Equations of State for Several Fluorocarbon Refrigerants

(First Report: Saturated and Critical Property Values)

By Hiroshi KONDO*, Koichi WATANABE** and Ichimatsu TANISHITA***

In accordance with the recent developments in refrigeration engineering, the necessity to utilize the fluorocarbon refrigerants has increased. Hence it becomes quite essential to establish the thermodynamically consistent formulations in wide ranges of state parameters of these substances. For this purpose, new correlations of the saturation pressure and of the saturated liquid density have been devised for six typical different fluorocarbons such as R-12, R-13, R-21, R-22, R-23 and R-C318.

Using these devised correlations with an aid of Caillietet-Mathias law, a set of most probable critical property values with their estimated uncertainties have also been derived. Additionally the necessity to derive the rational expressions for the thermodynamic consistency which have to be satisfied by the proposed formulations at the critical point is stressed and those expressions could be derived taking into consideration the estimated uncertainties of the critical property data.

1. Introduction

In accordance with the recent developments in refrigeration industry, the necessity and importance of the fluorocarbon refrigerants which are nonflammable, nontoxic and give high performance in refrigeration have increased. In connection with these recent tendencies, has been recognized the essential importance of the thermophysical property researches on fluorocarbon refrigerants.

Among the various kinds of the thermodynamic properties of refrigerant, the experimental P-v-T property is one of the most basic and important property data and some contributions have been made previously. In addition to those previous data, some more reliable new experimental P-v-T data have been reported recently for wide ranges of state parameters of several important fluorocarbon refrigerants.

On the other hand, the previously devised and reported equations of state for gaseous fluorocarbon refrigerants can be classified into three basic categories: (a) Beattie-Bridgeman type equations of state for the refrigerants R-11, R-12 and R-21, (b) Benedict-Webb-Rubin type equations of state for R-14, R-C318, etc., and (c) Martin-Hou type equations of state devised for various fluorocarbons such as R-12, R-13, etc. BB type of equation of state was proposed earlier and can be valid in some restricted region of the gaseous states. The other two types of equations of state, BWR and MH, can be proposed to cover some comparatively wider ranges of the gaseous states but they give poor coincidence with the experimental data either at high pressures above the critical pressure or in higher density region.

Therefore as a main purpose of the present study, it becomes necessary to establish some new and accurate formulation of the equations of state for typical fluorocarbon refrigerants in order to cover more extended regions of the state parameters especially taking into consideration the recently reported P-v-T data.

In the present paper, some considerations for the critical property data, such as the critical temperature, the critical pressure and the critical specific volume, of several fluorocarbons are made. And the new correlations of the saturation pressure with temperature as well as the correlations of the saturated liquid density of these fluorocarbons are presented as a preliminary approach to setting up the thermodynamically consistent formulations. Additionally some new criteria are proposed for the consistent thermodynamic relations among the critical property data which may be reported in general with some uncertainties of the measurements.

The discussions and considerations mentioned above concern the following six different kinds of fluorocarbon refrigerants: R-12(CCl3F2), R-13(CCl2F3), R-21(CHClF2), R-22(CHCIF3), R-23(CHF3) and R-C318(CF3).

2. Symbols and Units

A, B, C, D, E, F, m: numerical constants defined in the correlations of the saturation pressure, Eq. (3)

\[ C_i (i=1-4): \] numerical constants defined in the correlations of the saturated liquid density, Eq. (5)

\[ m_0: \] inclination (dP/dT) in g/cm²K of the rectilinear line on the T-P diagram

\[ P: \] pressure, kPa

\[ T: \] absolute temperature in Kelvin scale, K

\[ t: \] temperature in Celsius scale, °C

\[ v: \] specific volume, cm³/g

\[ \alpha_c: \] inclination of the saturation pressure curve at the critical point, (dP/dT)_{T=T_c}, kPa/K

\[ \delta_c: \] uncertainty of \( \alpha_c \) (dimensional)

\[ \delta_p: \] uncertainty of the critical density, g/cm³

\[ \delta_v: \] uncertainty of the saturated vapor density, g/cm³

\[ \delta_T_c: \] uncertainty of the critical temperature, K

\[ \delta_v_c: \] uncertainty of the critical specific volume, cm³/g

\[ \delta_P_c: \] uncertainty of the critical pressure, kPa

\[ \delta_p_c: \] uncertainty of the critical specific volume, cm³/g

\[ s: \] average percentage deviation of the saturation pressure data from Eq. (3), \%

\[ \epsilon_v: \] average percentage deviation of the experimental P values along the isochoros from the quadratic approximate expression of P with respect to T, \%

\[ \epsilon_P: \] average percentage deviation of the experimental saturated liquid density from Eq. (5), \%

\[ \rho: \] density, g/cm³

\[ \Delta_P: \] percentage deviation of the experimental saturation pressure from Eq. (3), \%

\[ \Delta_T: \] percentage deviation of the experimental saturated liquid density, \%

Subscripts

\[ c: \] property values at the critical point

\[ r: \] reduced property values due to the critical property data

\[ s: \] property values along the saturation pressure curve

\[ calc: \] calculated values due to the devised correlations
3. Correlations of the Saturation Pressure with Temperature

Although some certain correlations of the saturation pressure for the fluorocarbon refrigerants have been proposed up to now, almost all of them are established based upon their own experimental saturation pressure data only and hence they show rather drastic deviations from other experimental data sources reported by different investigators. Therefore, it is our present purpose to devise the correlational correlations of the saturation pressure as a function of temperature taking into consideration the possible amount of data sources.

Using the well-known Clapeyron-Clausius relation in thermodynamics, the following expression can easily be derived:

$$\frac{d(ln P_s)}{dT} = \frac{-\Delta H_s}{R \Delta s}$$

where $\Delta H_s$ and $R$ denote the latent heat of vaporization and the gas constant respectively, and $\Delta s_s$ denotes the difference of the compressibility factor values between the saturated vapor and the saturated liquid. Assuming the right-hand side of the above Eq. (1) to be expressed approximately as a polynomial of temperature, we can obtain

$$-\Delta H_s/(R \Delta s_s) = B_s \cdot C_s \cdot T^2 + D_s \cdot T + E_s \cdot T + F_s \cdot T + G_s$$

where $B_s$, $C_s$, $D_s$, $E_s$, $F_s$, and $G_s$ are the numerical constants.

Substituting Eq. (2) into Eq. (1) and integrating, a final form of the correlation of the saturation pressure with respect to temperature can be obtained as follows:

$$\log_{10}(P_s/P_0) = A_s + B_s \cdot T^2 + C_s \cdot T + D_s \cdot T + E_s \cdot T + F_s \cdot T + G_s$$

The numerical constants appearing in Eq. (3) are tabulated in Table 1 for the six kinds of fluorocarbons of present interest. In order to determine these numerical constants from A to F, usual least square fittings were applied and the usual numerical values for the constant m can also be determined to correspond to the minimum average deviations of the calculated saturation pressure values from the experimental data after varying m values between -10 and 10 with an interval of unity.

In Figs. 1 ~ 6, comparison of the computed saturation pressure by Eq. (3) with the experimental data is shown with an aid of the percentage deviation $\delta P_s$ defined by the expression,

$$\delta P_s = (P_s - P_s^{calc}) \times 100/P_s^{calc}$$

And it should be noted that the average deviation means the arithmetic mean of the absolute values of $\delta P_s$ by Eq. (4).

As is clear from Figs. 1 ~ 6, some satisfactory coincidence with respect to the substances such as R-13, R-21, R-22 and R-23 can be found between the available data and correlated Eq. (3) within ±0.5% except several data points. The coincidence between them is also found to be within ±0.7% and ±1.0% approximately for the other substances, R-12 and R-C318, respectively.

As typically shown in cases of the correlations proposed by Michels et al. (1) for R-12 and shown in Fig. 1 as well as that by Wagner (2) for R-23 and shown in Fig. 5, the previously established correlations of the saturation pressure are good in the restricted temperature range only where their own experimental data exist but they are not satisfactory for covering wider temperature ranges of practical importance. In contrast with these general features of the former correlations, the present correlations of the saturation pressure for six different fluorocarbons are representing the experimental data with satisfactory precision and they are valid in more extended temperature range of practical importance. So it may become necessary to reconcile those various correlations previously reported with the available experimental data in their application to the practical use.

4. Correlations of the Saturated Liquid Density

There exist some available experimental saturated liquid density data on six fluorocarbons of present interest which are, of course, not so much as the data on the saturation pressure.

The established correlations of the saturated liquid density in the present study are as follows:

$$\rho_s = 1 + \sum \frac{C_i}{(1 - T_s)^{D_i}} (n equals either 3 or 4)$$

As discussed in detail in the next section, it is essential to get these correlations in order to determine the critical specific volume with an aid of Cailletet-Mathias method. Hence, as a first step, assuming the reasonable $\rho_s$ values based upon the available data, the numerical constants $C_i$ in Eq. (5) can be found using the least square fittings and they are tabulated in Table 2.

In this procedure, the number of terms related to temperature is chosen as 6 and the better expression is taken between the case with n=3 and that with n=4.

As a next step, newly determined critical density $\rho_s$ values can be obtained as shown in Table 5 appearing later, using the established correlations, Eq. (5). And again using these newly determined $\rho_s$ values, the numerical constants in Eq. (5) can be determined by the least square fittings and they are given in Table 3. In these steps of the least square fittings, the number of terms, f, is taken from the case which shows the lowest average and maximum deviations of the correlations in the experimental saturated liquid density data and one of the typical results thus obtained for R-22 is shown in Fig. 7 as an example. Comparisons of the computed saturated liquid density values using the numerical constants given in Table 3, with the experimental data as well as the previously proposed correlations are shown in Figs. 8 ~ 13 for respective fluorocarbons. Just as in case of the saturation pressure, the percentage deviations of the saturated liquid density are also defined by the expression

$$\delta \rho = (\rho - \rho_{calc}) \times 100/\rho_{calc}$$

From Figs. 8 ~ 13, it is found that the deviations of the saturated liquid density values computed using the numerical constants given in Table 3 from the experimental data are quite satisfactory, being within ±0.1% for R-12 and R-21, mostly within ±0.3% for R-13 and R-22 and also ±0.5% for R-23 and R-C318 except several data points.

As is typically exhibited in Fig. 9 in comparison of the correlation by Albright and Martin (1) with the experimental data for R-13 and in Fig. 11 in comparison of the correlation by Benning and McHarness (2) with the experimental data for R-22, almost all of the correlations formerly proposed are satisfactory only in a certain restricted temperature range where their own experimental data exist but they show rather poor coincidence in the other temperature range with the experimental data by other investigators. On the other hand, the present correlations,

Table 1 Numerical constants for Eq.(3) for six fluorocarbons

<table>
<thead>
<tr>
<th></th>
<th>R-12</th>
<th>R-13</th>
<th>R-21</th>
<th>R-22</th>
<th>R-23</th>
<th>R-C318</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.663381</td>
<td>-0.811218</td>
<td>1.975906</td>
<td>-6.41094</td>
<td>19.28739</td>
<td>11.426073</td>
</tr>
<tr>
<td>B</td>
<td>-4.719416</td>
<td>-5.988753</td>
<td>-4.136897</td>
<td>-3.92257</td>
<td>3.045855</td>
<td>-0.283276</td>
</tr>
<tr>
<td>C</td>
<td>-9.974241</td>
<td>-14.97394</td>
<td>-6.57146</td>
<td>-0.497102</td>
<td>38.44235</td>
<td>38.01780</td>
</tr>
<tr>
<td>E</td>
<td>0.39845</td>
<td>-1.479150</td>
<td>-5.430614</td>
<td>1.736064</td>
<td>6.411557</td>
<td>0.00000</td>
</tr>
<tr>
<td>F</td>
<td>0.0</td>
<td>0.05536866</td>
<td>1.467754</td>
<td>0.00000</td>
<td>-2.18532x10^-1</td>
<td>0.543687</td>
</tr>
<tr>
<td>m</td>
<td>0.0</td>
<td>8.000000</td>
<td>3.000000</td>
<td>0.00000</td>
<td>-8.00000</td>
<td>-8.00000</td>
</tr>
</tbody>
</table>
Eq.(5), are much improved in this respect and they can reproduce the experimental data with quite satisfactory accuracy. And it should be also noted that the functional form of Eq.(5) is the so-called rational correlation to give the critical density at the critical point, besides the fact that Eq.(5) can cover more extended ranges of temperatures.

Fig. 1 Comparison of the saturation pressure for R-12 calculated by Eq. (3) with those by other correlations and experimental data

Fig. 2 Comparison of the saturation pressure for R-13 calculated by Eq. (3) with those by other correlations and experimental data

Fig. 3 Comparison of the saturation pressure for R-21 calculated by Eq. (3) with those by other correlations and experimental data

Fig. 4 Comparison of the saturation pressure for R-22 calculated by Eq. (3) with those by other correlations and experimental data

Fig. 5 Comparison of the saturation pressure for R-23 calculated by Eq. (3) with those by other correlations and experimental data

Fig. 6 Comparison of the saturated pressure for R-C318 calculated by Eq. (3) with those by other correlations and experimental data

Fig. 7 Relation between the deviations and the number of terms in Eq. (5)
Fig. 8 Comparison of the saturated liquid density for R-12 calculated by Eq. (5) with those by other correlations and experimental data

Fig. 9 Comparison of the saturated liquid density for R-13 calculated by Eq. (5) with those by other correlations and experimental data

Fig. 10 Comparison of the saturated liquid density for R-21 calculated by Eq. (5) with those by other correlations and experimental data

Fig. 11 Comparison of the saturated liquid density for R-22 calculated by Eq. (5) with those by other correlations and experimental data

Fig. 12 Comparison of the saturated liquid density for R-23 calculated by Eq. (5) with those by other correlations and experimental data

Fig. 13 Comparison of the saturated liquid density for R-C318 calculated by Eq. (5) with those by other correlations and experimental data

Table 2 A set of temporary-determined numerical constants in Eq.(5)

<table>
<thead>
<tr>
<th></th>
<th>R-12</th>
<th>R-13</th>
<th>R-21</th>
<th>R-22</th>
<th>R-23</th>
<th>R-C318</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_0 )</td>
<td>0.557 21</td>
<td>0.577 12</td>
<td>0.522 46</td>
<td>0.524 05</td>
<td>0.526 41</td>
<td>0.619 29</td>
</tr>
<tr>
<td>( C_1 )</td>
<td>1.637 910</td>
<td>1.240 331</td>
<td>1.961 792</td>
<td>1.986 256</td>
<td>0.473 101</td>
<td>1.082 011</td>
</tr>
<tr>
<td>( C_2 )</td>
<td>-3.617 633</td>
<td>-1.068 120</td>
<td>-0.827 025</td>
<td>-2.666 043</td>
<td>9.963 649</td>
<td>21.571 293</td>
</tr>
<tr>
<td>( C_3 )</td>
<td>9.010 066</td>
<td>7.273 865</td>
<td>3.187 867</td>
<td>16.623 658</td>
<td>0.166 305</td>
<td>-81.642 984</td>
</tr>
<tr>
<td>( C_4 )</td>
<td>-2.519 636</td>
<td>-6.570 318</td>
<td>-0.202 751</td>
<td>-37.204 846</td>
<td>20.894 645</td>
<td>161.536 25</td>
</tr>
<tr>
<td>( C_5 )</td>
<td>-8.959 300</td>
<td>0.506 687</td>
<td>-5.025 690</td>
<td>39.454 086</td>
<td>-23.375 202</td>
<td>-192.311 71</td>
</tr>
<tr>
<td>( n )</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3 A final set of numerical constants in Eq.(5)

<table>
<thead>
<tr>
<th></th>
<th>R-12</th>
<th>R-13</th>
<th>R-21</th>
<th>R-22</th>
<th>R-23</th>
<th>R-C318</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f )</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>( C_1 )</td>
<td>2.262 648</td>
<td>1.294 226</td>
<td>2.035 819</td>
<td>0.191 808</td>
<td>1.061 306</td>
<td>1.680 832</td>
</tr>
<tr>
<td>( C_2 )</td>
<td>-9.123 878</td>
<td>-2.245 147</td>
<td>-1.887 217</td>
<td>3.298 822</td>
<td>-5.761 352</td>
<td>27.505 074</td>
</tr>
<tr>
<td>( C_3 )</td>
<td>37.811 491</td>
<td>10.403 171</td>
<td>7.922 818</td>
<td>-3.658 531</td>
<td>33.836 463</td>
<td>-90.911 511</td>
</tr>
<tr>
<td>( C_4 )</td>
<td>-30.891 915</td>
<td>-12.432 404</td>
<td>-10.123 662</td>
<td>2.053 651</td>
<td>-35.338 526</td>
<td>104.268 884</td>
</tr>
<tr>
<td>( C_5 )</td>
<td>12.758 082</td>
<td>5.715 977</td>
<td>4.926 581</td>
<td>0.0</td>
<td>-62.215 819</td>
<td>78.911 109</td>
</tr>
<tr>
<td>( n )</td>
<td>4</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\( f \) and \( f \) are used.
5. Determination of the Property Values at the Critical Point

The equation of state proposed in the present study will be valid in wide ranges of the state parameters and so the critical points of the respective substances will be included in these ranges. Therefore the critical point is an essential state point with respect to these formulations and the thermodynamic consistency at the critical point has to be considered carefully.

However, some considerable critical property data have been reported on various fluorocarbons as listed in Table 4 for a typical example of R-23, and there exist some large amounts of discrepancy among the reported experimental data in contrast with the other important pure substances such as water and carbon dioxide.

The determination of the critical temperature is mostly done by observation of the disappearance of the meniscus of the gas-liquid interface. And as for the determination of the critical pressure, they have been obtained analytically from the correlations which were established based upon the experimental saturation pressure data.

In the present study, the critical temperature was determined by choosing one of the most reliable reported data (given with the asterisk in Table 4 for example) from the available data source. And if there exist more than two of the reliable data, the most probable critical temperature values can be understood to be found between them. The most probable critical temperatures thus evaluated for respective fluorocarbons are given in Table 5 and they must be described with some uncertainties \( \Delta T_c \) defined as follows:

\[
\Delta T_c = \left[ \text{[largest } T_c \text{ value among the available data]} \right] - \left[ \text{[estimated uncertainty with respect to this largest } T_c \text{ value]} \right] - \left[ \text{[smallest } T_c \text{ value among them]} \right] - \left[ \text{[estimated uncertainty with respect to this smallest } T_c \text{ value]} \right]
\]

(7)

The critical pressure \( \text{P}_c \) can be determined as the \( \text{P} \) value at \( T=T_c \) using the established correlation, Eq.(3). And the uncertainty \( \Delta \text{P}_c \) with respect to this critical pressure can also be described in the following form as is clear from Fig.14.

\[
\Delta \text{P}_c = \frac{\text{dP}/\text{dT}}{\Delta T_c} \times \Delta T_c + \text{eP}_c/100
\]

(8)

Generally speaking, there exists the largest amount of discrepancy among the critical specific volume data and it is usual to derive the \( \nu_c \) values of the certain kinds of pure substances with an aid of the so-called Calleit-Mathias method\(^{(34)}\) taking into consideration the relations between both \( \nu^* \) and \( \nu^* \) with respective temperature. So the similar application of the Calleit-Mathias method to the determination of the \( \nu_c \) values is also conducted in the following manner in this study.

As a first step, it is necessary to obtain some sufficient knowledge about the values of the saturated vapor specific volume \( V^* \). As is shown in Fig.15, fitting the approximate quadratic expression \( P=a+bT+cT^2 \) along the given isochores on the P-T diagram and extrapolating them to the saturation pressure curve, then a set of \( V^* \) values can be obtained corresponding to the set of \( P \) and \( T \) values at the saturated states as a result of iterative procedure. Suppose to define \( \Delta \nu \) as the average percentage deviation of the approximate quadratic expression from the available P-T data along the isochores, the uncertainty \( \Delta \nu \) corresponding to the \( V^* \) values thus obtained can be described by the following expression (refer to Fig.16).

\[
\Delta \nu = \frac{\nu}{\nu} \left( \text{mean} \frac{\Delta \nu}{\nu} \times 100 \right) / N
\]

(11)

Fig. 14 Method of obtaining \( \Delta \text{P}_c \)

Fig. 15 Extrapolation of the P-T data to the Saturation pressure curve

Fig. 16 Method of obtaining \( \Delta \nu \)

Table 4 Reported critical property data for R-23

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Year</th>
<th>Ref.</th>
<th>Critical temperature ( T_c )/°C</th>
<th>Critical pressure ( \text{P}_c )/psi (kg/cm²)</th>
<th>Critical specific volume ( \nu_c ) /cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruff, et al.</td>
<td>1936</td>
<td>(19)</td>
<td>32.8</td>
<td>49</td>
<td>1.94</td>
</tr>
<tr>
<td>Seger</td>
<td>1942</td>
<td>(30)</td>
<td>15</td>
<td>-</td>
<td>1.938</td>
</tr>
<tr>
<td>Whitney</td>
<td>1948</td>
<td>(31)</td>
<td>27</td>
<td>-</td>
<td>1.81</td>
</tr>
<tr>
<td>Plank</td>
<td>1956</td>
<td>(12)</td>
<td>29</td>
<td>46.50</td>
<td>2.01</td>
</tr>
<tr>
<td>Riedel</td>
<td>1957</td>
<td>(37)</td>
<td>29</td>
<td>51.60</td>
<td>1.89</td>
</tr>
<tr>
<td>Hou-Martin</td>
<td>1959</td>
<td>(21)</td>
<td>25.91*</td>
<td>49.32</td>
<td>1.904</td>
</tr>
<tr>
<td>Wagner</td>
<td>1968</td>
<td>(22)</td>
<td>26.3±0.1*</td>
<td>49.70±0.01</td>
<td>1.900</td>
</tr>
</tbody>
</table>
Where \( N \) denotes the number of the selected points for \( \rho^* \).

Then we can proceed to apply the Callettet-Mathias method to determine \( \rho_c \) values as shown in Fig.17(a), taking into consideration the existence of the uncertainties \( \delta \rho^* \) which is considered to be equivalent to \( \delta \rho^* \) and \( \delta \rho^* \) given by Eq.(10) respectively. So defining the inclination of the rectilinear line as \( m_0 = \delta \rho^*/\delta T = \delta \rho^*/\delta T = \delta \rho^*/\delta T \) in Fig.17(b), then the uncertainty \( \delta \rho^* \), with respect to the critical density can be given by the expression

\[
\delta \rho_c = (\rho^* + \delta \rho^*) m_0 /[2 \times 100] \times m_0 \delta T_c
\]

Therefore the critical specific volume \( \nu_c \) can be expressed with the uncertainty \( \delta \nu_c \) in the following form

\[
\nu_c = \delta \nu_c = 1/(\rho_c + \delta \rho_c) = 1/(\rho_c + \delta \rho_c/\rho_c)
\]

In Table 5, all of the critical property values obtained from the procedure described above are given for six fluorocarbons.

Among the obtained uncertainties of the critical temperature, the largest uncertainty is found at \( T = 0.25 \) \( \text{C} \) for R-23 and the smallest one as \( T = 0.05 \) \( \text{C} \) for R-12. As for the uncertainties of the critical pressure, the largest value of \( \pm 0.5 \% \) for R-23 and the smallest one of \( \pm 2.1 \% \) for R-13 are obtained. Similarly for the uncertainties of the critical specific volume, the largest one of \( \pm 0.5 \% \) for R-23 and the smallest one of \( \pm 1.3 \% \) for R-22 are also obtained. It is noteworthy that these uncertainties regarding the critical property data are well corresponding to the reported experimental accuracy of the measurements and therefore the present method of evaluation is recognized to be quite satisfactory.

6. Some Consideration upon the Thermodynamic Consistency of the Formulation at the Critical Point

It is well known that the equation of state for the pure substance which includes the critical point in its region of validity has to satisfy the four following thermodynamic conditions.

Assuming the equation of state given in a form

\[
P = P(\nu, T)
\]

these four different conditions are written as follows:

(i) \( P_c = P(\nu_c, T_c) \) .......................... (15)

(ii) \( (\partial P/\partial \nu)(T_c) = 0 \) .......................... (16)

(iii) \( (\partial P/\partial T)= (\partial P/\partial \nu)(T_c) \) .......................... (17)

(iv) \( (\partial T_p/\partial \nu)(T_c) = (\partial P/\partial T allowance) \) .......................... (18)

Moreover the critical property data are, in general, accompanied by the uncertainties mentioned above, the true critical point is only defined to exist in some region restricted by the following relations

- Critical pressure: \( P_c = \delta P_c \)
- Critical specific volume: \( \nu_c = \delta \nu_c \)
- Critical temperature: \( T_c = \delta T_c \)
- Inclination of the saturation pressure curve: \( \alpha_c = 1 \pm \delta \alpha_c \)

Hence it becomes necessary to reconsider the basic thermodynamic conditions given by Eqs.(15) \~(18) taking into account the additional restrictions given by Eq.(19).

1) Condition (i)

In this case, the dependent function \( P \) has to be satisfied by the expression

\[
\left| P - P(\nu_c, T_c) \right| \leq \delta P_c
\]

which is also rewritten in the following expression for our future convenience

\[
\Delta P_c = | P - P(\nu_c, T_c) | \leq \delta P_c
\]

2) Condition (ii)

The inclination of the saturation pressure curve at the critical point, \( \alpha_c \), must be restricted by the condition

\[
\left| 1 - \alpha_c \right| \leq \delta \alpha_c
\]

It should be noted that the uncertainty \( \delta \alpha_c \) becomes considerably large up to 0.02 ~ 0.1 because of the fact that most of the experimental data on the saturation pressure are obtained under the temperature well below the critical point. As an example, the computed \( \delta \alpha_c \) values due to the different reported correlations of the saturation pressure for R-22 are shown in Table 6.

3) Condition (iii)

The possible maximum uncertainty \( \Delta P \) with respect to the values of \( P \) from Eq.(14) at the critical point can be evaluated by the following expression

\[
\Delta P_c = \left| \left( P(\nu_c, T_c) \right) \right| \nu_c - | \delta \nu_c + 1 | \left( \partial P/\partial T_c \right) T_c - \delta T_c
\]

Here the uncertainty \( \Delta P_c \) has to be satisfied also with the restriction

\[
\Delta P_c + \delta P_c < \delta P_c
\]

Therefore we can obtain the following expression for \( \beta \) value using Eqs.(23) and (24).

\[
\beta < \delta P_c - \delta P_c / \delta \nu_c
\]

4) Condition (iv)

Taking into account the effects up to the second derivatives of the uncertainties \( \delta \nu_c \) and \( \delta T_c \) at the critical point, the possible maximum uncertainty of pressure \( \Delta P_c \) can also be derived as follows:

Table 5 Critical property values with estimated uncertainty

<table>
<thead>
<tr>
<th>Substance</th>
<th>Critical temperature ( t_c, \text{K} )</th>
<th>Critical pressure ( P_c, \text{atm} )</th>
<th>Critical specific volume ( \nu_c, \text{cm}^3/\text{mol} )</th>
<th>Critical density ( \rho_c, \text{g/cm}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-12</td>
<td>112.00 ± 0.05</td>
<td>42.18 ± 0.17</td>
<td>7.89 ± 0.005</td>
<td>2.558 ± 0.001</td>
</tr>
<tr>
<td>R-13</td>
<td>28.81 ± 0.06</td>
<td>39.46 ± 0.11</td>
<td>7.75 ± 0.005</td>
<td>3.079 ± 0.001</td>
</tr>
<tr>
<td>R-21</td>
<td>179.43 ± 0.08</td>
<td>52.86 ± 0.12</td>
<td>9.38 ± 0.002</td>
<td>5.529 ± 0.000</td>
</tr>
<tr>
<td>R-22</td>
<td>96.10 ± 0.10</td>
<td>50.49 ± 0.17</td>
<td>1.913 ± 0.002</td>
<td>7.52 ± 0.000</td>
</tr>
<tr>
<td>R-23</td>
<td>25.15 ± 0.25</td>
<td>49.51 ± 0.38</td>
<td>8.194 ± 0.007</td>
<td>8.527 ± 0.002</td>
</tr>
<tr>
<td>R-24</td>
<td>318</td>
<td>28.39 ± 0.161</td>
<td>6.215 ± 0.0088</td>
<td>6.616 ± 0.003</td>
</tr>
</tbody>
</table>

Table 6 Comparison of \( \alpha_c \) values for R-12

<table>
<thead>
<tr>
<th>Investigators</th>
<th>( \alpha_c/\alpha_c )</th>
<th>( \Delta \alpha_c = 1 - \alpha_c/\alpha_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>McNair et al.</td>
<td>0.9706</td>
<td>0.044</td>
</tr>
<tr>
<td>Bohr &amp; Halsey</td>
<td>0.7295</td>
<td>0.007</td>
</tr>
<tr>
<td>Kells et al.</td>
<td>0.7170</td>
<td>0.001</td>
</tr>
<tr>
<td>Rombo and Gessen</td>
<td>0.7145</td>
<td>0.003</td>
</tr>
<tr>
<td>Average of above four</td>
<td>0.7173</td>
<td>0.000</td>
</tr>
<tr>
<td>Calculated value due</td>
<td>0.7170</td>
<td>0.001</td>
</tr>
<tr>
<td>to Eq.(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gilkey et al.</td>
<td>0.6765</td>
<td>0.056</td>
</tr>
</tbody>
</table>
\[ \Delta P_C = \beta \delta V_c + \alpha T_c - \{[(\beta^2P) \delta V_c + \alpha T_c] \nu V_c + [(\beta^2P) \delta T_c] \nu T_c \} + 2 \{[(\beta^2P) \delta V_c + \alpha T_c] \nu V_c + [(\beta^2P) \delta T_c] \nu T_c \} \]

\[ T = T_c + \{[(\beta^2P) \delta V_c + \alpha T_c] \nu V_c + [(\beta^2P) \delta T_c] \nu T_c \} \]

As well as for the condition (ii), \( \Delta P_C \) defined by Eq.(26) has to satisfy the following restriction

\[ \Delta P_C + \Delta P_{C2} < \delta P_{C} \] ............................. (27)

Hence 3 value must obey the next condition obtained from Eqs. (26) and (27)

\[ \frac{[\beta^2P] \delta V_c - \Delta P_C - \delta T_c - \{[(\beta^2P) \delta V_c + \alpha T_c] \nu V_c + [(\beta^2P) \delta T_c] \nu T_c \} \nu V_c}{\delta T_c} - \frac{[\beta^2P] \delta V_c - \Delta P_C - \delta T_c - \{[(\beta^2P) \delta V_c + \alpha T_c] \nu V_c + [(\beta^2P) \delta T_c] \nu T_c \} \nu V_c}{\delta T_c} \] ............................. (28)

In conclusion, the thermodynamic consistency which is essential to the formulation given by Eq.(14) can be satisfied and reduced to the four thermodynamic conditions given by Eqs. (20), (22), (25) and (28), if there exist any uncertainties \( \delta P_C \), \( \delta V_c \) and \( \delta T_c \) with respect to the critical pressure, the critical specific volume and the critical temperature. However, it is selfevident that Eqs.(20) and (25) will be satisfied automatically whenever Eq.(28) can be satisfied, so we can understand the necessary restrictions are Eqs.(22) and (28) for the thermodynamic consistency at the critical point.

7. Conclusions

The equation of state proposed in the present study can be valid in wider ranges of the state parameters of six typical fluorocarbons than those proposed by other investigators previously and the critical points of these substances are included in these ranges of their validity. On the other hand, reported experimental data on the critical properties show some considerable amount of discrepancy among them. Therefore, in the present study, some rational procedure to evaluate the most probable critical property data and their estimated uncertainties is proposed for the typical fluorocarbons.

In conjunction with the present purpose of this work, the new correlations of the saturation pressure as well as those of the saturated liquid density for those substances are also established. These newly derived correlations of both properties can cover more extended ranges of temperatures than those reported previously and they show quite satisfactory coincidence with the available data in contrast with the previous works. Additionally the necessity to derive the rational expressions for the thermodynamic consistency which have to be satisfied by the proposed formulation at the critical point is stressed and those conditional expressions, Eqs. (22) and (28), are derived taking into consideration the existing uncertainties of the critical property data on respective substances.

References