International Journal of Thermophysics, Vol. 27, No. 1, January 2006 (© 2006)
DOI: 10.1007/s10765-006-0036-3

Corresponding States Relationships of *PVT* Properties of Working Fluids[1]

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A new corresponding states compressibility factor, defined as $\hat{Z}_r = (1-Z)/(1-Z_c)$, and a new generalized prediction method for the *PVT* properties of fluids of interest using water as a reference fluid are proposed on the basis of the corresponding states principle. The values of the specific volumes of 23 working fluids, including CFCs, HCFCs, HFCs, HCs, NH_3, etc., were investigated in the gas-phase region, the supercritical region, and the saturated-gas region with water as the reference fluid. The average deviations of the investigated fluids from literature results are generally within 1%.

KEY WORDS: corresponding states principle; prediction method; *PVT* relationships; working fluids.

1. INSTRUCTION

PVT relationships involve the fundamental thermophysical properties for working fluids. One of the most important estimation methods for *PVT* relations is the corresponding states principle [1], which defines dimensionless variables, $V_r = V/V_C$, $P_r = P/P_C$, and $T_r = T/T_C$, and assumes $V_{r1} = V_{r2}$ if $P_{r1} = P_{r2}$ and $T_{r1} = T_{r2}$ for two different fluids. However, the corresponding states critical compressibility factor is assumed as $Z_C = 0.270$ in traditional corresponding states principle, which will result in large prediction deviations for polar fluids, such as water and ammonia, in the critical region and along the saturation line. Therefore, it is of interest to extend

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[1] Paper presented at the Seventh Asian Thermophysical Properties Conference, August 23–28, 2004, Hefei and Huangshan, Anhui, P. R. China.

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the corresponding states principle for PVT predictions with high accuracy over the whole PVT region. In our former studies [2–6], the generalized prediction functions of the enthalpy of saturated liquids, the latent heat and enthalpy of evaporation of saturated gases, the density of saturated gases, and the density of saturated liquids were developed on the basis of a new corresponding states temperature transformation. The authors also developed a corresponding states method with four parameters to predict the specific volume behavior [7]. However, it is not very convenient because some parameters of the three reference fluids in some regions are not sufficient even though this method has high accuracy. However, the new corresponding states method presented in this paper needs only one reference fluid, and can overcome differences in the critical compressibility factor Z_C for different working fluids.

2. NEW CORRESPONDING STATES PARAMETERS

2.1. Corresponding States Compressibility Factor, $\hat{Z}_r$

The new corresponding states compressibility factor is defined as

$$\hat{Z}_r = \frac{1 - Z}{1 - Z_C} \tag{1}$$

where $Z = PV/RT$ is the compressibility factor and the subscript "C" denotes the critical state. $\hat{Z}_r$ is the ratio of the difference between the compressibility factor of the ideal gas ($Z = 1$) and the real compressibility factor Z to the difference between the compressibility factor of the ideal gas and the critical compressibility factor Z_C. It gives the corresponding states relationship of compressibility factors for different fluids. It is obvious that $\hat{Z}_r = 0$ for the ideal gas ($P_r \to 0$) and $\hat{Z}_r = 1$ at the critical point for any fluid.

2.2. Corresponding States Saturated Compressibility Factor, $\hat{Z}_{sr}$

The corresponding states saturated compressibility factor is defined as

$$\hat{Z}_{sr} = \frac{1 - Z_s}{1 - Z_C} \tag{2}$$

where Z_s is the saturated compressibility factor and the subscript "s" denotes the saturated state. Equation (2) expresses the generalized corresponding states relationship of compressibility factors at the saturated state.

2.3. Corresponding States Pressure, P_r

The corresponding states pressure is

$$P_r = \frac{P}{P_C} \tag{3}$$

It is suitable to express the corresponding states pressure by Eq. (3) because the pressure of the ideal gas is approximately zero.

2.4. Corresponding States Temperature

The corresponding states temperature is defined as

$$\hat{T}_{sr} = \frac{T}{T_s} \tag{4}$$

For $P_r \leqslant 1$, it is possible for a fluid to be in the saturated phase region; therefore, $\hat{T}_{sr}$ is the corresponding states temperature for a saturated point. T_s is the saturated temperature at pressure P. For $P_r \geqslant 1$, the fluid is in the supercritical region, and T_s is the pseudo-saturated temperature at pressure P.

3. RELATIONSHIP OF CORRESPONDING STATES SATURATED TEMPERATURE T_{sr} AND CORRESPONDING STATES PRESSURE P_r

The corresponding states saturated temperature at the corresponding states pressure P_r is defined as

$$T_{sr} = \frac{T_s}{T_C} \tag{5}$$

The relationship of the corresponding states temperature T_{sr} and the corresponding pressure states P_r is written as

$$T_{sr} = P_r^{(a + bP_r^{0.095})} \tag{6}$$

where

$$a = 0.061 Z_C^{0.15} \tag{7}$$

$$b = \left(\frac{0.1549}{1+\omega} - a \right) 10^{0.095(1+\omega)} \tag{8}$$

with ω is the acentric factor.

Table I. Average Absolute Deviations for Predicted Saturated Temperatures by Eq. (6) from Literature Data for Working Fluids

Fluids:	H_2^a	O_2^a	N_2^a	NH_3^a	CH_4^a	$C_2H_4^a$	$C_2H_6^a$	$C_3H_6^a$
T_r	0.6–1.0	0.45–1.0	0.51–1.0	0.49–1.0	0.48–1.0	0.38–1.0	0.4–1.0	0.36–1.0
AAD (%)[c]	0.326	0.141	0.055	0.072	0.163	0.112	0.106	0.149
Fluids:	$C_3H_8^a$	$C_4H_{10}^a$	i-$C_4H_{10}^a$	R11[a]	R113[a]	R114[a]	R115[a]	R12[a]
T_r	0.54–1.0	0.32–1.0	0.28–1.0	0.29–1.0	0.5–1.0	0.5–1.0	0.46–1.0	0.45–1.0
AAD (%)	0.127	0.178	0.367	0.289	0.208	0.210	0.269	0.190
Fluids:	R123[a]	R125[b]	R12B1[a]	R13[a]	R134[a]	R13B1[a]	R14[a]	R142b[a]
T_r	0.57–1.0	0.54–1.0	0.41–1.0	0.3–1.0	0.65–1.0	0.48–1.0	0.3–1.0	0.52–1.0
AAD (%)	0.096	0.189	0.116	0.174	0.058	0.132	0.149	0.126
Fluids:	R143a[b]	R152a[a]	R21[a]	R22[a]	R227ea[b]	R23[a]	R32[b]	H_2O^a
T_r	0.47–1.0	0.53–1.0	0.5–1.0	0.47–1.0	0.59–1.0	0.3–1.0	0.39–1.0	0.43–1.0
AAD (%)	0.148	0.140	0.188	0.197	0.147	0.199	0.091	0.085

[a] Data were calculated by Propath Database 11.1 [9].
[b] Data were calculated by NIST Refprop 6.01 [10].
[c] $\text{AAD}/\% = \frac{1}{n}\sum_{i=1}^{n} \left|(T_{\text{cal}} - T_{\text{ref}})/T_{\text{ref}}\right| \times 100.$

Equation (6) was tested with 32 fluids and the average absolute deviations were less then 0.4% as shown in Table I. The T_s for the corresponding states temperature, defined as Eq. (4), can be calculated at any pressure by Eqs. (5) and (6).

4. CORRESPONDING STATES COMPRESSIBILITY FACTOR, $\hat{Z}_r$

The generalized function of the corresponding states compressibility factor difference $\hat{Z}_r$ can be written as

$$\hat{Z}_r = f(P_r, \hat{T}_{sr}) \tag{9}$$

Although the detailed functional form is not given from Eq. (9), the *PVT* relationships for a fluid of interest can be calculated from the *PVT* properties of a reference fluid using the above equation based on the following corresponding states principle.

Table II. Average Absolute Deviations for Predicted Specific Volumes from Literature Data for Working Fluids

Fluids:	NH_3	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	i–C_4H_{10}
T_r	0.5–1.6	0.55–1.6	0.45–1.5	0.45–1.6	0.55–1.5	0.6–1.5	0.6–1.6	0.6–1.6
P_r	0.0–4.42	0.0–4.0	0.0–3.62	0.0–4.0	0.0–1.99	0.0–3.28	0.0–4.0	0.0–3.62
AAD (%)[a]	0.525	1.099	0.849	0.319	0.628	0.612	0.500	0.392
Fluids:	R11	R113	R114	R115	R12	R123	R13	R134a
T_r	0.6–1.0	0.6–1.0	0.6–1.2	0.6–1.3	0.6–1.2	0.6–1.0	0.55–1.5	0.65–1.2
P_r	0.01–1.09	0.01–1.2	0.0–1.99	0.0–2.20	0.0–1.8	0.01–1.0	0.01–3.28	0.02–2.2
AAD (%)	0.781	0.879	0.518	0.557	0.515	0.586	1.18	0.534
Fluids:	R13b1	R14	R142b	R152a	R21	R22	R23	
T_r	0.55–1.6	0.55–1.6	0.6–1.1	0.6–1.1	0.6–1.0	0.59–1.2	0.59–1.4	
P_r	0.0–2.97	0.01–3.28	0.0–0.81	0.0–0.70	0.01–1.21	0.0–2.2	0.01–3.28	
AAD (%)	0.571	1.16	0.654	0.291	0.882	0.412	0.660	

[a] $\mathrm{AAD}/\% = \frac{1}{n}\sum_{i=1}^{n}\left|(V_{\mathrm{cal}} - V_{\mathrm{ref}})/V_{\mathrm{ref}}\right| \times 100.$

5. NEW CORRESPONDING STATES PRINCIPLE

If $P_{r1} = P_{r2}$ and $\hat{T}_{sr1} = \hat{T}_{sr2}$, we have

$$\hat{Z}_{r1} = \hat{Z}_{r2} \tag{10}$$

In this study, water was selected as the reference fluid because its *PVT* properties are known with high accuracy over a broad *PVT* region. The subscript “1” denotes the reference fluid, water, and the subscript “2” denotes the investigated fluid.

The values of the specific volumes of 23 working fluids, including CFCs, HCFCs, HFCs, HCs, and NH_3, were investigated in the gas-phase region, supercritical region, and saturated-gas region with water as the reference fluid. The average deviations of the investigated fluids from literature values are generally within 1% as shown in Table II. The *PVT* properties of water and the investigated 23 fluids were calculated by Propath Database 11.1 [9].

6. CONCLUSIONS

A new corresponding states compressibility factor $\hat{Z}_r$ and a corresponding states temperature for the saturated point $\hat{T}_{sr}$ were defined, and then a new generalized corresponding states method for predicting *PVT* properties of working fluids was presented here. This method overcomes the shortcomings of the conventional corresponding states method, and provides accurate predictions at the critical point and for the ideal-gas state for different working fluids and has high accuracy in the gaseous phase and supercritical regions. The new method extends the corresponding states theory and can be used to calculate the *PVT* properties of gases, but its accuracy in the liquid region is not satisfactory.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (Grant No. 50336020).

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