favor of the preference of TWU and PR EOS over other remaining EOS's in predicting densities of all mentioned refrigerants in both super and sub critical regions. Typically, this refrigerant is known to offer advantages such as ozone depleting potential equal to zero, Global warming potential equal to 140, and no toxic.

**Keywords**—Refrigerant; cooling systems; Sub-Critical Regions; volumetric properties; efficiency

## I. INTRODUCTION

**B**UILDING Cooling Systems – effective heat rejection is necessary to maintain the efficiency of the refrigeration system. If outdoor heat rejection equipment is damaged, operating inefficiently, or its access to suitable flow of air is reduced, the effectiveness in rejecting heat is thereby reduced as a consequence. This in turn has the effect of reducing refrigeration efficiency, and reducing the cooling capacity of the system as a whole.

Such refrigeration equipment may turn off and on under the action of its own high temperature or pressure cut-out, often without satisfying the building cooling load. This will

increase the wear and tear on the equipment and will also reduce the service life of the plant.

### *Plant Inefficiency*

For cooling systems effective indoor heat exchange is necessary to maintain the efficiency of the refrigeration system. The assessor will examine the heat exchange equipment to see if it is damaged, or its access to adequate airflow is otherwise reduced, thus the effectiveness in transferring heat to the refrigeration system is reduced. This has the effect of reducing refrigeration efficiency, and reducing the cooling capacity of the system. It may cause the refrigeration equipment to turn off and on under the action of its low temperature or pressure cut-out, often without satisfying the building cooling load, observations that the assessor has will be noted on the above factors and invariably the overall asset rating for the system will be reduced as a consequence. It is recommended that the refrigeration system is serviced prior to an inspection so that the best possible efficiency gains can be met, thus improving the energy efficiency rating for the plant. Equipment that performs poorly will be noted by the assessor and may appear as a recommendation to replace or upgrade component parts as a result. Such reports are advisory.

Note that all air-conditioning systems with an effective rated output of more than 12kw rating must be regularly inspected by an Energy Assessor. The inspections must be a maximum of five years apart.

## II. HOME AND CONSUMER USE

With the invention of synthetic refrigerants based mostly on a chlorofluorocarbon (CFC) chemical, safer refrigerators were possible for home and consumer use. Freon is a trademark of the Dupont Corporation and refers to these CFC, and later hydro chlorofluorocarbon (HCFC) and hydrofluorocarbon (HFC), refrigerants developed in the late 1920s. These refrigerants were considered at the time to be less harmful than the commonly used refrigerants of the time, including methyl formate, ammonia, methyl chloride, and sulfur dioxide. The intent was to provide refrigeration equipment for home use without danger: these CFC refrigerants answered that need. However, in the 1970s the compounds were found to be reacting with atmospheric ozone, an important protection against solar ultraviolet radiation, and their use as a refrigerant worldwide was curtailed in the Montreal Protocol of 1987.

### III. HISTORY

Since van der Waals (1873) proposed his well-known cubic equation of state over a century ago, numerous equations of state have been proposed to calculate the thermodynamic properties of both pure components and mixtures in vapor and liquid phases.

The ability of a CEOS to correlate the phase equilibria of mixtures depends not only on the mixing rule, but also on the alpha function. Remarkable success in the development of a generalized alpha function was shown by Soave (1972). He recognized that a prerequisite for the correlation of the phase equilibria of mixtures is the correlation of the vapor pressures of the pure components. The Soave modification of the Redlich and Kwonog (1949) equation has been a major success in correlation of the phase behavior of multi-component systems containing non-polar and slightly polar components. The Soave approach was subsequently used in work by Peng and Robinson (1976). This also helped the PR equation to become one of the most widely used equations of state in industry for correlating the vapor – liquid equilibria (VLE) of systems containing non-polar and slightly polar components.

Equations of state play an important role in chemical engineering design and they have assumed an expanding role in the study of the phase equilibria of fluids and fluid mixtures. Originally, equations of state were used mainly for pure components. When first applied to mixtures, they were used only for mixtures of nonpolar (Soave, 1972; Peng and Robinson, 1976) and slightly polar compounds (Huron et al., 1978; Asselineau et al., 1978; Graboski and Daubert, 1978). Since then, equations of state have developed rapidly for the calculation of phase equilibria in non-polar and polar mixtures. The advantage of the equations of state method is its applicability over wide ranges of temperature and pressure to mixtures of diverse components, from the light gases to heavy liquids. They can be used for the representation of vapour-liquid, liquid-liquid and supercritical fluid phase equilibria and they can be also applied to the gas, liquid and supercritical phases without encountering any conceptual difficulties. Many equations of state have been proposed in the literature with either an empirical, semi-empirical or theoretical basis. Comprehensive reviews can be found in the works of Martin (1979), Gubbins (1983), Tsionopoulos and Heidman (1985) [9], Han et al. (1988), Anderko (1990), Sandler (1994) and Donohue and Economou (1995).

### IV. REVIEW OF EQUATIONS OF STATE

#### A. Van der Waals EOS

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad (1)$$

Where  $p$  represents pressure,  $T$  is temperature,  $V_m$  is molar volume and  $R$  is the molar gas constant. The parameter  $a$  is a measure of the attractive forces between the molecules and the parameter  $b$  is a measure of the size of the molecules (hard body term). Both adjustable parameters  $a$  and  $b$  can be obtained from the critical properties of the fluid. The van

der Waals equation can be regarded as a “hard-sphere (repulsive) + attractive” term equation of state composed from the contribution of repulsive and attractive intermolecular interactions, respectively.

It gives a qualitative description of the vapour and liquid phases and phase transitions (Van Konynenburg and Scott, 1980), but it is rarely sufficiently accurate for critical properties and phase equilibria calculations. A simple example is that for all fluids, the critical compressibility predicted by Eq.(1) is 0.375, whereas the real value for different hydrocarbons varies from 0.24 to 0.29. The van der Waals equation has been superseded by a large number of other, more accurate equations of state.

Where  $a$ ,  $b$  and  $R$  are constants that depend on the specific material. They can be calculated from the critical properties as:

$$a = 0.421875 \frac{R^2 T_c^2}{P_c} \quad (2)$$

$$b = 0.125 \frac{RT_c}{P_c} \quad (3)$$

Proposed in 1873, the van der Waals equation of state was one of the first to perform markedly better than the ideal gas law. In this landmark equation  $a$  is called the attraction parameter and  $b$  the repulsion parameter or the effective molecular volume. While the equation is definitely superior to the ideal gas law and does predict the formation of a liquid phase, the agreement with experimental data is limited for conditions where the liquid forms. While the van der Waals equation is commonly referenced in text-books and papers for historical reasons, it is now obsolete. Other modern equations of only slightly greater complexity are much more accurate. Van der Waals equation may be considered as the ideal gas law, “improved” due to two independent reasons:

1. Molecules are thought as particles with volume, not material points. Thus  $V$  cannot be too little, less than some constant. So we get  $(V - b)$  instead of  $V$ .

2. While ideal gas molecules do not interact, we consider molecules attracting others within a distance of several molecules' radii. It makes no effect inside material, but surface molecules attract to inside. We see this as diminishing of pressure on the outer shell (which is used in the ideal gas law), so we write  $(P + \text{something})$  instead of  $P$ . To evaluate this 'something', let's examine addition force acting on an element of gas surface.

#### B. Redlich-Kwong EOS

Introduced in 1949 the Redlich-Kwong [4] equation of state was a considerable improvement over other equations of the time. It is still of interest primarily due to its relatively simple form. While superior to the van der Waals equation of state, it performs poorly with respect to the liquid phase and thus cannot be used for accurately calculating vapor-liquid equilibria. However, it can be used in conjunction with separate liquid-phase correlations for this purpose.. The

Redlich-Kwong equation is adequate for calculation of gas phase properties when the ratio of the pressure to the critical pressure (reduced pressure) is less than about one-half of the ratio of the temperature to the critical temperature (reduced temperature). The Redlich-Kwong EOS by Redlich and Kwong is a modification of the Van der Waals EOS it should only be used in order to demonstrate the inabilities of simple EOS, because better EOS exist. Use of this EOS only requires the input of  $T_c$  and  $P_c$ .

The parameters  $a$  and  $b$  (for each component):

$$p = \frac{RT}{v-b} - \frac{a}{\sqrt{T}v(v+b)} \quad (4)$$

$$a = 0.42748 \frac{R^2 T_c^{2.5}}{P_c} \quad (5)$$

$$b = \frac{0.0778 RT_c}{P_c} \quad (6)$$

### C. Peng-Robinson EOS

The Peng-Robinson equation is particularly accurate for predicting the properties of hydrocarbons, including the behavior of mixtures and vapor-liquid equilibrium..

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (7)$$

The Peng-Robinson equation was developed in 1976 in order to satisfy the following goals:

1. The parameters should be expressible in terms of the critical properties and the acentric factor.
2. The model should provide reasonable accuracy near the critical point, particularly for calculations of the Compressibility factor and liquid density.
3. The mixing rules should not employ more than a single binary interaction parameter, which should be independent of temperature pressure and composition.
4. The equation should be applicable to all calculations of all fluid properties in natural gas processes.

For the most part the Peng-Robinson equation exhibits performance similar to the Soave equation, although it is generally superior in predicting the liquid densities of many materials, especially nonpolar ones.

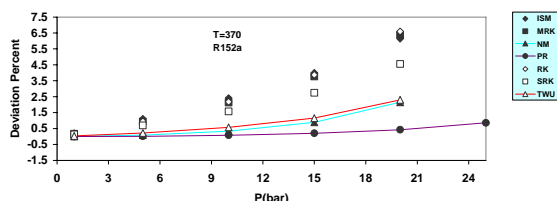


Fig. 1 Deviation plot of the calculated vapor density from the literature data for refrigerant R152a in super-critical ( $T= 500$  K) region.

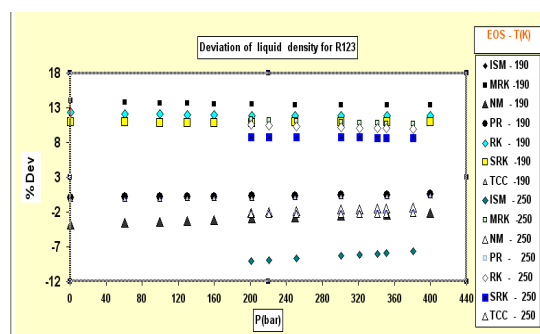


Fig. 2 The calculated liquid density of R152a and R123 at different temperatures and pressures using aforementioned equations of state from literature data.

### V. DISCUSSION OF RESULTS

1- The present work is devoted to evaluating seven cubic equations of state (EOS) in predicting gas and liquid phase thermodynamic properties of several refrigerants both in super and sub-critical regions.

2- Refrigerants include R22, R32, R123, R124, R125, R134a, R141b, R143, and R152a and equations of state, considered here, are Ihm-Song-Mason (ISM), Peng-Robinson (PR), Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK)[2], Modified Redlich-Kwong (MRK), Nasrifar-Moshfeghian (NM), and Twu-Coon[7]- Cunningham (TCC).

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