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Prediction and Correlations of Residual Entropy of Superheated Vapor for Pure Compounds

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Abstract

Prediction of accurate values of residual entropy (S^R) is necessary step for the calculation of the entropy. In this paper, different equations of state were tested for the available 2791 experimental data points of 20 pure superheated vapor compounds (14 pure nonpolar compounds + 6 pure polar compounds). The Average Absolute Deviation (AAD) for S^R of 2791 experimental data points of the all 20 pure compounds (nonpolar and polar) when using equations of Lee-Kesler, Peng-Robinson, Virial truncated to second and to third terms, and Soave-Redlich-Kwong were 4.0591, 4.5849, 4.9686, 5.0350, and 4.3084 J/mol.K respectively. It was found from these results that the Lee-Kesler equation was the best (more accurate) one compared with the others, but this equation is sometimes not very preferable. It was noted that SRK equation was the closest one in its accuracy to that of the Lee-Kesler equation in calculating the residual entropy S^R of superheated vapor, but it was developed primarily for calculating vapor-liquid equilibrium and to overcome this problem, efforts were directed toward the possibility of modifying SRK equation to increase its accuracy in predicting the residual entropy as much as possible. The modification was made by redefining the parameter α in SRK equation to be a function of reduced pressure, acentric factor, and polarity factor for polar compounds in addition to be originally function of reduced temperature and n parameter –which is also function of acentric factor– by using statistical methods. This correlation is as follows:

$$\alpha = [1+n(\gamma)]^2 \qquad , \qquad \gamma = -0.920338\ P_r^{-0.34091} + 0.064049\ T_r^{\,4}\omega + 0.370002\ \omega - P_r^{0.996932} Tr^{-4}\chi$$

This new modified correlation decreases the deviations in the results obtained by using SRK equation in calculating S^R when comparing with the experimental data. The AAD for 2791 experimental data points of 20 pure compounds is 4.3084 J/mol.K while it becomes 2.4621 J/mol.K after modification. Thus SRK equation after this modification gives more accurate results for residual entropy of superheated vapor of pure 20 compounds than the rest of the equations mentioned above.

Keywords: entropy, residual entropy, superheated vapor, equation of state, reduced temperature, reduced pressure, acentric factor, and polarity factor.

Introduction

Thermodynamics has been called by many “the science of energy and entropy”. However, unlike energy, the word entropy is seldom heard in everyday conversation; energy and entropy play important roles in thermal systems engineering [1].

Although there are many ways to introduce the concept of entropy, the simplest is just to deal with its utility; namely: a mathematical tool to describe the direction in which things actually occur and if it occurs spontaneously or not. It is one of the thermodynamic properties of fluids that are essential for the design process equipments that calculate the heat and work requirements of industrial process. Also the analysis of the performance of compressors or expanders requires knowledge of the entropy behavior. Neither energy nor entropy can be measured directly on energy or entropy meter, so values are usually expressed in relation to an arbitrary reference state depending on the experimental data of another property that can be measured experimentally such as temperature and pressure denoted by **T** and **P**, respectively [2, 3].

One of the important ways to obtain the entropy data for pure substances at various states is the experimental data usually available in graphical or tabular forms, but for graphical it is a more complicated method in practical use compared with the property tables that when simply provide very accurate information about the properties, but they are very bulky and vulnerable to typographical errors [2] and many times some interpolations between two pressures or temperatures are needed to obtain the value of a thermodynamic property of entropy at certain points. Also for the phase of superheated vapor, it is so difficult reaching the conditions of high pressures or temperatures for many compounds in laboratory. Thus a more practical and desirable approach is based on **E**quation **o**f **s**tate (**EOS**).

Pure gases are categorized into [4]:

1. **Nonpolar gases** which include:
   a. Simple fluids with spherical molecules $\omega=0$ such as Argon, Krypton,
   b. Quantum gases having $\omega<0$ such as He, H_2, and
   c. Other nonpolar fluids which have $\omega>0$ such as Benzene, Propane.
2. **Polar gases** that can be subdivided into:
   a. Non-hydrogen bonding compounds such as Ketones, and Aldehydes, and
   b. Hydrogen bonding compounds (a bond forms between the H atom attached to Oxygen atom in one molecule with the Oxygen atom of another molecule) such as Alcohols, and Water.

In addition to acentricity, the polar compounds are characterized by the presence of dipole moment arises from positive and negative charges that are present in the molecule.

There is no precise recommended method for calculating entropy or residual entropy for superheated vapor. This work involves studying the deviation in calculated entropy values from its actual values (obtained by available experimental data for different compounds: polar and nonpolar gases) and then stating which method is more suitable than the others.

EOS (Models)

The most convenient method of representing the properties or the behavior of a substance, is by a mathematical expression; that is, an equation which represent the (P-V-T) behavior of a fluid. A general form of such an expression known as EOS is:

$$f(P,V,T)=0 \qquad \ldots(1)$$

1. Soave-Redlich-Kwong (*SRK*) Equation

Soave [5, 6] in 1972 introduced a modification on the Redlich-Kwong (*RK*) equation of state ; this modification has been successful in extending the applicability of *RK* equation to be applied with high accuracy for wide range of non-polar and slightly polar components. The temperature dependent term $a/T^{0.5}$ of the *RK* equation was altered to include both the temperature and the acentric factor by Soave; the *SRK* equation is [7]:

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)} \quad \text{...(2)}$$

Where the factor α is an empirical function determined from the vapor-pressure data of pure hydrocarbons.
The *SRK* equation for residual entropy is:

$$\frac{S^R}{R} = \ln[Z-B] - \frac{BD}{a\alpha A}\ln\left(1+\frac{B}{Z}\right) \quad \text{...(3)}$$

The cubic form in terms of compressibility factor is:

$$Z^3 - (1-B)Z^2 + \left(A - B^2 - B\right)Z - AB = 0 \quad \text{...(4)}$$

Where

$$A = 0.42747\alpha\frac{P_r}{T_r^2},\ B = 0.08664\frac{P_r}{T_r} \quad \text{...(5)}$$

$$a = 0.42747\frac{R^2T_c^2}{P_c}, b = 0.08664\frac{RT_c}{P_c} \quad \text{...(6)}$$

$$\alpha = \left[1 + n\left(1 - T_r^{0.5}\right)\right]^2 \quad \text{...(7a)}$$

$$n = 0.48508 + 1.55171\omega - 0.1561\omega^2 \quad \text{...(7b)}$$

and $D = na\sqrt{\alpha T_r}$ ...(8)

2. Peng-Robinson (*PR*) Equation

The equation of Peng and Robinson in 1976 [8] is rather structurally similar to the SRK and, like the SRK, requires only the critical constants and the acentric factor for its application for a pure fluid. This equation of state was developed primarily for vapor liquid equilibrium predictions. Peng-Robinson modified the standard form as follows [7]:

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b) + b(V-b)} \quad \text{...(9)}$$

The *SRK* equation for residual entropy is:

$$\frac{S^R}{R} = \ln[Z-B] - \frac{BD}{2.828\,a\alpha A}\ln\left(\frac{Z+2.414B}{Z-0.414B}\right) \quad \text{...(10)}$$

The cubic form in terms of compressibility factor is:

$$Z^3 - (1-B)Z^2 + \left(A - 3B^2 - 2B\right)Z - \left(AB - B^2 - B^3\right) = 0 \quad \text{...(11)}$$

Where $A = 0.45724\alpha\frac{P_r}{T_r^2}, B = 0.07780\frac{P_r}{T_r}$ ...(12)

$$a = 0.45724\frac{R^2T_c^2}{P_c}, b = 0.07780\frac{RT_c}{P_c}$$

$$\alpha = \left[1 + n\left(1 - T_r^{0.5}\right)\right]^2 \quad \text{...(13)}$$

$$n = 0.37464 + 1.5422\omega - 0.26992\omega^2 \quad \text{...(14)}$$

also, $D = na\sqrt{\alpha T_r}$ ...(15)

3. Lee-Kesler Equation

Lee and Kesler in (1975) [9] developed an analytical correlation, based on Pitzer's three-parameter corresponding states principle [10] to provide increased accuracy and covering the whole range of Tr and Pr of practical interest in hydrocarbon processing. It is to be noted that the original correlations by Pitzer et al. were limited to reduced temperatures above 0.8. Pitzer et al. correlations for the compressibility factor of a fluid whose acentric factor is ω are given by the following equation:

$$Z = Z^{(0)} + \omega Z^{(1)} \qquad \ldots(16)$$

Where $Z^{(0)}$ is the compressibility factor of a simple fluid and $Z^{(1)}$ corrects $Z^{(0)}$ for the effects of nonspherical intermolecular forces (primarily dispersion and overlap). $Z^{(0)}$ and $Z^{(1)}$ are assumed functions of T_r and Pr. However, Lee and Kesler found that the compressibility factor of any fluid is a function of the compressibility of a simple fluid ($Z^{(0)}$), the compressibility of a reference fluid ($Z^{(r)}$), and the acentric factor, where $Z^{(0)}$ and $Z^{(r)}$ are functions of T_r and Pr and the correlation of Lee and Kesler takes the form:

$$Z = Z^{(0)} + \frac{\omega}{\omega^r}\left(Z^{(r)} - Z^{(0)}\right) \qquad \ldots(17)$$

Where $\omega^r=0.3978$ and it is the acentric factor for reference fluid, and the correction term $Z^{(1)}$ in eq. (16) is obviously equivalent to $(Z^{(r)} - Z^{(0)}) / \omega^r$ this expression is convenient since both $Z^{(r)}$ and $Z^{(0)}$ are given by the same equation with, however, different constants. Lee and Kesler chose n-octane as the heavy reference fluid since it is the heaviest hydrocarbon for which there are accurate (P-V-T) and enthalpy data over a wide range of conditions [9, 11].

The function for both the simple fluid $Z^{(0)}$ and the reference fluid $Z^{(r)}$ are derived through a combination of experimental data and a reduced form of the modified Benedict-Webb-Rubin [9, 11] equation of state with a different set of constants that are scheduled in Table (1).

$$Z = \left(\frac{P_r V_r}{T_r}\right) = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right) \qquad \ldots(18)$$

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \qquad \ldots(19)$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \qquad \ldots(20)$$

$$D = d_1 + \frac{d_2}{T_r} \qquad \ldots(21)$$

Table 1, Constants for Calculating Equation (18) [9]

constants	Simple Fluid (0)	Reference Fluid (r)
b_1	0.1181193	0.2026579
b_2	0.265729	0.331511
b_3	0.15479	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0.0	0.016901
c_4	0.042724	0.041577
$d_1\times10^4$	0.155488	0.48736
$d_2\times10^4$	0.623689	0.0740336
β	0.65392	1.226
γ	0.060167	0.03754

For calculating Z for the fluid of interest given at T and P, first the appropriate values of T_r (T/T_c) and P_r (P/P_c) are calculated by using critical properties of the fluid. From the simple fluid constants in Table (1), eq. (18) solves V_r –which is not the correct reduced volume for the fluid of interest, but rather a pseudo–reduced volume– by the trial and error method when V_r is defined as (P_cV/RT_c), which can be considered the initial guess for the calculation, or from the first equality of eq. (18) the initial guess can be taken as:

$$V_r = Z\frac{T_r}{P_r} \qquad \ldots(22)$$

The previous equation was depended by Paul and Francis [12] in preparing their computer program for the tables of

Lee and Kesler*. After trial and error calculation the obtained value of $V_r = V_r^{(0)}$ for simple fluid and when employed in the first equality of eq. (18), $Z^{(0)}$ is calculated for simple fluid. This process is then repeated using the reference fluid constants with the same T_r and P_r values of the fluid of interest to find $V_r = V_r^{(r)}$ and $Z^{(r)}$ for the reference fluid. Finally, with $Z^{(0)}$ from the first calculation and $Z^{(r)}$ from the second, the compressibility factor Z for the fluid of interest is determined from eq. (17) [9].

The residual entropy is derived from eq. (18):

$$\frac{S-S^{ig}}{R}+\ln\left(\frac{P}{P^*}\right)=\ln(Z)-\frac{b_1+\left(b_3/T_r^2\right)+\left(2b_4/T_r^3\right)}{V_r}-\frac{c_1-\left(2c_3/T_r^3\right)}{2V_r^2}-\frac{d_1}{5V_r^5}+2E \quad \ldots(23)$$

* Paul and Francis [12] took the initial guess for Z of eq. (23) equal to 0.2 but in this research which concentrates on the vapor phases especially superheated vapor the initial Z value taken equal to 1 because for vapor phases at high reduced temperatures and pressures the Z value often more than unity [13].

Where:

$$E=\frac{c_4}{2T_r^3\gamma}\left\{\beta+1-\left(\beta+1+\frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right)\right\} \quad \ldots(24)$$

After determining $V_r^{(0)}$ and $Z^{(0)}$ for the simple fluid at the T_r and P_r appropriate for the fluid of interest, and employing eq. (23) with the simple fluid constants in table (1), $(S\text{-}S^{ig})/R$ is calculated. This term represents $[(S\text{-}S^{ig})/R]^{(0)}$ in this calculation and Z in eq. (23) is $Z^{(0)}$. Then, when repeating the same calculation, using the same T_r and P_r and the values of $V_r^{(r)}$ and $Z^{(r)}$ for the reference fluid also determined previously, but employing the reference fluid constants from Table (1), eq. (23) allows the calculation of $[(S\text{-}S^{ig})/R]^{(r)}$. Now, determining the residual entropy function for the fluid of interest from:

$$\left[\frac{\left(S-S^{ig}\right)}{R}+\ln\left(\frac{P}{P^*}\right)\right]=\left[\frac{\left(S-S^{ig}\right)}{R}+\ln\left(\frac{P}{P^*}\right)\right]^{(0)}+\left(\frac{\omega}{\omega^r}\right)\left\{\left[\frac{\left(S-S^{ig}\right)}{R}+\ln\left(\frac{P}{P^*}\right)\right]^{(r)}-\left[\frac{\left(S-S^{ig}\right)}{R}+\ln\left(\frac{P}{P^*}\right)\right]^{(0)}\right\} \quad \ldots(25)$$

4. Virial Equation

The virial equation of state, also called the virial expansion, is the most interesting and versatile of the equations of state which are used to describe the (P-V-T) properties of a fluid and its importance is due to that it has a sound theoretical basis. It is a polynomial series in pressure or in inverse volume whose coefficients are functions only of T for a pure fluid. Virial coefficients are classified into many truncated forms according to the order of the term series. The consistent forms for the initial terms are:

$$Z=\frac{PV}{RT}=1+\frac{B(T)}{V}+\frac{C(T)}{V^2}+\frac{D(T)}{V^3} \quad \ldots(26a)$$

$$=1+B\rho+C\rho^2+D\rho^3 \quad \ldots(26b)$$

$$=1+B'P+C'P+D'P+ \quad \ldots(26c)$$

The coefficient B or B' is called the second virial coefficient; C or C' is called the third virial coefficient, and so on. In practice, since not all of the coefficients of the virial series are known, and only data of the second virial coefficients are plentiful in the literature, terms above the third virial coefficient are rarely used in chemical thermodynamics and the series is usually limited in practice up to moderate pressures. However, the advantages of the virial equation could be increased if quantitative information were available on the third virial coefficient [3, 14, 15].

4.1. Relations Between the Virial Coefficients

The virial expansion for P is:

$$P=\frac{RT}{V}\left(1+\frac{B(T)}{V}+\frac{C(T)}{V^2}+\frac{D(T)}{V^3}\cdots\right) \quad ...(27)$$

The coefficients of the expansion in pressure are related to the coefficients of the expansion in density (*1/V*) as follows [16]:

$$B=RTB' \quad \Rightarrow \quad B'=\frac{B}{RT} \quad ...(28a)$$

$$C=(RT)^2\left(C'+B'^2\right) \quad \Rightarrow \mathrm{C}'=\frac{\left(\mathrm{C}-\mathrm{B}^2\right)}{(\mathrm{RT})^2} \quad ...(28b)$$

The first step of the derivation of these relations is by solving the original virial expansion for *P* above and then by equating the two virial expansions, and finally by substituting this expression for *P* into the pressure form-side of resulting equation to obtain:

$$1+B\frac{1}{V}+C\frac{1}{V^2}+\cdots=1+B'RT\frac{1}{V}+B'RTB\frac{1}{V^2}$$
$$+C'(RT)^2\frac{1}{V^2}+\cdots \quad ...(29)$$

Both sides of equation (29) are power series in 1/V (third and higher powers of *1/V* were omitted because the second power is the highest power used by the common references). Since the two power series must be equal, the coefficients of each power of *1/V* must be the same on both sides. This comparison provides the relations between the coefficients [15].

4.2. Second Virial Coefficient

Correlation of second virial coefficient of both polar and nonpolar systems is presented by [4, 15].

$$Z=1+\frac{B}{V}=1+B'P=1+\frac{BP}{RT} \quad \ldots (30)$$

Tsonopoulos correlation for *B* is:

$$B=\frac{RT_c}{P_c}\left(B^{(0)}+\omega B^{(1)}\right) \quad ...(31)$$

$$B^{(0)}=0.1445-\frac{0.33}{T_r}-\frac{0.1385}{T_r^2}-\frac{0.0121}{T_r^3}-\frac{0.000607}{T_r^8} \quad \ldots(32)$$

$$B^{(1)}=0.0637-\frac{0.331}{T_r^2}-\frac{0.423}{T_r^3}-\frac{0.008}{T_r^8} \quad \ldots(33)$$

4.3. Third Virial Coefficient

At high pressures -above 1500 kPa- equations (26a, b, and c) may be truncated after three terms [13]:

$$Z=1+\frac{B}{V}+\frac{C}{V^2}=1+B'P+C'P^2 \quad \ldots(34)$$

Orbey-Vera correlation for *C* is:

$$C=\left(\frac{RT_c}{P_c}\right)^2\left(C^{(0)}+\omega C^{(1)}\right) \quad ...(35)$$

$$C^{(0)}=0.01407+\frac{0.02432}{T_r^{2.8}}-\frac{0.00313}{T_r^{10.5}} \quad ...(36)$$

$$C^{(1)}=-0.02676+\frac{0.0177}{T_r^{2.8}}+\frac{0.04}{T_r^3}-\frac{0.003}{T_r^6}-\frac{0.00228}{T_r^{10.5}} \quad \ldots(37)$$

By using the residual properties, the final expression of the residual entropy after derivation can be expressed as [13]:

$$\frac{S-S^{ig}}{R}=-\left(\frac{dB}{dT}\left(\frac{P}{R}\right)-\frac{1}{2}\left[C-T\frac{dC}{dT}-\left(B^2-2BT\frac{dB}{dT}\right)\right]\left(\frac{P}{RT}\right)^2+\cdots\right) \quad \ldots(38)$$

The aim of the present work is to calculate the residual entropy by using Lee-Kesler, Peng-Robinson, Virial truncated to B or to C terms, and Soave-Redlich-Kwong equations to determine the deviation from the actual residual entropy using statistical methods to modify the best equation depending on the shape of particle (ω) in addition to the polarity factor (χ) for the polar gases in order to come out with an equation that predicts the residual entropy for different types of superheated vapor of pure gases with high agreement with experimental data.

Acentric Factor

In 1955, Pitzer [10] observed that the reduced vapor pressures of molecules with acentric force fields are lower than that of simple fluids, and the difference is greater for the molecules of greater acentricity. Pitzer noted that all vapor pressure data for the simple fluids (Ar, Kr, and Xe) lie on the same line when plotted as $\log_{10} P_r^{sat}$ vs. $1/T_r$ and that the line passes through $\log_{10} P_r^{sat} = -1.0$ at $T_r = 0.7$. This is illustrated in Fig. (1).

Data for other fluids define other lines whose location can be fixed in relation to the line of simple fluids. Thereupon, Pitzer defined the acentric factor ω (a third parameter) of a substance by [15]:

$$\omega = -1 - \log_{10}\left(P_r^s\right)_{T_r=0.7} \qquad ...(39)$$

Therefore ω can be determined for any fluid from Tc, Pc, and a single vapor-pressure measurement was made at Tr = 0.7 which is near the normal boiling point of most substances, so the importance of choosing Tr = 0.7 that was adopted by Pitzer not only provides numerical simplicity ($\log_{10}P_r^{sat} = -1$ for simple fluids) but also is beneficial because vapor pressure data are most commonly available at near atmospheric pressure [15].

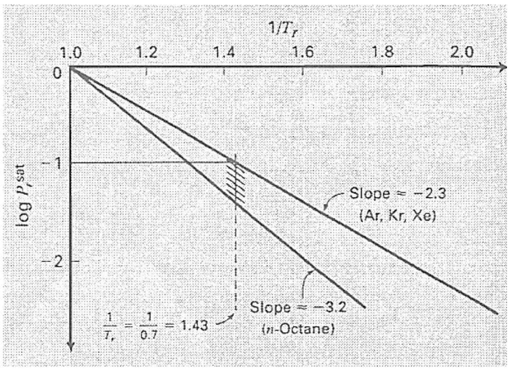

Fig.1, Approximate temperature dependence of the reduced vapor pressure [15]

Polarity Factor of Halm and Stiel

Because the vapor pressure formed the basis for the definition of the acentric factor, this property was chosen as the starting point for the extension of the normal fluid approach to polar fluids to obtaining polarity factor χ which is an empirical parameter for polar substances similar to the acentric factor for normal fluids. The factor χ is defined to be zero for normal fluids and can be expressed for polar fluids as follows:

$$\chi = \log P^s{}_r\Big|_{T_r=0.6} + 1.552 + 1.7\omega \quad \ldots(40)$$

Values of χ can be obtained from the literatures for some polar compounds[17, 18].

Calculation of Entropy for Superheated Region

The calculation of entropy for superheated region needing four steps in a calculational path leading from an initial to a final state of a system as obtained in equation below:

$$\Delta S = \Delta S_v + \int_{T_1}^{T_2} C_P^{ig}\frac{dT}{T} - R\ln\frac{P_2}{P_1} + S_2^R - S_1^R \quad \ldots(41)$$

Thus, in Fig. (2) the actual path from state 1 to state 2 – the dashed line – is replaced by a four-step calculational path; these steps visualize the sum of four changes represented by the sequence of isothermal and isobaric steps:

$$S_2 - S_1 = \left(S_2 - S_2^{ig}\right) + \left(S_2^{ig} - S_1^{ig}\right) + \left(S_1^{ig} - S_1^{v}\right) + \left(S_1^{v} - S_1\right) \qquad \ldots(42)$$

- **Step** 1 → 1^v: The transformation of saturated liquid at (T_1, P_1) to saturated vapor at T_1 and P_1:

$$S_1^v - S_1 = \Delta S_v$$

Saturated entropy of vapor can be calculated by converting saturated liquid at reference T and P to saturated actual gas at the same T and P by using the entropy of vaporization at the normal boiling point ΔS^v after scaling it with the reference temperature by Watson relation [15]

$$\frac{\Delta H_{v1}}{\Delta H_{v2}} = \left(\frac{1 - T_{r1}}{1 - Tr_2}\right)^{0.38} \qquad \ldots(43)$$

In ref. [13], some of the better estimation methods were tested for several different compounds as hydrocarbons, alcohols, rare gases, oxides and other polar compounds and useful comparison between these methods (Giacalone, Riedel, Chen, and Vetere) and experimental values of ΔH_v were obtained. This comparison shows that the average absolute percentage error of Giacalone, Riedel, Chen, and Vetere methods are 2.8, 1.8, 1.7, and 1.6, respectively. Therefore, the present investigation employs the more accurate one Vetere method eq. (44) to calculate ΔH^v at the normal boiling point and it is scaled with eq. (43)

$$\Delta H_{vb} = RT_c T_{br} \frac{0.4343 \ln P_c - 0.69431 + 0.89584 T_{br}}{0.37691 - 0.37306 T_{br} + 0.15075 P_c^{-1} T_{br}^{-2}} \qquad \ldots(44)$$

to obtain ΔHv at the reference temperature, then calculating ΔSv by dividing ΔHv by the reference temperature.

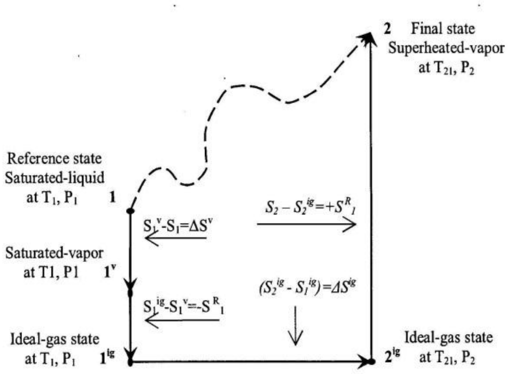

Fig.2, Calculational path for entropy change

- **Step** 1^v → 1^{ig}: A hypothetical process that transforms a real gas into an ideal gas at T_1 and P_1 by using suitable residual entropy of an equation of state.

$$S_1^{ig} - S_1^v = -S_1^R$$

- **Step** 1^{ig} → 2^{ig}: Changes in the ideal-gas state from (T_1, P_1) to (T_2, P_2). For this process:

$$\Delta S^{ig} = S_2^{ig} - S_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

In the present work C_p^{ig} is calculated by:

$$\frac{C_p^{ig}}{R} = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \qquad \ldots(45)$$

This polynomial provides simplicity in use and it also covers good range of temperatures. The data related to eq. (45) for some pure compounds are listed in (Appendix A- section c) of ref. [1٣].

- **Step** 2^{ig} → 2: Another hypothetical process that transforms the ideal gas back into a real gas at T_2 and P_2:

$$S_2 - S_2^{ig} = S_2^R$$

Therefore, Equation (42) is the result of the totality of the entropy changes for the above four steps.

Selecting the Optimum EOS for the Present Work [19]

The conflict between accuracy and simplicity is a big dilemma in the development of an equation of state. Despite the wide use of high-speed computers, the simplicity is still highly desired for easy and unequivocal applications of the equation to complex problems. So, for most calculations, the empirical approach is often better than the more complex theoretical approach in view of accuracy as well as minimum data requirements. Often, virialequation – which truncates to second or to third term – can only be considered useful from the first form and employed in the present work. In addition to the Soave-Redlich-Kwong equation (SRK) and Peng-Robinson equation (PR) as the models of cubic equations of state from the second form which have valuable applications in most common use today, Lee and Kesler equation represents –although it is including some complexity– the easiest example of the third form that was also used in the present work.

The **A**verage **A**bsolute **D**eviation for residual entropy AAD in (J/mol.K) is defined as follows:

$$AAD = \frac{\sum \left| (S^R{}_{experimental} - S^R{}_{calculated}) \right|}{n} \quad ...(46)$$

AAD is considered as a factor for a comparison between the different methods that were used for calculating actual residual entropy of superheated vapor for different compounds. It is calculated in (J/mol.K) because when it is calculated in (J/g. K) it was very decimal and the imparity of deviations of using the equations was not perceptible. Also, the dimensionless deviation can be obtained by dividing AAD by R (gas constant) which is denoted by AAD/R.

In addition, the **A**verage **A**bsolute **P**ercentage **D**eviation for entropy AAD% is defined as follows:

$$AAD\% = \frac{\sum \left| (S_{experimental} - S_{calculated}) / S_{experimental} \right| \times 100\%}{n} \quad ...(47)$$

which is considered as a factor for comparison between the different methods that were associated in determining the actual entropy of superheated vapor for different compounds.

Results and Discussion [19]

1. Application of the EOS for Compounds

1.1. Classification of the Application of EOS into Regions

Five different equations of state were applied for calculating residual entropy (S^R) in comparison for all experimental data of pure compounds that supported the present investigation as expressed earlier. To have an insight of the precision of these equations with the range of T_r and Pr, a summary of the results classified into three regions is presented as follows:

Region 1)

T_r **< 1, and** P_r **< 1** include 14 compounds involving 859 experimental data points (9 nonpolar compounds with 431 experimental data points and 5 polar compounds with 428 experimental data points) from the 2791 experimental data points of the all 20 compounds.

Region 2)

T_r **> 1, and** P_r **< 1** include the 20 compounds involving 1501 experimental data points (14 nonpolar compounds with 921 exp. data points and 6 polar compounds with 580 exp. data points) from the all 2791 exp. data points of the all 20 compounds.

Region 3)

$T_r > 1$, **and** $P_r > 1$ include 13 compounds involving 431 experimental data points (10 nonpolar compounds with 308 experimental data points and 3 polar compounds with 123 experimental data points) from the all 2791 experimental data points of the all 20 compounds. Although this region represents the supercritical region, but the knowledge of the accuracy of employing these equations in comparison with the accuracy of the modified equation in the present work for this region is advantageous for some available experimental data.

1.2. Total Region

This region represents all three regions and consists of 20 compounds involving 2791 experimental data points (14 nonpolar compounds with 1660 experimental data points and 6 polar compounds with 1131 experimental data points).

2. Modification of EOS [19]

2.1. Selecting the Optimum EOS for the Modification

Although Lee-Kesler equation proved to be better than Soave-Redlich-Kwong, Peng-Robinson, and Virial equations for the prediction of residual entropy of superheated vapor for the most of compounds used in this investigation, but it is more useful if the errors can be reduced to value less than those obtained with Lee-Kesler equation.

The modification of any equation is usually done for the equation that proved to be the most accurate. The more accurate one is Lee-Kesler equation, but it is very difficult to modify it, so Soave-Redlich-Kwong equation which is the nearest one in accuracy to the Lee-Kesler equation was selected for modification.

Table 2, The existence of the compounds in three regions

	Non polar compounds	regions		Non polar compounds	regions
1	Argon	1, 2, 3	12	n-Hexane	1, 2, 3
2	Methane	2, 3	13	n-Heptane	1, 2, 3
3	Oxygen	2, 3	14	n-Octane	1, 2, 3
4	Nitrogen	2, 3		Polar compounds	regions
5	Ethane	2, 3			
6	Cyclo-propane	1, 2	1	Refrigerant 12	1,2
7	Propane	1, 2, 3	2	Isopentane	2, 3
8	Acetylene	1, 2	3	Ammonia	1, 2
9	Neo-pentane	1, 2	4	Refrigerant 152a	1, 2
10	Benzene	1, 2	5	Refrigerant 134a	1, 2, 3
11	Carbon dioxide	2, 3	6	Water	1, 2, 3

2.2. Modification of Soave-Redlich Kwong Equation [19]

Soave-Redlich-Kwong equation was derived mainly to calculate vapor-liquid equilibria, so all attention was concentrated on that purpose in its derivation, and therefore, there is still room for improving it for superheated vapor.

The modification would be based on modifying α parameter of SRK equation which is the function of reduced temperature and also on acentric factor which is included in parameter n:

$$\alpha = \left[1 + n\left(1 - T_r^{0.5}\right)\right]^2 \text{ SRK eq. parameter} \quad \ldots(7a)$$

Figs. (2) to (5) show clearly that the values of pressures or reduced pressures influence the value of α although the temperature is constant.

Thus α in Soave equation can be considered a function of temperature, pressure and acentric factor and its equation would be written as [19]:

$$\alpha = \left[1 + n(\gamma)\right]^2 \text{ new form of } \alpha \text{ parameter} \quad \ldots(48a)$$

$$\gamma = g_1 \Pr^{g_2} + g_3 Tr^4 \omega + g_4 \omega - \Pr^{g_5} Tr^{-4} \chi \quad \ldots(48b)$$

The coefficients of this equation had been determined by using statistical methods. These coefficients were calculated with the aid of computer program on non-linear estimation of statistica software fitting to minimize the error obtained for calculating new α for two selected compounds.

In the present work, n-octane and water were used in the fitting. By trying many different equations, it was found that equation (48b) was the optimum equation for predicting γ with lowest error. The coefficients of eq. (48b) are listed in Table (3).

Table 3, Coefficients of equation (48b)

coefficient	value	coefficient	value
g_1	-0.920338	g_4	0.370002
g_2	-0.034091	g_5	0.9906321
g_3	0.064049	----	----

The modification was made by comparing the experimental values of residual entropy of superheated vapor with the values calculated by Soave equation which was obtained by using all original parameters of Soave equation except γ parameter which is inserted in the computer program empirically and remain varying until the deviation between the inserted value of γ with the calculated value by Soave equation for each experimental data point- approached to zero (% error of $(S^R_{exp.}-S^R_{cal.}) \leq 0.00001$).

The new equation of α gives a higher accuracy where the overall **AAD** was 2.4621 J/mol.K for residual entropy and the (**AAD%**) was 1.1083 for entropy, for all compounds studied in the present work.

The main reason for choosing the mentioned two compounds (n-octane, and water) in the fitting of the experimental data was due to their molecular nature that n-octane represents the normal nonpolar gases which was considered having the highest ω > 0 in comparison with the other used compounds in the present work and thus to be able of controlling the other compounds of less ω and has no polarity properties found (χ = 0). On the other hand, water represents the polar compounds which have in addition to ω > 0 the polarity properties χ > 0 and also it has the highest χ among others. The only way for obtaining the experimental values of the parameter γ is by all empirical trial and error method which needs great time to obtain any value. Therefore, the modification was limited to only these mentioned two types of gases which were used to predict the new α parameter equation that gives more accuracy in calculating S^R and S for all data points (2791) experimental data points for all 20 nonpolar and polar gases employed in the present work.

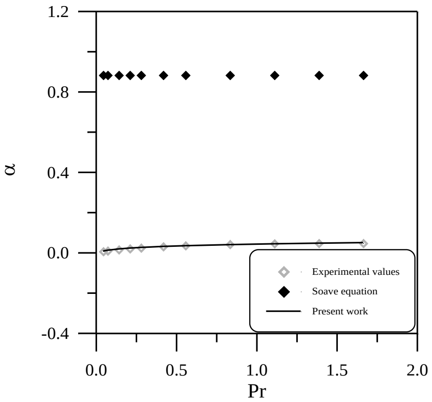

Fig.2, The relation between the values of parameter α and P_r for n-octane at T_r =1.3

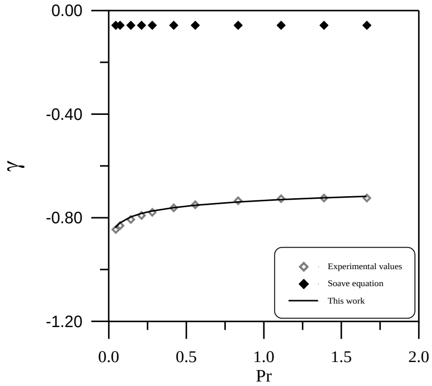

Fig.3, The relation between the values of parameter γ and P_r for n-octane at T_r =1.3

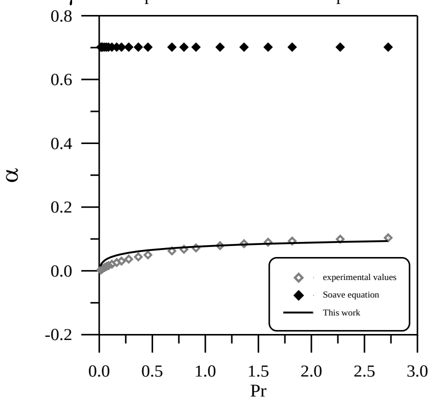

Fig.4, The relation between the values of parameter α and P_r for water at T_r =1.349

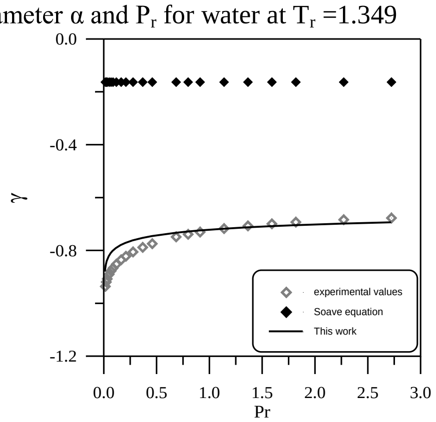

Fig.5, The relation between the values of parameter γ and P_r for water at T_r =1.349

Table 4a, Summary of application of EOS through 3 regions individually

Region 1 at (Tr < 1 and Pr <1) No. of points in region 1 is (859)			
Equations used	AAD for S^R (J/mol.K)	AAD/R for S^R	AAD% for S
L-K	4.8377	0.5819	1.7033
P-R	5.2743	0.6344	1.9060
Virial truncated to B)	5.2816	0.6353	1.9657
Virial truncated to C)	5.2197	0.6278	1.9547
S-R-K	5.1998	0.6254	1.8723
This work	2.9180	0.3510	1.0974

Region 2 at (Tr > 1 and Pr <1) No. of points in region 2 is (1501)			
Equations used	AAD for S^R (J/mol. K)	AAD/R for S^R	AAD% for S
L-K	3.9300	0.4727	1.7892
P-R	4.1422	0.4982	1.8790
Virial truncated to B)	4.3718	0.5258	2.0988
Virial truncated to C)	4.3709	0.5257	2.1102
S-R-K	4.0144	0.4828	1.8171
This work	2.4077	0.2896	1.1475

Region 3 at (Tr > 1 and Pr >1) No. of points in region 3 is (431)			
Equations used	AAD for S^R (J/mol. K)	AAD/R for S^R	AAD% for S
L-K	2.9571	0.3557	1.5221
P-R	4.7524	0.5716	2.7529
Virial truncated to B)	6.4233	0.7726	4.6412
Virial truncated to C)	6.9797	0.8395	5.0765
S-R-K	3.5325	0.4249	2.1336
This work	1.7430	0.2096	0.9935

Table 4b, Summary of Application of EOS through whole regions. (from $T_r < 1$ & $P_r < 1$ to $T_r > 1$ & $P_r > 1$)

All regions (1, 2, and 3) No. of points for all regions (2791)			
Equations used	AAD for S^R (J/mol. K)	AAD/R for S^R	AAD% for S
L-K	4.0591	0.4882	1.7215
P-R	4.5849	0.5515	2.0223
Virial truncated to B)	4.9686	0.5976	2.4505
Virial truncated to C)	5.0350	0.6056	2.5204
S-R-K	4.3084	0.5182	1.8850
This work	2.4621	0.2961	1.1083

Discussion

The entropy of a pure compound cannot be directly measured but is calculated from other properties. It is a function of both temperature and pressure; in general, it increases with the increase in temperature and decreases with the increase in pressure at constant temperature. At zero pressure, all gases behave ideally, and the ideal gas state entropy is remaining dependent on pressure.

The residual entropy term $S\text{-}S^{ig}$ is the difference between the entropy of a compound at certain P and T and that of an ideal gas state at the same conditions. In the absence of P-V-T data for the compounds of interest, or if the data do not cover the conditions under which engineering calculations are to be made, generalized correlations which express Z as a function of T_r and P_r were found to be of great value in estimating residual properties as residual entropy based on a modified theory of corresponding states.

The usual method available for predicting the residual entropy of superheated vapor for pure compounds is by employing the equation of state. In the present work the equations of state employed were: L-K, P-R, S-R-K, and Virial truncated to second and to third terms equations. It is well known that the evaluation of any correlation or prediction method is done by comparing the calculated values for any equation used with those of the experimental data normally limited and mostly not covering wide range of temperatures and pressures for any certain compound. The deviation between the experimental data and results of prediction or correlation method determines the accuracy of the method and this accuracy in the present work was represented as mentioned in the previous section by AAD% for entropy and AAD J/mol.K for residual entropy. Tables (4a) and (4b) show the AAD% and the AAD in J/mol.K for the calculated entropy and calculated residual entropy respectively of the superheated vapor for nonpolar and polar compounds as compared with experimental values.

1. Comparison of the Results with the Experimental Data [19]

Comparing the results that are shown in tables (4a) and (4b) indicate that the L-K equation gives higher accuracy for predicting SR as compared with the P-R, Virial truncated to second or third terms, and S-R-K equations using the experimental data points of the present study.

The AAD% for calculating the entropy of superheated vapor for 14 nonpolar compounds of 1660 data points are 1.389%, 1.397%, 1.4918%, 1.5237%, and 1.3799% when using L-K, P-R, Virial truncated to second or third terms, S-R-K respectively, while the AAD for calculating the residual entropy of superheated vapor of these compounds by using these equations are 4.6277, 4.9243, 4.9782, 4.9501, and 4.7665 J/mol.K respectively. Further more the AAD% for calculating the entropy of superheated vapor for 6 polar compounds of 1131 data points are 2.2096%, 2.9399%, 3.8575%, 3.9833, and 2.6263% when using L-K, P-R, Virial truncated to second or third terms, S-R-K respectively, while the AAD for calculating the residual entropy of superheated vapor of these compounds by using these equations are 3.2247, 4.0867, 4.9546, 5.1597, and 3.6359 J/mol.K respectively.

The AAD% for calculating the entropy of superheated vapor for all the compounds of 2791 data points are 1.7215%, 2.0223%, 2.4505%, 2.5204%, and 1.8850% when using L-K, P-R, Virial truncated to second or third terms, S-R-K respectively, while the AAD for calculating the residual entropy of superheated vapor of these compounds by using these equations are 4.0591, 4.5849, 4.9686, 5.0350, and 4.3084 J/mol.K, respectively.

2. The Modified Equation [19]

Although the better results were obtained by L-K equation, but this equation is sometimes not very preferable, because it needs more time and not easy to apply as cubic equations of state.S-R-K equation showed also a very good accuracy closest to that of the L-K equation in calculating the residual entropy S^R of superheated vapor. Thus efforts were directed to modify S-R-K equation to increase its accuracy as much as possible and to be more accurate than the original Soave-Redlich-Kwong and even the L-K equation. This may be done by using a statistical program and statistical methods that give the suitable form of correlation.

Many attempts were done to develop S-R-K equation to this purpose, and the best correlation of this modification was obtained in section 3.6 which proved a very good accuracy for most compounds under study.

The modification was applied for 20 pure compounds of 2791 experimental data points (nonpolar and polar compounds). It reduced the AAD% and AAD of Soave-Redlich-Kwong equation for 1660 experimental data points of 14 nonpolar compounds from 1.3799% to 0.9592% and from 4.7665 to 2.8247 J/mol.K, respectively. While it reduced the AAD% and AAD of Soave-Redlich-Kwong equation for 1131 experimental data points of 6 polar compounds from 2.6263% to 1.3270% and from 3.6359 to 1.9299 J/mol.K, respectively. On the other hand, it reduced the AAD% and AAD of Soave-Redlich-Kwong equation for all the 20 pure compounds under study from 1.8850% to 1.1083% and from 4.3084 to 2.4621 J/mol.K respectively as shown in Table (4b).

<u>Examples of Nonpolar Compounds:</u>

For octane, the AAD% and AAD by using SRK equation were 2.0085% and 12.0160 J/mol.K respectively, while they were 0.3711% and 2.1418 J/mol.K respectively when using the modified SRK equation. For nitrogen, the AAD% and AAD by using SRK equation were 0.4308% and 0.7276 J/mol.K respectively, while they were 0.2925% and 0.4956 J/mol.K respectively when using the modified SRK equation.

<u>Examples of Polar Compounds</u>:

For water, the AAD% and AAD by using SRK equation were 5.1695% and 6.2356 J/mol.K respectively, while they were 2.4539% and 3.2028 J/mol.K respectively when using the modified SRK equation. For refrigerant (134a), the AAD% and AAD by using SRK equation were 3.0307% and 5.8645 J/mol.K respectively, while they were 1.2397 % and 2.3752 J/mol.K respectively when using the modified SRK equation.

For polar compounds when applying the modified SRK equation without considering polarity effect term, the deviation from the experimental data was more than that when considering polarity effect term as shown in tables (4a) and (4b). Although this increase was not very significant, but in practical use more accuracy is desirable.

The interesting features of the developed equation in the present work for calculating the residual entropy are:

1. It is a rather simple equation that achieved good results for both nonpolar and polar compounds.
2. It needs only well-known properties of pure compounds (T_c, P_c, ω, and for polar compounds χ) for each compound.

The new correlation gives very good accuracy for calculating S^R of the compounds shown in tables (4a) and (4b) by a comparison with the experimental data approximately over the whole temperature and pressure ranges tested. Where the conditions tested for temperature are up to $T_r > 2$ and for pressure raised for some compounds are up to $P_r > 2$.

Figures (2) to (5) show the relation either between residual entropy with pressure at constant temperature or between residual entropy with temperature at constant pressure for the results obtained using this new method of correlation and other equations used comparing with the experimental data.

Tables (4a) and (4b) show the comparison of the results of deviations from the experimental data of n-octane and water when using Lee-Kesler, Peng-Robinson, Soave-Redlich-Kwong equations of state, and the new correlation of this work. Although virial equation was employed in this study but its results showed high deviations from the experimental values obtained in comparison with deviations of other equations employed.

Conclusions

1. Different equations of state were used to predict the residual entropy of superheated vapor for pure compounds. They are Lee-Kesler, Peng-Robinson, Soave-Redlich-Kwong and Virial truncated to second and to third terms equations of state. The results indicate that Lee-Kesler equation is the most accurate equation among these five equations, SRK equation is the closest one in its accuracy to the Lee-Kesler, and the virial equation (truncated to second or to third terms) gave highest deviations from the experimental values which prescribed the need to listing its results in tables.

2. New modification was made by redefining the parameter α in Soave equation to be a function of reduced pressure, acentric factor, and polarity factor for polar compounds in addition to be the original function of reduced temperature and n parameter –which is also the function of acentric factor– by using statistical methods. This correlation is as follows:

$$\alpha = [1 + n(\gamma)]^2$$

$$\gamma = -0.920338\ P_r^{-0.34091} + 0.064049\ T_r^{4}\omega - 0.370002\ \omega - P_r^{0.996932}\ Tr^{-4}\chi$$

a. The AAD of 1660 experimental data points of 14 pure nonpolar compounds obtained from this correlation was 2.8247 J/mol.K in comparison with those obtained from Lee-Kesler, Peng-Robinson, Virial truncated to second and to third terms, and Soave-Redlich-Kwong methods were 4.6277, 4.9243, 4.9782, 4.9501, and 4.7665 J/mol.K, respectively.

b. The AAD of 1131 experimental data points of 6 pure polar compounds obtained from this correlation was 1.9299 J/mol.K, in comparison with those obtained when using the same equations above were 3.2247, 4.0867, 4.9546, 5.1597, and 3.6359 J/mol.K respectively.

c. The AAD of 2791 experimental data points of all the 20 pure compounds obtained from this correlation was 2.4621 J/mol.K in comparison with those obtained from Lee-Kesler, Peng-Robinson, Virial truncated to second and to third terms, and Soave-Redlich-Kwong methods were 4.0591, 4.5849, 4.9686, 5.0350, and 4.3084 J/mol.K, respectively.

Acknowledgement

To all these who try to understand the philosophy of entropy and interpret why it intrudes in everything in our lives

Nomenclature

Variable Notations

A, B, Constants used in the cubic EOS, eq.(4) and eq. (11), B, B′, Second Virial Coefficient, cm^3/mol^2, b, c, d, Coefficients of eq.(23), C, C′, Third Virial Coefficient, Cm^6/mol^3, C_p, Heat capacity at constant pressure, J/mol.K, $g_1,g_2,..g_5$, Coefficients of eq. (48b), n, Constant used in the cubic EOS, eq.(4) and eq. (11), P, Pressure, kPa, R, Universal gas constant, J/mol.K,, S, Entropy, J/mol.K, T, Temperature, K, V, Volume,m^3, Z, Compressibility factor.

Abbreviations

AD, absolute deviations for S^R ,J/(mol.K), AD%,absolute percentage deviation for S, AD/R, absolute deviation for S^R divided by R, AAD, Average Absolute Deviation for S^R,J/(mol.K) AAD%, Average Absolute Percentage Deviation for S, AAD/R, Average Absolute Deviation per R for S^R, EOS, Equation Of State, LK, Lee-Kesler equation, M.wt., Molecular weight, PR Peng-Robinson equation, RK, Redlich-Kwong equation, Ref., Reference, SRK, Soave-Redlich-Kwong equation**.**

Greek Letters

α, Constant Used in cubic equations of state, β, Parameter used in equation (2-57)., γ, Constant used in equation (18), γ, Parameter used in equation (48a), ω, Acentric factor.,χ, Polarity factor of eq. (40).

Superscripts

ig, Ideal gas, R, Residual, sat., Saturated state, (0), Simple Fluid Equation (17), (r), Reference Fluid Equation (17).

Subscripts

b, Boiling point, c, Critical property , cal., Calculated value, exp.,=,Experimental value, g, Gas state, l, Liquid state, r, Reduced property r, Reference fluid, v, vaporization.

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