GENERAL EQUATIONS FOR THE CALORIC FUNCTIONS OF GASES AND LIQUIDS

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A generalized thermal equation of state is used in deriving equations for the major caloric functions of gases and liquids.

Information on the caloric parameters of gases and liquids is required for many calculations in heat engineering, physical chemistry, and chemical technology; however, no reasonably accurate general relationships have been published for the caloric functions of many substances, particularly ones covering wide ranges in the state parameters. The caloric functions are the internal energy, enthalpy, entropy, and specific heat; and these can be derived from the thermal equation of state [1, 2].

One determines the differences between the parameters at a specified temperature and specified pressure and the values of the same at the identical temperature but at standard pressure. We have devised a new form of the principle of corresponding states, which uses the thermodynamic correlation factor β [3].

It has been found [4] that this factor β has advantages over the correlation factors used by Pitzer, Lidersen, and Riedel. First of all, the general relationships derived from this quantity describe the measurements very closely. Secondly, the normal boiling point T_b, the critical temperature T_c, and the critical pressure P_c, which are used to calculate β, are usually determined with high accuracy. Thirdly, β is dependent on the normal boiling point and on the critical parameters. On the other hand, Pitzer's acentricity factor ω is related only to the reduced saturation vapor pressure at a temperature close to the normal boiling point, while Lidersen's critical compressibility coefficient Z_c and Riedel's factor α_c are related only to the properties of the substance in the critical region. The thermodynamic parameters of a gas or liquid should be discussed in terms of the density in dimensionless form in the development of generalized methods. The critical density is not usually known with very high precision, and it is not required to calculate β, so the reduction parameter for the density in this form of the corresponding-state principle is the density at the point on the surface corresponding to the ideal-gas state but having the critical P and T, namely, $\rho^* = P_s/RT_s$. Therefore, the thermal equation of state is put as

$$F(P_R,\ T_R,\ \rho_R,\ \beta) = 0, \tag{1}$$

where $P_R = P/P_s$, $T_R = T/T_s$, and $\rho_R = \rho/(\rho^*/Z'_c)$ are the reduced pressure, temperature, and density; $\beta = \log(9.8692\ P_s)/(T_s/T_b - 1)$, where P_s is in MPa.

The explicit form of (1) for the gas phase has been derived [5] by referring Hirschfelder's equation [1] to a form containing the dimensionless variables used in (1).

The mean error in determining the density is 0.5-2% for $T_R = 0.50$-10 and $P_R = 0.001$-40, while the maximum errors are 2-7%. The average error increases in the critical region.

The density of the liquid is [6] given by

$$P_{RL}(\rho_R, T_R) = P_{Rv}(\rho_R, T_R) - P_{Rv}(\rho_{RLs}, T_R) + P_{Rs}(T_R), \tag{2}$$

where P_{Rv} is the reduced pressure derived from the equation of state for the gas phase, while P_{Rs} is reduced saturation vapor pressure.

The average error in determining the density is 2-5% for $T_R = 0.50$-0.95 and $P_R = 0.001$-200.

The thermal equation of state [5, 6] has been used to derive analytic relationships for the corrections ΔH to the enthalpy and ΔC_v and ΔC_p to the specific heats in the ideal-gas state, which can be utilized in computer calculations.

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TABLE 1. Values of a_{ij} in (6), (7), and (24)

j	i					
	−1	0	1	2	3	4
			for (6)			
0		326,541	−1057,877	506,483	1180,881	−972,679
1		−161,248	385,597	395,106	−1521,434	917,107
2		14,726	12,707	−238,894	422,798	−213,899
			for (7)			
0		81,348	−233,388	22,445	390,725	−263,767
1		−51,885	115,053	102,168	−388,431	225,504
2		2,199	9,569	−68,776	107,867	−51,281
			for (24)			
0	59,72363	−827,48582	4050,6713	−8313,8258	5683,4209	
1	−74,92164	1000,6369	−4744,6394	9513,4966	−6499,6167	
2	30,944836	−398,0132	1825,107	−3561,3245	2412,364	
3	−4,192988	58,373	−231,338	437,5681	−291,1894	

TABLE 2. Coefficients K_{ij} Appearing in the Equations for the Caloric Parameters

i	j			
	0	1	2	3
0	0	$88{,}5-3{,}12\,m$	$-124{,}46+3{,}84\,m+0{,}363\,m^2$	$44{,}4-5{,}22\,m$
1	0	$-313{,}3+13{,}42\,m$	$429-9{,}84\,m-1{,}815\,m^2$	$-156{,}9+18{,}92\,m$
2	0	$408{,}9-21{,}54\,m$	$-528{,}8+1{,}98\,m+3{,}63\,m^2$	$204{,}3-25{,}44\,m$
3	$5{,}5-m$	$-237{,}4+15{,}3\,m$	$233+15{,}7\,m-3{,}63\,m^2$	$-115{,}5+15\,m$
4	$-2{,}25-\frac{\alpha'_{cv}}{2}+m$	$47{,}8-4{,}06\,m$	$\frac{\alpha'_{cv}}{2}-27{,}05-16{,}18m+1{,}815m^2$	$23{,}7-3{,}26\,m$
5	0	0	$-8{,}44+4{,}50\,m-0{,}363\,m^2$	0

The reduced density is $\rho_R \leq 1$ in the low-density region, and one can write the enthalpy as

$$\left(\frac{H^0-H}{RT}\right)_T = -Z_c\int\limits_0^{\rho_R}\left[\frac{P_R}{T_R}-\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R}\right]\frac{d\rho_R}{\rho_R^2}-\frac{Z_cP_R}{\rho_RT_R}+1. \tag{3}$$

In the case of a gas for which $\rho_R \geq 1$, the integration region is split into two zones:

$$\left(\frac{H^0-H}{RT}\right)_T = \left(\frac{H^0-H_1}{RT}\right)_T - Z_c\int\limits_1^{\rho_R}\left[\frac{P_R}{T_R}-\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R}\right]\frac{d\rho_R}{\rho_R^2}-\frac{Z_c}{T_R}\left[\frac{P_R}{\rho_R}-P_{R1}\right]. \tag{4}$$

The quantity $(H^0-H_1)/RT$ calculated from (3) is substituted into the result of integration with $\rho_R = 1$.

The equation of state for the low-density range allows one to calculate the density of the saturated vapor ρ_{R_V} if the saturation vapor pressure P_{R_S} is known; from ρ_{R_V} and P_{R_S} we can readily derive an expression for the enthalpy of the vapor on the saturation line, and then the Clausius–Clapeyron equation can be used to derive an expression for the enthalpy of the liquid on the saturation line. For that purpose, it is necessary to know the saturation vapor pressure and the density of the liquid on the saturation line. Although the density of the saturated vapor can be calculated from the equation of state, more reliable results are obtained if it is determined in a fashion as independent as that for ρ_{R_L} and P_{R_S}. One can use generalized equations derived within the framework of the new principle of corresponding states by means of the correlation factor β:

saturation vapor pressure [7],

$$\log P_R = [\beta + A_0 + A_1(T_R-\delta)^2 + A_2(T_R-\delta)^4]\left(1-\frac{1}{T_R}\right),$$
$$\delta = B_0 + B_1\beta + B_2\beta^2 + B_3\beta^3, \tag{5}$$

where $B_0 = 0.34154$; $B_1 = -0.08934$; $B_2 = 0.13317$; $B_3 = -0.018205$; $A_0 = -0.015$; $A_1 = 1.397$; and $A_2 = 5.813$;

density of liquid on saturation line [8],

$$\rho_{RL} = \frac{\rho_L Z_c'}{P_c/RT_c} = Z_c' \sum_{i=0}^{4} \sum_{j=0}^{2} a_{ij} \beta^j T_R^i;$$

density of gas on saturation line [8],

$$\rho_{Rv} = \frac{\rho_v Z_c'}{P_c/RT_c} = Z_c' \exp\left(\sum_{i=0}^{4} \sum_{j=0}^{2} a_{ij} \beta^j T_R^i \right). \tag{7}$$

Table 1 gives the values of the a_{ij}, which allow one to calculate the enthalpy of the liquid via the equation of state for the latter:

$$\left(\frac{H^0 - H}{RT} \right) = -Z_c \int_{\rho_{RL}}^{\rho_R} \left[\frac{P_R}{T_R} - \left(\frac{\partial P_R}{\partial T_R} \right)_{\rho_R} \right] \frac{d\rho_R}{\rho_R^2} - \frac{Z_c}{T_R} \left[\frac{P_R}{\rho_R} - \frac{P_{Rs}}{\rho_{RL}} \right] + Z_c \left(\frac{1}{\rho_{Rv}} - \frac{1}{\rho_{RL}} \right) \frac{dP_{Rs}}{dT_R} + \left(\frac{H^0 - H_v}{RT} \right). \tag{8}$$

The value for $(H^\circ - H_V)/RT$ is calculated from (3) with ρ_{RV} replacing ρ_R.

The final equations for the enthalpy differ for each of the regions, as in the case of the equation of state:

I. All T_R, $\rho_R \leq 1$

$$\left(\frac{H^0 - H}{RT} \right) = Z_c' \left[\rho_R \left(\frac{2K_0}{T_R} + \frac{3K_1}{T_R^2} \right) + K_2 \rho_R^2 \left(1 - \frac{2}{T_R^2} \right) \right] - \frac{b\rho_R - b'\rho_R^2}{1 - b\rho_R + b'\rho_R^2},$$

$$K_0 = 5.5,\ K_1 = m - K_0,\ K_2 = 0.5\,(1 - K_0 - \alpha_{cv}' + 2m), \tag{9}$$

$$b = \frac{3m^2 - 6m - 1}{m(3m - 1)},\quad b' \quad \frac{m - 3}{3m - 1},\ \rho_R = \frac{\rho}{P_c/RT_c} \cdot Z_c',$$

$$Z_c' = 1.2484 - 0.3317\beta + 0.03407\beta^2 - 0.85767/\beta;\quad \alpha_{cv}' = -3 + 3.676\beta;$$

$$m = 43.164 - 272.73\,(Z_c') + 706.63\,(Z_c')^2 - 705.41\,(Z_c')^3.$$

II. $T_R \geq 1$, $\rho_R > 1$

$$\left(\frac{H^0 - H}{RT} \right) = -Z_c' \sum_{j=0}^{3} T_R^{(j-2)} \left\{ \frac{\Omega_j(\rho_R)}{\rho_R} - \Omega_j(1) - (j-2)\,[W_j(\rho_R) - W_j(1)] \right\} + \left(\frac{H^0 - H_1}{RT} \right), \tag{10}$$

$$\Omega_j(\rho_R) = \frac{K_{0j} + K_{1j}\rho_R + K_{2j}\rho_R^2 + K_{3j}\rho_R^3 + K_{4j}\rho_R^4 + K_{5j}\rho_R^5}{\rho_R},$$

$$W_j(\rho_R) = \frac{-0.5K_{0j} - K_{1j}\rho_R + K_{2j}\rho_R^2 \ln\rho_R + K_{3j}\rho_R^3 + 0.5K_{4j}\rho_R^4 + 0.3333K_{5j}\rho_P^5}{\rho_R^2},$$

and $\Omega_j(1)$ and $W_j(1)$ are the values of Ω_j and W_j for $\rho_R = 1$; $(H^0 - H_1)/RT$ is defined by (9) subject to $\rho_R = 1$; Table 2 gives the values of the K_{ij}.

III. $T_R < 1$, $\rho > 1$

$$\left(\frac{H^0 - H}{RT} \right) = -Z_c' \sum_{j=0}^{3} T_R^{(j-2)} \left\{ \frac{\Omega_j(\rho_R)}{\rho_R} - \frac{\Omega_j(\rho_{RL})}{\rho_{RL}} - (j-2)\,[W_j(\rho_R) \right.$$

$$\left. - W_j(\rho_{RL})] - (j-1)\,(\rho_R^{-1} - \rho_{RL}^{-1})\,\Omega_j(\rho_{RL}) \right\} + Z_c'\,(\rho_R^{-1} - \rho_{RL}^{-1}) \frac{d\rho_{RL}}{dT_R}$$

$$\times \sum_{j=0}^{3} T_R^{(j-1)} R_j(\rho_{RL}) + Z_c'\,(\rho_{Rv}^{-1} - \rho_R^{-1}) \frac{dP_{R_s}}{dT_R} + \left(\frac{H^0 - H_v}{RT} \right), \tag{11}$$

$$R_j(\rho_{RL}) = \frac{-K_{0j} + K_{2j}\rho_{RL}^2 + 2K_{3j}\rho_{RL}^3 + 3K_{4j}\rho_{RL}^4 + 4K_{5j}\rho_{RL}^5}{\rho_{RL}^2},$$

where $\Omega_j(\rho_{RL})$ and $W_j(\rho_{RL})$ are as in (10) subject to the condition $\rho_R = \rho_{RL}$; $(H^0-H_v)/RT$ is determined by (9) subject to $\rho_R = \rho_{Rv}$; P_{Rs}, ρ_{RL}, ρ_{Rv}, dP_{Rs}/dT_R, and $d\rho_{RL}/dT_R$ are determined by (5)-(7).

In calculating K_{40} and K_{42} one should replace α'_{cv} by $\alpha'_{cL} = 27.63-20.345\beta + 7.031\beta^2-0.8827\beta^3$:

For the specific heat:

I. All T_R, $\rho_R \le 1$

$$\left(\frac{C_v^0 - C_v}{R}\right) = -Z_c' \frac{(2K_1\rho_R - K_2\rho_R^2)}{T_R^2}, \tag{12}$$

$$\left(\frac{\partial P_R}{\partial \rho_R}\right)_{T_R} = -2\left(K_0 + \frac{K_1}{T_R}\right)\rho_R + 3K_2\left(-T_R + \frac{1}{T_R}\right)\rho_R^2 + \frac{T_R(1-b'\rho_R^2)}{Z_c'(1-b\rho_R+b'\rho_R^2)^2},$$

$$\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R} = \frac{K_1\rho_R^2}{T_R^2} - K_2\left(1+\frac{1}{T_R^2}\right)\rho_R^3 + \frac{\rho_R}{Z_c'(1-b\rho_R+b'\rho_R^2)}.$$

II. $T_R \ge 1$, $\rho_R > 1$

$$\left(\frac{C_v^0 - C_v}{R}\right) = -Z_c' \frac{2K_1 - K_2}{T_R^2} + Z_c' \sum_{j=0}^{3} (j-1)(j-2) T_R^{(j-2)} [W_j(\rho_R) - W_j(1)], \tag{13}$$

$$\left(\frac{\partial P_R}{\partial \rho_R}\right)_{T_R} = \sum_{i=0}^{3} T_R^{(j-1)} R_j(\rho_R), \quad \left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R} = \sum_{j=0}^{3} (j-1) T_R^{(j-2)} \Omega_j(\rho_R).$$

III. $T_R < 1$, $\rho_R > 1$

$$\begin{aligned}\left(\frac{C_v^0 - C_v}{R}\right) = {} & Z_c' \sum_{j=0}^{3} (j-1)(j-2) T_R^{(j-2)} [W_j(\rho_R) - W_j(\rho_{RL})] \\ & + Z_c'(\rho_R^{-1} - \rho_{RL}^{-1}) \sum_{j=0}^{3} \Big\{ j-1)(j-2)\,\Omega_j(\rho_{RL})\, T_R^{(j-2)} \\ & + \left[2(j-1) T_R^{(j-1)} \frac{d\rho_{RL}}{dT_R} + T_R^j \frac{d^2\rho_{RL}}{dT_R^2}\right] R_j(\rho_{RL}) \Big\} - Z_c' \rho_{Rv}^{-2} \frac{d\rho_{Rv}}{dT_R} \\ & \times \left(T_R \frac{dP_{Ps}}{dT_R} - P_{Rs}\right) + Z_c' \left(\frac{d\rho_{RL}}{dT_R}\right)^2 \sum_{j=0}^{3} T_R^j \Big\{ \rho_{RL}^{-2} R_j(\rho_{RL}) + (\rho_R^{-1} - \rho_{RL}^{-1}) \\ & \times \left[\frac{dR_j(\rho_R)}{d\rho_R}\right]_{\rho_{RL}} \Big\} - Z_c'(\rho_R^{-1} - \rho_{Rv}^{-1})\, T_R \frac{d^2 P_{Rs}}{dT_R^2} + \left(\frac{C_v^0 - C_{vv}}{R}\right),\end{aligned} \tag{14}$$

$$\left(\frac{\partial P_R}{\partial \rho_R}\right)_{T_R} = \sum_{i=0}^{3} T_R^{(j-1)} R_j(\rho_R),$$

$$\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R} = \sum_{j=0}^{3} (j-1) T_R^{(j-2)} [\Omega_j(\rho_R) - \Omega_j(\rho_{RL})] - \frac{d\rho_{RL}}{dT_R} \sum_{j=0}^{3} T_R^{(j-1)} R_j(\rho_{RL}) + \frac{dP_{Rs}}{dT_R},$$

$$\frac{dR_j(\rho_R)}{d\rho_R} = 2K_{0j}\rho_R^{-3} + 2K_{3j} + 6K_{4j}\rho_R + 12K_{5j}\rho_R^2,$$

where $(C_V^0 - C_{VV})/R$ is defined by (12) subject to $\rho_R = \rho_{Rv}$; P_{Rs}, ρ_{RL}, ρ_{Rv}, dP_{Rs}/dT_R, $d\rho_{RL}/dT_R$, $d\rho_{Rv}/dT_R$, d^2P_{Rs}/dT_R^2 and $d^2\rho_{RL}/dT_R^2$ are defined by (5)-(7). Similarly, one should use α'_{cv} for the enthalpy of the gas and α'_{cL} for the enthalpy of the liquid.

The following formula converts from C_V to C_P:

$$\left(\frac{C_p^0 - C_p}{R}\right) = \left(\frac{C_v^0 - C_v}{R}\right) - \frac{Z_c' T_R}{\rho_R^2}\left[\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R}^2 \Big/ \left(\frac{\partial P_R}{\partial \rho_R}\right)_{T_R}\right] + 1. \tag{15}$$

From (9)-(14) we obtain the enthalpy and specific heat for the gas and liquid on the saturation line:

$$\left(\frac{H^0 - H_{vs}}{RT}\right) = Z_c'\left[\rho_{Rv}\left(\frac{2K_0}{T_R} + \frac{3K_1}{T_R^2}\right) + K_2\rho_{Rv}^2\left(1 - \frac{2}{T_R^2}\right) - \frac{b\rho_{Rv} - b'\rho_{Rv}^2}{1 - b\rho_{Rv} + b'\rho_{Rv}^2}\right], \tag{16}$$

$$\left(\frac{H^0 - H_{vs}}{RT}\right) = Z_c'(\rho_{Rv}^{-1} - \rho_{RL}^{-1})\frac{dP_{Rs}}{dT_R} + \left(\frac{H^0 - H_{vs}}{RT}\right). \tag{17}$$

The enthalpy of the liquid is calculated as the enthalpy of the gas with the addition of the enthalpy difference arising from the phase transition, which is defined by the Clausius–Clapeyron equation. A more accurate result is obtained if the enthalpy of the gas is combined with the latent heat of evaporation, which is [9] defined by

$$\frac{L}{RT_c} = Af(1 - T_R) = A[2{,}4 + 51.68(1 - T_R) - 199{,}54(1 - T_R)^2 + 490.28(1 - T_R)^3 - 599.84(1 - T_R)^4 + 280.1(1 - T_R)^5], \tag{18}$$

where $A = -0.2883 + 0.3371\beta$; then

$$\left(\frac{H^0 - H_{Ls}}{RT}\right) = \left(\frac{H_{vs} - H_{Ls}}{RT}\right) + \left(\frac{H^0 - H_{vs}}{RT}\right) = \frac{A}{T_R} f(1 - T_R) + \left(\frac{H^0 - H_{vs}}{RT}\right). \tag{19}$$

The specific heat of the gas is

$$\left(\frac{C_v^0 - C_{vv}}{R}\right) = -Z_c'\frac{2K_1\rho_{Rv} - K_2\rho_{Rv}^2}{T_R^2},$$

$$\left(\frac{\partial P_R}{\partial \rho_R}\right)_{T_R} = -2\left(K_0 + \frac{K_1}{T_R}\right)\rho_{Rv} + 3K_2\left(-T_R + \frac{1}{T_R}\right)\rho_{Rv}^2 + \frac{T_R(1 - b'\rho_{Rv}^2)}{Z_c'(1 - b\rho_{Rv} + b'\rho_{Rv})^2},$$

$$\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R} = \frac{K_1\rho_{Rv}^2}{T_R^2} - K_2\left(1 + \frac{1}{T_R^2}\right)\rho_{Rv}^3 + \frac{\rho_{Rv}}{Z_c'(1 - b\rho_{Rv} + b'\rho_{Rv}^2)}. \tag{20}$$

The specific heat of the liquid is

$$\left(\frac{C_v^0 - C_{vLs}}{R}\right) = -Z_c'\rho_{Rv}^{-2}\frac{d\rho_{Rv}}{dT_R}\left[T_R\frac{dP_{Rs}}{dT_R} - P_{Rs}\right] + Z_c'\left(\frac{d\rho_{RL}}{dT_R}\right)^2\sum_{j=0}^{3} T_R^j[\rho_{RL}^{-2}R_j(\rho_{RL})]$$

$$- Z_c'(\rho_{RL}^{-1} - \rho_{Rv}^{-1})T_R\frac{d^2P_{Rs}}{dT_R^2} + \left(\frac{C_v^0 - C_{vv}}{R}\right),$$

$$\left(\frac{\partial P_R}{\partial \rho_R}\right)_{T_R} = \sum_{j=0}^{3} T_R^{(j-1)}R_j(\rho_{RL}), \tag{21}$$

$$\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R} = -\frac{d\rho_{RL}}{dT_R}\sum_{j=0}^{3} T_R^{(j-1)}R_j(\rho_{RL}) + \frac{dP_{Rs}}{dT_R},$$

The analytical expressions for $(H^\circ - H)/RT_c$ and $(C_p^0 - C_p)/R$ indicate that the error in determing the corrections for deviation from ideal behavior are on average 2-5% for the enthalpy and specific heat of the gas; these corrections are very small in this case by comparison with the ideal-gas functions.

The integration must be carried through the coexistence curve in the expressions for $(H^\circ - H)/RT$ and $(C_V^0 - C_V)/R$, which introduces considerable computational errors into the final result. Therefore, it is desirable to integrate from the saturation line into the single-phase region for the liquid state (region III), for which purpose one can use generalized empirical expressions of adequate accuracy for the coexistence curve.

Then we have for the enthalpy

$$\left(\frac{H^0 - H}{RT}\right) = \left(\frac{H^0 - H_{Ls}}{RT}\right) + \left(\frac{H_{Ls} - H}{RT}\right), \tag{22}$$

TABLE 3. Values Derived from (9), (10), and (22) with Data for the Pressure Corrections to the Ideal-Gas Enthalpy

Compound	Parameter ranges		Error, %		No. of points	Ref.
	T_R	p_R	av.	max.		
Methane	0,52—5,2	0,02—22	4,55	8,23	15	[12]
Methane	1,8	0,75—3,0	7,73	8,85	5	[13]
Propane	0,84—1,6	0,02—14	2,30	5,16	12	[12]
Propane	0,54—1,5	0,32—3,2	4,53	8,90	30	[14]
Propane	0,99—1,3	0,32—1,6	4,63	9,54	8	[15]
Isobutane	1,34	0,27—4,2	2,06	2,79	5	[12]
n-Pentane	0,78—1,3	0,40—2,9	5,35	10,2	20	[16]
n-Octane	0,74—0,99	0,55—3,9	6,49	9,6	12	[16]
n-Hexadecane	0,74—0,84	0,12—6,8	6,87	11,6	6	[16]
Propylene	1,0—1,2	0,21—33	3,41	6,9	15	[12]
Benzene	0,75—1,1	0,28—2,0	6,66	13,7	20	[16]

where

$$\left(\frac{H_{Ls}-H}{RT}\right)=-Z_c'\sum_{j=0}^{3}T_R^{(j-2)}\left\{\frac{\Omega_j(\rho_R)}{\rho_R}-\frac{\Omega_j(\rho_{RL})}{\rho_{RL}}-(j-2)[W_j(\rho_R)-W_j(\rho_{RL})]-(j-1)(\rho_R^{-1}-\rho_{RL}^{-1})\,\Omega_j(\rho_{RL})\right\}+$$

$$+Z_c'(\rho_R^{-1}-\rho_{RL}^{-1})\frac{d\rho_{RL}}{dT_R}\sum_{j=0}^{3}T_R^{(j-1)}R_j(\rho_{RL})-Z_c'(\rho_R^{-1}-\rho_{RL}^{-1})\frac{dR_{Rs}}{dT_R},$$

and $(H^0-H_{Ls})/RT$ is defined by (19).

The calculation for the specific heat is from

$$\left(\frac{C_p^0-C_p}{R}\right)=\left(\frac{C_p^0-C_{ps}}{R}\right)+\left(\frac{C_{ps}-C_p}{R}\right). \tag{23}$$

The value of $(C_p^0-C_{ps})/R$ can be calculated from the following generalized equation [10]:

$$\left(\frac{C_p^0-C_{ps}}{R}\right)=-\sum_{i=-1}^{3}\sum_{j=0}^{3}a_{ij}\beta^j(1-T_R)^i. \tag{24}$$

Table 1 gives the values of the a_{ij} for (24).

The equation of state gives the correction

$$\left(\frac{C_{vs}-C_v}{R}\right)=Z_c'\sum_{j=0}^{3}(j-1)(j-2)\,T_R^{(j-2)}\,[W_j(\rho_R)-W_j(\rho_{RL})]$$

$$+Z_c'(\rho_R^{-1}-\rho_{RL}^{-1})\sum_{j=0}^{3}\left\{(j-1)(j-2)\,\Omega_j(\rho_{RL})\,T_P^{(j-2)}\right.$$

$$\left.+\left[2(j-1)\,T_R^{(j-1)}\frac{d\rho_{RL}}{dT_R}+T_R^j\frac{d^2\rho_{RL}}{dT_R^2}\right]R_j(\rho_{RL})\right\}$$

$$+Z_c'(\rho_R^{-1}-\rho_{RL}^{-1})\left(\frac{d\rho_{RL}}{dT_R}\right)^2\sum_{j=0}^{3}T_R^j\left(\frac{dR_j(\rho_R)}{d\rho_R}\right)_{\rho_{RL}}+Z_c'(\rho_{RL}^{-1}-\rho_R^{-1})\,T_R\frac{d^2P_{Rs}}{dT_R^2}, \tag{25}$$

which can then be converted to the correction

$$\left(\frac{C_{ps}-C_p}{R}\right)=\left(\frac{C_{vs}-C_v}{R}\right)-Z_c'T_R\left\{\frac{1}{\rho_R^2}\left[\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R}^2\Big/\left(\frac{\partial P_R}{\partial\rho_R}\right)_{TR}\right]\right.$$

$$\left.-\frac{1}{\rho_{RL}^2}\left[\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R}^2\Big/\left(\frac{\partial P_R}{\partial\rho_R}\right)_{T_R}\right]_{\rho_{RL}}\right\}.$$

TABLE 4. Comparison of Values Calculated from (12), (13), and (23) with Pressure Corrections for the Ideal-Gas Isobaric Specific Heat [12]

Compound	Parameter ranges		Error, %		No. of points
	T_R	P_R	av.	max.	
Methane	1,57—5,25	0,02—22	12,2	18,7	16
Ethane	1,05—1,65	0,02—10	7,27	12,7	12
Propane	0,84—1,63	0,02—14	8,53	15,8	18
Isobutane	1,34	0,02—4,1	11,3	17,0	6
Propylene	1,02—1,20	0,02—54	11,4	16,6	19
Benzene	0,66—0,85	1,02—11	9,61	12,3	8
Butan-1, 3-diene	0,97	0,11—0,33	9,83	13,4	3
Oxygen	0,52—6,46	0,02—20	13,2	20,7	26
Nitrogen	0,63—7,92	0,03—30	13,7	21,3	25

The first set of partial derivatives within the curly brackets may be derived from (14), while the second can be derived from (21).

This method of calculating the enthalpy and specific heat of the liquid provides much higher accuracy, and the generalized relationships apply for wide ranges in the state parameters. Tables 3 and 4 compare the calculated values with measured ones for T_R = 0.5-8 and pressures up to P_R = 50. The thermal equation of state can also be used to calculate the fugacity f and entropy S for all three regions. The final expressions for the fugacity take the form:

I. All $T_R, \rho_R \le 1$

$$\ln\frac{f}{P_c} = -Z_c'\left[2\rho_R\left(\frac{K_0}{T_R}+\frac{K_1}{T_R^2}\right)+1{,}5K_2\rho_R^2\left(1-\frac{1}{T_R^2}\right)\right]$$

$$+\frac{b\rho_R-b'\rho_R^2}{1-b\rho_R+b'\rho_R^2}+\ln(\rho_R T_R)-0{,}5\ln(1-b\rho_R+b'\rho_R^2)+K_3\tan^{-1}(K_3)+K_3\tan^{-1}(K_4\rho_R-K_3)-\ln Z_c', \qquad (26)$$

where the values of K_0, K_1, K_2, b, and b' are calculated as for the enthalpy and specific heat, and $K_3 = b/(4b'-b^2)^{1/2}$ and $K_4 = 2b'/(4b'-b^2)^{1/2}$.

II. $T_R \ge 1$, $\rho_R > 1$

$$\ln\frac{f}{P_c} = Z_c'\sum_{j=0}^{3}T_R^{(j-2)}\left[\frac{\Omega_j(\rho_R)}{\rho_R}-\Omega_j(1)+W_j(\rho_R)-W_j(1)\right]+\ln\frac{f_1}{P_c}. \qquad (27)$$

where $\ln f_1/P_c$ is defined by (26) with $\rho_R = 1$; $\Omega_j(\rho_R)$, $\Omega_j(1)$, $W_j(\rho_R)$, and $W_j(1)$ are the same functions as for the enthalpy and specific heat.

III. $T_R < 1$, $\rho_R > 1$

$$\ln\frac{f}{P_c} = Z_c'\sum_{j=0}^{3}T_R^{(j-2)}\left[\frac{\Omega_j(\rho_R)}{\rho_R}-\frac{\Omega_j(\rho_{RL})}{\rho_{RL}}+W_j(\rho_R)-W_j(\rho_{RL})\right]+\ln\frac{f_v}{P_c}, \qquad (28)$$

where $\ln f_v/P_c$ is defined by (26) subject to $\rho_R = \rho_{Rv}$.

The expressions for the enthalpy and fugacity readily give the entropy:

$$\left(\frac{S^0-S}{R}\right)=\left(\frac{H^0-H}{RT}\right)+\ln\frac{f}{P_c}+\ln P_c. \qquad (29)$$

The calculations require a knowledge of the normal boiling point T_b, the critical temperature T_c, and the critical pressure P_c, as well as of the ideal-gas functions.

Therefore, the equation of state previously derived has been used in generalized analytic expressions for the enthalpy, fugacity, and specific heats C_v and C_p for pure nonpolar substances; the accuracy of these equations is such as to make them suitable for engineering and technological calculations. The expressions can be extended to polar substances by applying appropriate corrections to the thermodynamic correlation factor β. In the case of a mixture, one should use the pseudocritical temperature and pressure instead of the true T_c and P_c for the individual substances [4].

NOTATION

H	is the enthalpy;
S	is the entropy;
C_v	is the specific heat at constant volume;
C_p	is the specific heat at constant pressure;
f	is the fugacity;
L	is the latent heat of vaporization;
ρ	is the density;
P	is the pressure;
T	is the temperature;
β	is the thermodynamic correlation factor;
ω	is the acentric factor;
Z_c	is the critical coefficient of compressibility;
Z'_c, α'_c	are the equation parameters;
R	is the universal gas content.

Indices

b	is the normal boiling point;
c	is the critical point;
R	is the reduced value;
v	is the gas;
L	is the liquid;
s	is the saturation line;
0	is the ideal 1 gas state;
1	is the value for $\rho_R = 1$.

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