Helmholtz型状態式による熱物性値の計算方法

赤坂 亮

平成17年12月26日

1 緒言

近年，作動媒体や冷媒としての用途が期待される物質に対し，新たに報告された実測値情報を元に，続々とHelmholtz型状態式が提案されている．表1は1980年以降に発表された主なHelmholtz型状態式である．

Table 1: Helmholtz function equation of states for important fluids in industry

Fluid	Reference	Year
Ammonia	Tillner-Roth et al. [1]	1993
Argon	Tegeler et al. [2]	1999
Butane	Bücker and Wagner [3]	2004
Carbon Dioxide	Span and Wagner [4]	1996
Cyclohexane	Penoncello et al. [5]	1995
Ethane	Bücker and Wagner [3]	2004
Ethylene	Smukala et al. [6]	2000
Fluorine	de Reuck [7]	1990
Isobutane	Bücker and Wagner [3]	2004
	Miyamoto and Watanabe [8]	2001
Methane	Setzmann and Wagner [9]	1991
Methanol	de Reuck and Craven [10]	1993
Neon	Katti et al. [11]	1986
Nitrogen	Span et al. [12]	2000
Oxygen	Schmidt and Wagner [13]	1985
Propane	Miyamoto and Watanabe [14]	2000
Propylene	Angus et al. [15]	1980
R-11	Jacobsen et al. [16]	1992
R-113	Marx et al. [17]	1992
R-12	Marx et al. [17]	1992
R-124	de Vries et al. [18]	1995
R-125	Sunaga et al. [19]	1998
	Tillner-Roth and Yokozeki [20]	1997
R-134a	Tillner-Roth and Baehr [21]	1994
	Tillner-Roth and Yokozeki [20]	1997
R-143a	Lemmon and Jacobsen [22]	2000
	Tillner-Roth and Yokozeki [20]	1997
R-22	Kamei et al. [23]	1995
R-23	Penoncello et al. [24]	2003
R-32	Tillner-Roth and Yokozeki [20]	1997
Sulfur Hexafluoride	de Reuck et al. [25]	1991
Water	Wagner and Pruß [26]	2002
Air (as pseude pure fluid)	Lemmon et al. [27]	2000

Helmholtz 自由エネルギーは Canonical 関数の一つであるから，四則演算と微分演算のみですべての熱力学的性質を導くことができる．本稿では Tillner-Roth ら提案した HFC 系冷媒に対する Helmholtz 型状態式 [20] を例として，微分演算の結果およびそれを用いた熱力学的状態量の導出方法を示す．

また，飽和蒸気圧および臨界定数について，実際の状態式に基づく具体的な数値計算手順を説明する．Helmholtz 型状態式について論じた文献の多くは，微分演算の結果までは示しているものの，飽和蒸気圧などの具体的な計算手順まで述べたものは少ない．本稿で示した計算方法は，他の Helmholtz 型状態式に対してもほぼそのままの形で適用することができる．

2 状態式

Tillner-Roth らが提案した R32，R125，R134a および R143a に対する状態式は，温度 T および密度 ρ を独立変数として次式のように表される．

$$\Phi(\tau,\delta) = \frac{a}{RT} = \Phi^\circ(\tau,\delta) + \Phi^r(\tau,\delta) \tag{1}$$

ここで，$\tau = T_c/T$ および $\delta = \rho/\rho_c$ であり，T_c および ρ_c はそれぞれ臨界温度および臨界密度である．また，Φ° は理想気体状態における Helmholtz 自由エネルギーであり，Φ^r は実在流体と理想気体状態との Helmholtz 自由エネルギーの偏差（残留 Helmholtz 自由エネルギー）である．Φ° および Φ^r はそれぞれ以下のように表現される（係数 a_i° および a_i の値は省略）．

$$\Phi^\circ(\tau,\delta) = \ln\delta + a_0^\circ + a_1^\circ\tau + a_2^\circ\ln\tau + \Phi^*(\tau) \tag{2}$$

$$\Phi^*(\tau) = \begin{cases} \displaystyle\sum_{i=3}^{N^\circ} a_i^\circ \ln[1-\exp(-n_i\tau)] & \text{(R32 および R125)} \\ \displaystyle\sum_{i=3}^{N^\circ} a_i^\circ \tau^{n_i} & \text{(R134a および R143a)} \end{cases} \tag{3}$$

$$\Phi^r(\tau,\delta) = \sum_{i=1}^{N_1} a_i\delta^{d_i}\tau^{t_i} + \sum_{i=N_1+1}^{N_2} a_i\delta^{d_i}\tau^{t_i}\exp(-\delta^{e_i}) \tag{4}$$

以下に微分演算の結果を示す．

1 階微分

$$\Phi_\delta^\circ = \left(\frac{\partial\Phi^\circ}{\partial\delta}\right)_\tau = \frac{1}{\delta} \tag{5}$$

$$\Phi_\tau^\circ = \left(\frac{\partial\Phi^\circ}{\partial\tau}\right)_\delta = \begin{cases} a_1^\circ + \dfrac{a_2^\circ}{\tau} + \displaystyle\sum_{i=3}^{N^\circ} a_i^\circ \frac{n_i}{\exp(n_i\tau)-1} & \text{(R32 および R125)} \\ a_1^\circ + \dfrac{a_2^\circ}{\tau} + \displaystyle\sum_{i=3}^{N^\circ} a_i^\circ n_i\tau^{n_i-1} & \text{(R134a および R143a)} \end{cases} \tag{6}$$

$$\Phi_\delta^r = \left(\frac{\partial\Phi^r}{\partial\delta}\right)_\tau = \sum_{i=1}^{N_1} a_i d_i\delta^{d_i-1}\tau^{t_i} + \sum_{i=N_1+1}^{N_2} a_i\exp(-\delta^{e_i})(d_i - e_i\delta^{e_i})\,\delta^{d_i-1}\tau^{t_i} \tag{7}$$

$$\Phi_\tau^r = \left(\frac{\partial\Phi^r}{\partial\tau}\right)_\delta = \sum_{i=1}^{N_1} a_i t_i\delta^{d_i}\tau^{t_i-1} + \sum_{i=N_1+1}^{N_2} a_i t_i\exp(-\delta^{e_i})\,\delta^{d_i}\tau^{t_i-1} \tag{8}$$

2 階微分

$$\Phi^\circ_{\delta\delta} = \left(\frac{\partial^2\Phi^\circ}{\partial\delta^2}\right)_\tau = -\frac{1}{\delta^2} \tag{9}$$

$$\Phi^\circ_{\tau\tau} = \left(\frac{\partial^2\Phi^\circ}{\partial\tau^2}\right)_\delta = \begin{cases} -\dfrac{a^\circ_2}{\tau^2} - \displaystyle\sum_{i=3}^{N^\circ} a^\circ_i \frac{n_i^2\exp(-n_i\tau)}{[1-\exp(-n_i\tau)]^2} & \text{(R32 および R125)} \\ -\dfrac{a^\circ_2}{\tau^2} - \displaystyle\sum_{i=3}^{N^\circ} a^\circ_i n_i(n_i-1)\tau^{n_i-2} & \text{(R134a および R143a)} \end{cases} \tag{10}$$

$$\Phi^\circ_{\tau\delta} = \left[\frac{\partial}{\partial\delta}\left(\frac{\partial\Phi^\circ}{\partial\tau}\right)_\delta\right]_\tau = 0 \tag{11}$$

$$\Phi^r_{\delta\delta} = \left(\frac{\partial^2\Phi^r}{\partial\delta^2}\right)_\tau = \sum_{i=1}^{N_1} a_i d_i(d_i-1)\delta^{d_i-2}\tau^{t_i} + \sum_{i=N_1+1}^{N_2} a_i\exp(-\delta^{e_i})[d_i^2 - d_i - e_i\delta^{e_i}(2d_i+e_i-1-e_i\delta^{e_i})]\,\delta^{d_i-2}\tau^{t_i} \tag{12}$$

$$\Phi^r_{\tau\tau} = \left(\frac{\partial^2\Phi^r}{\partial\tau^2}\right)_\delta = \sum_{i=1}^{N_1} a_i t_i(t_i-1)\delta^{d_i}\tau^{t_i-2} + \sum_{i=N_1+1}^{N_2} a_i t_i(t_i-1)\exp(-\delta^{e_i})\,\delta^{d_i}\tau^{t_i-2} \tag{13}$$

$$\Phi^r_{\tau\delta} = \left[\frac{\partial}{\partial\delta}\left(\frac{\partial\Phi^r}{\partial\tau}\right)_\delta\right]_\tau = \sum_{i=1}^{N_1} a_i d_i t_i\delta^{d_i-1}\tau^{t_i-1} + \sum_{i=N_1+1}^{N_2} a_i t_i(d_i - e_i\delta^{e_i})\exp(-\delta^{e_i})\,\delta^{d_i-1}\tau^{t_i-1} \tag{14}$$

3 熱力学的性質の導出

3.1 圧力

次の関係を用いる.

$$\left(\frac{\partial a}{\partial v}\right)_T = -P \tag{15}$$

$a = RT(\Phi^\circ + \Phi^r)$ より

$$\left(\frac{\partial a}{\partial v}\right)_T = \left(\frac{\partial a}{\partial\delta}\right)\left(\frac{\partial\delta}{\partial v}\right) = RT\left(\frac{\partial\delta}{\partial v}\right)\left(\Phi^\circ_\delta + \Phi^r_\delta\right)$$

ここで, $\delta = \rho/\rho_c = 1/(\rho_c v)$ であるから,

$$\left(\frac{\partial\delta}{\partial v}\right) = -\frac{1}{\rho_c v^2} = -\frac{\rho^2}{\rho_c} = -\rho\delta \tag{16}$$

したがって,

$$\left(\frac{\partial a}{\partial v}\right)_T = -RT\rho\delta\left(\frac{1}{\delta} + \Phi^r_\delta\right) = -RT\rho\,(1 + \delta\Phi^r_\delta)$$

以上より

$$\frac{P}{RT\rho} = 1 + \delta\Phi^r_\delta \tag{17}$$

3.2 エントロピ

次の関係を用いる．

$$\left(\frac{\partial a}{\partial T}\right)_v = -s \tag{18}$$

ここで，

$$\left(\frac{\partial a}{\partial T}\right)_v = \left(\frac{\partial a}{\partial \tau}\right)\left(\frac{\partial \tau}{\partial T}\right)$$

であり，

$$\begin{aligned}\left(\frac{\partial a}{\partial \tau}\right) &= \frac{\partial}{\partial \tau}\left[\frac{RT_c}{\tau}(\Phi^\circ + \Phi^r)\right] \\ &= -\frac{RT_c}{\tau^2}(\Phi^\circ + \Phi^r) + \frac{RT_c}{\tau}(\Phi^\circ_\tau + \Phi^r_\tau) \\ &= -\frac{RT_c}{\tau}\left[\frac{1}{\tau}(\Phi^\circ + \Phi^r) - (\Phi^\circ_\tau + \Phi^r_\tau)\right]\end{aligned} \tag{19}$$

$$\left(\frac{\partial \tau}{\partial T}\right) = -\frac{T_c}{T^2} = -\frac{\tau}{T} \tag{20}$$

であるから，

$$\left(\frac{\partial a}{\partial T}\right)_v = R\tau\left[\frac{1}{\tau}(\Phi^\circ + \Phi^r) - (\Phi^\circ_\tau + \Phi^r_\tau)\right] = R\left[\Phi^\circ + \Phi^r - \tau(\Phi^\circ_\tau + \Phi^r_\tau)\right] \tag{21}$$

したがって，

$$\frac{s}{R} = \tau(\Phi^\circ_\tau + \Phi^r_\tau) - \Phi^\circ - \Phi^r \tag{22}$$

3.3 内部エネルギー，エンタルピおよび Gibbs 自由エネルギー

$u = a + Ts$ であるから，式 (1) および (22) より，

$$\frac{u}{RT} = \frac{a}{RT} + \frac{s}{R} = \tau(\Phi^\circ_\tau + \Phi^r_\tau) \tag{23}$$

また，$h = u + Pv$ であるから，式 (17) および (23) より，

$$\frac{h}{RT} = \frac{u}{RT} + \frac{Pv}{RT} = \frac{u}{RT} + \frac{P}{RT\rho} = 1 + \tau(\Phi^\circ_\tau + \Phi^r_\tau) + \delta\Phi^r_\delta \tag{24}$$

さらに，$g = h - Ts$ であるから，式 (22) および (24) より，

$$\begin{aligned}\frac{g}{RT} &= \frac{h}{RT} - \frac{s}{R} \\ &= 1 + \tau(\Phi^\circ_\tau + \Phi^r_\tau) + \delta\Phi^r_\delta - \left[\tau(\Phi^\circ_\tau + \Phi^r_\tau) - \Phi^\circ - \Phi^r\right] \\ &= 1 + \Phi^\circ + \Phi^r + \delta\Phi^r_\delta\end{aligned} \tag{25}$$

3.4 定積比熱

定積比熱 c_v の定義式

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial \tau}\right)\left(\frac{\partial \tau}{\partial T}\right) \tag{26}$$

において,

$$\left(\frac{\partial u}{\partial \tau}\right) = \frac{\partial}{\partial \tau}\left[RT\tau\left(\Phi^{\circ}_{\tau} + \Phi^{r}_{\tau}\right)\right] = \frac{\partial}{\partial \tau}\left[RT_c\left(\Phi^{\circ}_{\tau} + \Phi^{r}_{\tau}\right)\right] = RT_c\left(\Phi^{\circ}_{\tau\tau} + \Phi^{r}_{\tau\tau}\right) \tag{27}$$

したがって,

$$\frac{c_v}{R} = -\tau^2\left(\Phi^{\circ}_{\tau\tau} + \Phi^{r}_{\tau\tau}\right) \tag{28}$$

3.5 定圧比熱

以下の関係を用いる.

$$ds = \frac{c_v}{T}dT + \left(\frac{\partial P}{\partial T}\right)_v dv \tag{29}$$

$P = \text{const.}$ の条件下において両辺を T で微分すれば

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_v}{T} + \left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_P \tag{30}$$

となる. $c_p = T\,(\partial s/\partial T)_P$ であることから,

$$c_p = c_v + T\left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_P \tag{31}$$

独立変数が (T, v) であるから, $(\partial P/\partial T)_v$ は容易に求まる. $(\partial v/\partial T)_P$ を計算する.

triple product rule より,

$$\left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial v}{\partial P}\right)_T\left(\frac{\partial T}{\partial v}\right)_P = -1 \tag{32}$$

これから,

$$\left(\frac{\partial T}{\partial v}\right)_P = -\frac{1}{\left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial v}{\partial P}\right)_T} \tag{33}$$

または,

$$\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial v}{\partial P}\right)_T \tag{34}$$

式 (34) を式 (31) に代入する.

$$c_p = c_v - T\left(\frac{\partial P}{\partial T}\right)_v^2\left(\frac{\partial v}{\partial P}\right)_T = c_v - T\left(\frac{\partial P}{\partial T}\right)_v^2 \bigg/ \left(\frac{\partial P}{\partial v}\right)_T \tag{35}$$

ここで，

$$P = RT\rho(1+\delta\Phi^r_\delta) = \frac{RT_c\rho_c\delta}{\tau}(1+\delta\Phi^r_\delta)$$

であるから，

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial P}{\partial \tau}\right)\left(\frac{\partial \tau}{\partial T}\right) = -\frac{\tau}{T}\left[-\frac{RT_c\rho_c\delta}{\tau^2}(1+\delta\Phi^r_\delta) + \frac{RT_c\rho_c\delta}{\tau}\delta\Phi^r_{\delta\tau}\right]$$
$$= R\rho(1+\delta\Phi^r_\delta - \delta\tau\Phi^r_{\delta\tau}) \tag{36}$$

また，

$$\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial P}{\partial \delta}\right)\left(\frac{\partial \delta}{\partial v}\right) = -\rho\delta\left[\frac{RT_c\rho_c}{\tau}(1+\delta\Phi^r_\delta) + \frac{RT_c\rho_c\delta}{\tau}(\Phi^r_\delta + \delta\Phi^r_{\delta\delta})\right]$$
$$= -RT\rho^2(1+2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta}) \tag{37}$$

式 (35)，(36) および (37) より

$$\frac{c_p}{R} = \frac{c_v}{R} + \frac{(1+\delta\Phi^r_\delta - \delta\tau\Phi^r_{\delta\tau})^2}{1+2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta}} \tag{38}$$

3.6 音速

音速 w は次式で定義される.

$$w^2 = \left(\frac{\partial P}{\partial \rho}\right)_s \tag{39}$$

triple product rule より

$$\left(\frac{\partial P}{\partial \rho}\right)_s\left(\frac{\partial s}{\partial P}\right)_\rho\left(\frac{\partial \rho}{\partial s}\right)_P = -1 \tag{40}$$

であるから，

$$\left(\frac{\partial P}{\partial \rho}\right)_s = -\frac{1}{\left(\frac{\partial s}{\partial P}\right)_\rho\left(\frac{\partial \rho}{\partial s}\right)_P} = -\left(\frac{\partial P}{\partial s}\right)_\rho\left(\frac{\partial s}{\partial \rho}\right)_P \tag{41}$$

ここで，

$$\left(\frac{\partial P}{\partial s}\right)_\rho = \left(\frac{\partial P}{\partial T}\right)_\rho \Big/ \left(\frac{\partial s}{\partial T}\right)_\rho = \frac{T}{c_v}\left(\frac{\partial P}{\partial T}\right)_\rho \tag{42}$$

また，

$$\left(\frac{\partial s}{\partial \rho}\right)_P = \left(\frac{\partial s}{\partial T}\right)_P\left(\frac{\partial T}{\partial \rho}\right)_P = \frac{c_p}{T}\left(\frac{\partial T}{\partial v}\right)_P\left(\frac{\partial v}{\partial \rho}\right)_P = -\frac{c_p v^2}{T}\left(\frac{\partial T}{\partial v}\right)_P \tag{43}$$

以上より，

$$\left(\frac{\partial P}{\partial \rho}\right)_s = \gamma v^2\left(\frac{\partial P}{\partial T}\right)_\rho\left(\frac{\partial T}{\partial v}\right)_P \tag{44}$$

ただし，$\gamma = c_p/c_v$ である．さらに，式 (33) より

$$\left(\frac{\partial T}{\partial v}\right)_P = -\left(\frac{\partial P}{\partial v}\right)_T \Big/ \left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial P}{\partial v}\right)_T \Big/ \left(\frac{\partial P}{\partial T}\right)_\rho \tag{45}$$

であるから，結局

$$w^2 = -\gamma v^2 \left(\frac{\partial P}{\partial v}\right)_T = -\frac{\gamma}{\rho^2}\left[-RT\rho^2(1 + 2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta})\right] \tag{46}$$

または

$$\frac{w^2}{RT} = \gamma(1 + 2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta}) \tag{47}$$

4 飽和状態

4.1 条件式

飽和状態においては気液両相の圧力および Gibbs 自由エネルギーが等しいので，以下の 2 式が成り立つ．

$$P_\ell = P_v \tag{48}$$

$$g' = g'' \tag{49}$$

式 (17) より，

$$P_\ell = RT\rho'\left[1 + \delta'\left(\Phi^r_\delta\right)'\right] \tag{50}$$

$$P_v = RT\rho''\left[1 + \delta''\left(\Phi^r_\delta\right)''\right] \tag{51}$$

ただし，$\left(\Phi^r_\delta\right)' = \Phi^r_\delta(\tau, \delta')$ および $\left(\Phi^r_\delta\right)'' = \Phi^r_\delta(\tau, \delta'')$ である．また，式 (25) および (49) より，

$$\delta'\left(\Phi^r_\delta\right)' + (\Phi^\circ)' + (\Phi^r)' = \delta''\left(\Phi^r_\delta\right)'' + (\Phi^\circ)'' + (\Phi^r)''$$

または，

$$\delta'\left(\Phi^r_\delta\right)' + (\Phi^r)' + \ln\delta' = \delta''\left(\Phi^r_\delta\right)'' + (\Phi^r)'' + \ln\delta'' \tag{52}$$

以上より，与えられた温度 T における飽和液密度 ρ' および飽和蒸気密度 ρ'' を求めるには，以下の 2 式を同時に満たす δ' および δ'' を求めればよい．

$$\delta''\left[1 + \delta''\left(\Phi^r_\delta\right)''\right] - \delta'\left[1 + \delta'\left(\Phi^r_\delta\right)'\right] = 0 \tag{53}$$

$$\left[\delta''\left(\Phi^r_\delta\right)'' + (\Phi^r)'' + \ln\delta''\right] - \left[\delta'\left(\Phi^r_\delta\right)' + (\Phi^r)' + \ln\delta'\right] = 0 \tag{54}$$

飽和蒸気圧 P_s は式 (50) もしくは (51) から計算する．

4.2 計算方法

2 元の Newton-Raphson 法を用いる．$M(\delta) = \delta\left[1 + \delta\Phi^r_\delta\right]$ および $N(\delta) = \delta\Phi^r_\delta + \Phi^r + \ln\delta$ とし，$\mathcal{M}$ および $\mathcal{N}$ をそれぞれ以下のように定義する．

$$\mathcal{M}(\delta', \delta'') = M(\delta'') - M(\delta') = \delta''\left[1 + \delta''\left(\Phi^r_\delta\right)''\right] - \delta'\left[1 + \delta'\left(\Phi^r_\delta\right)'\right] \tag{55}$$

$$\mathcal{N}(\delta', \delta'') = N(\delta'') - N(\delta') = \left[\delta''\left(\Phi^r_\delta\right)'' + (\Phi^r)'' + \ln\delta''\right] - \left[\delta'\left(\Phi^r_\delta\right)' + (\Phi^r)' + \ln\delta'\right] \tag{56}$$

適当な δ' および δ'' の推定値をそれぞれ $\Delta\delta'$ および $\Delta\delta''$ だけ修正した値が真の根であるとすれば，

$$\mathcal{M}(\delta' + \Delta\delta', \delta'' + \Delta\delta'') = \mathcal{M}(\delta', \delta'') - \Delta\delta' \left.\frac{dM}{d\,\delta}\right|_{\delta=\delta'} + \Delta\delta'' \left.\frac{dM}{d\,\delta}\right|_{\delta=\delta''} = 0 \tag{57}$$

$$\mathcal{N}(\delta' + \Delta\delta', \delta'' + \Delta\delta'') = \mathcal{N}(\delta', \delta'') - \Delta\delta' \left.\frac{dN}{d\,\delta}\right|_{\delta=\delta'} + \Delta\delta'' \left.\frac{dN}{d\,\delta}\right|_{\delta=\delta''} = 0 \tag{58}$$

すなわち，

$$\begin{bmatrix} M_\delta(\delta') & -M_\delta(\delta'') \\ N_\delta(\delta') & -N_\delta(\delta'') \end{bmatrix} \begin{bmatrix} \Delta\delta' \\ \Delta\delta'' \end{bmatrix} = \begin{bmatrix} \mathcal{M} \\ \mathcal{N} \end{bmatrix}$$

これから，

$$\begin{bmatrix} \Delta\delta' \\ \Delta\delta'' \end{bmatrix} = \frac{1}{\Delta} \begin{bmatrix} -N_\delta(\delta'') & M_\delta(\delta'') \\ -N_\delta(\delta') & M_\delta(\delta') \end{bmatrix} \begin{bmatrix} \mathcal{M} \\ \mathcal{N} \end{bmatrix} \tag{59}$$

ただし，

$$\Delta = -M_\delta(\delta')N_\delta(\delta'') + M_\delta(\delta'')N_\delta(\delta') \tag{60}$$

なお，

$$M_\delta = \frac{dM}{d\delta} = 1 + 2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta} \tag{61}$$

$$N_\delta = \frac{dN}{d\delta} = 2\Phi^r_\delta + \delta\Phi^r_{\delta\delta} + \frac{1}{\delta} \tag{62}$$

である．

5 臨界点

5.1 条件式

臨界点では次の 2 式が満足されなければならない．

$$\left(\frac{\partial P}{\partial v}\right)_T = 0 \tag{63}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0 \tag{64}$$

式 (37) より，

$$\left(\frac{\partial P}{\partial v}\right)_T = -RT\rho_c^2\delta^2\,(1 + 2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta})$$

さらに，

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = -RT\rho_c^2\left[2\delta(1 + 2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta}) + \delta^2(2\Phi^r_\delta + 4\delta\Phi^r_{\delta\delta} + \delta^2\Phi^r_{\delta\delta\delta})\right]$$

したがって，式 (63) および (64) が同時に満足されるためには，

$$1 + 2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta} = 0 \tag{65}$$

$$2\Phi^r_\delta + 4\delta\Phi^r_{\delta\delta} + \delta^2\Phi^r_{\delta\delta\delta} = 0 \tag{66}$$

であればよい．

5.2 計算方法

式 (65) および (66) も 2 元の Newton-Raphson 法で解くことができる.

$$\mathcal{M}(\tau,\delta) = 1 + 2\delta\Phi^r_\delta + \delta^2\Phi^r_{\delta\delta} \tag{67}$$

$$\mathcal{N}(\tau,\delta) = 2\Phi^r_\delta + 4\delta\Phi^r_{\delta\delta} + \delta^2\Phi^r_{\delta\delta\delta} \tag{68}$$

とし, 適当な τ および δ の推定値をそれぞれ $\Delta\tau$ および $\Delta\delta$ だけ修正した値が真の根であるとすれば,

$$\mathcal{M}(\tau+\Delta\tau,\delta+\Delta\delta) = \mathcal{M} + \Delta\tau\mathcal{M}_\tau + \Delta\delta\mathcal{M}_\delta = 0 \tag{69}$$

$$\mathcal{N}(\tau+\Delta\tau,\delta+\Delta\delta) = \mathcal{N} + \Delta\tau\mathcal{N}_\tau + \Delta\delta\mathcal{N}_\delta = 0 \tag{70}$$

ただし, $\mathcal{M}_\tau = (\partial\mathcal{M}/\partial\tau)_\delta$, $\mathcal{M}_\delta = (\partial\mathcal{M}/\partial\delta)_\tau$, $\mathcal{N}_\tau = (\partial\mathcal{N}/\partial\tau)_\delta$ および $\mathcal{N}_\delta = (\partial\mathcal{N}/\partial\delta)_\tau$ である. 式 (69) および (70) より,

$$\begin{bmatrix} \mathcal{M}_\tau & \mathcal{M}_\delta \\ \mathcal{N}_\tau & \mathcal{N}_\delta \end{bmatrix} \begin{bmatrix} \Delta\tau \\ \Delta\delta \end{bmatrix} = \begin{bmatrix} -\mathcal{M} \\ -\mathcal{N} \end{bmatrix}$$

であるから,

$$\begin{bmatrix} \Delta\tau \\ \Delta\delta \end{bmatrix} = -\frac{1}{\Delta} \begin{bmatrix} \mathcal{N}_\delta & -\mathcal{M}_\delta \\ -\mathcal{N}_\tau & \mathcal{M}_\tau \end{bmatrix} \begin{bmatrix} \mathcal{M} \\ \mathcal{N} \end{bmatrix} \tag{71}$$

ここで,

$$\Delta = \mathcal{M}_\tau\mathcal{N}_\delta - \mathcal{M}_\delta\mathcal{N}_\tau \tag{72}$$

なお, $\mathcal{M}_\tau$, $\mathcal{M}_\delta$, $\mathcal{N}_\tau$ および $\mathcal{N}_\delta$ の計算式は次のようになる.

$$\mathcal{M}_\tau = 2\delta\Phi^r_{\delta\tau} + \delta^2\Phi^r_{\delta\delta\tau} \tag{73}$$

$$\mathcal{M}_\delta = 2\Phi^r_\delta + 4\delta\Phi^r_{\delta\delta} + \delta^2\Phi^r_{\delta\delta\delta} \tag{74}$$

$$\mathcal{N}_\tau = 2\Phi^r_{\delta\tau} + 4\delta\Phi^r_{\delta\delta\tau} + \delta^2\Phi^r_{\delta\delta\delta\tau} \tag{75}$$

$$\mathcal{N}_\delta = 6\Phi^r_{\delta\delta} + 6\delta\Phi^r_{\delta\delta\delta} + \delta^2\Phi^r_{\delta(4)} \tag{76}$$

$$\Phi^r_{\delta\delta\tau} = \sum_{i=1}^{N_1} a_i t_i d_i (d_i - 1)\delta^{d_i-2}\tau^{t_i-1} + \sum_{i=N_1+1}^{N_2} a_i t_i \exp(-\delta^{e_i})\,\delta^{d_i-2}D(\delta)\tau^{t_i-1} \tag{77}$$

$$\Phi^r_{\delta\delta\delta} = \sum_{i=1}^{N_1} a_i d_i (d_i - 1)(d_i - 2)\delta^{d_i-3}\tau^{t_i} + \sum_{i=N_1+1}^{N_2} a_i \exp(-\delta^{e_i})\,\delta^{d_i-3}E(\delta)\tau^{t_i} \tag{78}$$

$$\Phi^r_{\delta\delta\delta\tau} = \sum_{i=1}^{N_1} a_i t_i d_i (d_i - 1)(d_i - 2)\delta^{d_i-3}\tau^{t_i-1} + \sum_{i=N_1+1}^{N_2} a_i t_i \exp(-\delta^{e_i})\,\delta^{d_i-3}E(\delta)\tau^{t_i-1} \tag{79}$$

$$\Phi^r_{\delta(4)} = \sum_{i=1}^{N_1} a_i d_i (d_i - 1)(d_i - 2)(d_i - 3)\delta^{d_i-4}\tau^{t_i} + \sum_{i=N_1+1}^{N_2} a_i \exp(-\delta^{e_i})\,\delta^{d_i-4}\tau^{t_i}\left[(d_i - 3 - e_i\delta^{e_i})E(\delta) + \delta\frac{dE}{d\delta}\right] \tag{80}$$

$$D(\delta) = d_i^2 - d_i - e_i\delta^{e_i}(2d_i + e_i - 1 - e_i\delta^{e_i}) \tag{81}$$

$$E(\delta) = (d_i - 2 - e_i\delta^{e_i})D(\delta) + \delta\frac{dD}{d\delta} \tag{82}$$

$$\frac{dD}{d\delta} = -e_i^2\delta^{e_i-1}(2d_i + e_i - 1 - 2e_i\delta^{e_i}) \tag{83}$$

$$\frac{dE}{d\delta} = -e_i^2\delta^{e_i-1}D(\delta) + (d_i - 1 - e_i\delta^{e_i})\frac{dD}{d\delta} + \delta\frac{d^2D}{d\delta^2} \tag{84}$$

$$\frac{d^2D}{d\delta^2} = -e_i^2\delta^{e_i-2}(e_i - 1)(2d_i + e_i - 1 - 2e_i\delta^{e_i}) + 2e_i^4\delta^{2e_i-2} \tag{85}$$

参考文献

[1] R. Tillner-Roth, F. Harms-Watzenberg, and H. D. Baehr, (1993), *DKVTagungsbericht*, 20, 167.

[2] C. Tegeler, R. Span, and W. Wagner, (1999), *J. Phys. Chem. Ref. Data*, 28, 779.

[3] D. Bücker and W. Wagner, *J. Phys. Chem. Ref. Data*, (in press, 2004).

[4] R. Span and W. Wagner, (1996), *J. Phys. Chem. Ref. Data*, 25, 1509.

[5] S. G. Penoncello, A. R. H. Goodwin, and R. T Jacobsen, (1995), *Int. J. Thermophys*, 16, 519.

[6] J. Smukala, R. Span, and W. Wagner, (2000), *J. Phys. Chem. Ref. Data*, 29, 1053.

[7] K. M. de Reuck, (1990), *International Thermodynamic Tables of the Fluid State-11 Fluorine, International Union of Pure and Applied Chemistry*, Pergamon Press, Oxford.

[8] H. Miyamoto and K. Watanabe, (2001), *Int. J. Thermophys*, 23, 477.

[9] U. Setzmann and W. Wagner, (1991), *J. Phys. Chem. Ref. Data*, 20, 1061.

[10] K. M. de Reuck and R. J. B. Craven, (1993), *International Thermodynamic Tables of the Fluid State-12 Methanol, International Union of Pure and Applied Chemistry*, Blackwell Scientific Publications, London.

[11] R. S. Katti, R. T Jacobsen, R. B. Stewart, and M. Jahangiri, (1986), *Adv. Cryo. Eng.*, 31, 1189.

[12] R. Span, E. W. Lemmon, R. T Jacobsen, W. Wagner, and A. Yokozeki, (2000), *J. Phys. Chem. Ref. Data*, 29, 1361.

[13] R. Schmidt and W. Wagner, (1985), *Fluid Phase Equilib.*, 19, 175.

[14] H. Miyamoto and K. Watanabe, (2000), *Int. J. Thermophys.*, 21, 1045.

[15] S. Angus, B. Armstrong, and K. M. de Reuck, (1980), *International Thermodynamic Tables of the Fluid State-7 Propylene, International Union of Pure and Applied Chemistry*, Pergamon Press, Oxford.

[16] R. T. Jacobsen, S. G. Penoncello, and E. W. Lemmon, (1992), *Fluid Phase Equilib.* 80, 45.

[17] V. Marx, A. Pruß, and W. Wagner, (1992), *Fortschr.-Ber. VDI, Dusseldorf: VDIVerlag*, 19, 57.

[18] B. de Vries, R. Tillner-Roth, and H. D. Baehr, (1995), *19th International Congress of Refrigeration, The Hague, The Netherlands, International Institute of Refrigeration*, Vol. IVa, 582.

[19] H. Sunaga, R. Tillner-Roth, H. Sato, and K. Watanabe, (1998), *Int. J. Thermophys.*, 19, 1623.

[20] R. Tillner-Roth, J. Li, A. Yokozeki, H. Sato and K. Watanabe, (1998), *Thermodynamic Properties of Pure and Blended Hydrofluorocarbon (HFC) Refrigerants*, Japan Society of Refrigerating and Air Conditioning Engieers.

[21] R. Tillner-Roth and H. D. Baehr, (1994), *J. Phys. Chem. Ref. Data*, 23, 657.

[22] E. W. Lemmon and R. T Jacobsen, (2000), *J. Phys. Chem. Ref. Data*, 29, 521.

[23] A. Kamei, S. W. Beyerlein, and R. T Jacobsen, (1995), *Int. J. Thermophys.*, 16, 1155.

[24] S. G. Penoncello, E. W. Lemmon, R. T Jacobsen, and Z. Shan, (2003), *J. Phys. Chem. Ref. Data*, 32, 1473.

[25] K. M. de Reuck, R. J. B. Craven, and W. A. Cole, (1991), *Report on the Development of an Equation of State for Sulphur Hexafluoride*, IUPAC Thermodynamic Tables Project Centre, London.

[26] W. Wagner and A. Pruß, (2002), *J. Phys. Chem. Ref. Data*, 31, 387.

[27] E. W. Lemmon, R. T Jacobsen, S. G. Penoncello, and D. G. Friend, (2000), *J. Phys. Chem. Ref. Data*, 29, 331.