Performance Comparison of Four-Parameter Correlation Equations of the Enthalpy of Vaporization

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ABSTRACT: A few commonly used correlation equations of the enthalpy of vaporization essential to the analysis of refrigeration cycles are reviewed. A new four-parameter correlation equation is proposed assuming that the enthalpy of vaporization could be represented with a linear form of the temperature and an additional function which slowly decreases as the temperature increases. It is not a common practice to measure the enthalpy of vaporization by experiment; therefore, performance of the new correlation is examined using numeric data from the ASHRAE tables for 22 pure substance refrigerants. The new correlation equation and other existing ones are fitted to the data optimizing the root mean squared deviation. All data points are weighted equally and NBP (normal boiling point) is used as a fixed point since the NBP is important for refrigeration application. The new four-parameter equation yields an average absolute deviation of 0.05% for 22 refrigerants which is smaller than those of other four-parameter equations, such as Guermouche-Vergnaud (0.08%), Aerebrot (0.13%), Radoz-Lyderson (0.08%), and Somayajulu four-parameter equation (0.08%).

———— Nomenclature ————

a : linear coefficient
Δh : enthalpy of vaporization [kJ/kg]
i : data number, term number
k : exponent
l : exponent or coefficient
m : exponent or coefficient
N : number of data points
n : exponent or coefficient
R : gas constant [kJ/kgK]
T : saturation temperature [K]
Z : compressibility factor

Greek symbols

α : critical exponent or constant
β : critical exponent or constant
γ : constant
θ : function of temperature($= 1 - T_r$)
τ : function of temperature($= 1/T_r - 1$)
Δ : critical exponent

Subscripts

b : normal boiling point
c : critical point
cal : calculated
r : reduced
t : triple pojnt
tbl : property table value

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1. Introduction

Refrigeration cycles, in general, transfer heat from a lower temperature body to a higher temperature body using the latent heat which a working fluid accepts or rejects during its phase change processes. Therefore, calculation of the enthalpy of vaporization is considered to be essential for a cycle analysis. Calculation of the enthalpy also affects the evaluation of the heat transfer coefficients since the enthalpy of vaporization is involved in most of the correlations for prediction of phase change heat transfer.

It is not a common practice to measure the enthalpy of vaporization by experiment. Most of the so-called experimental values come from the Clapeyron equation or the saturation condition determined by an equation of state. These approaches are rather complicated so that, when only simple hand calculation is necessary, it is desirable to have a correlation independent of any equation of state. Watson equation[1] is typical of various correlations found in the literature.[2-11]

In this study, first, some of independent correlations of the enthalpy of vaporization are reviewed. Then a new correlation is introduced and is compared with the existing correlations. It is our aim to improve the method of calculation and reproduction of the enthalpy of vaporization for each pure substances.

2. Vaporization enthalpy correlations

Based on available data, it is usual to propose a correlation which expresses the enthalpy of vaporization as a function of temperature. For this purpose, we have simple two-parameter Watson equation.[1]

$$\frac{\Delta h}{\Delta h_b} = \left(\frac{1 - T_r}{1 - T_{br}}\right)^n \tag{1}$$

where Δh_b is the enthalpy of vaporization at

NBP (normal boiling point) and T_{br} is the reduced temperature at NBP ($= T_b / T_c$). The value of exponent, n is known to be about 0.38, but the optimal value lies in the range of 0.23 ~0.41 depending on the substance.[3]

Recently Meyra et al.[2] proposed the following equation (MKZ) similar to the Watson.

$$\frac{\Delta h}{\Delta h_t} = \left(\frac{1 - T_r}{1 - T_{tr}}\right)^{Z_c^2[(T_r - T_{tr})/(1 - T_{tr})] + Z_c} \tag{2}$$

where Δh_t is the value at the triple point (TP), T_{tr} is the reduced temperature ($= T_t / T_c$) at TP, Z_c being a universal critical ratio. Equation (2) has a constraint that the curve should pass the TP. When TP data is not available, data point at the lowest temperature could be used instead.

As a three-parameter equation, Majer et al.[5] suggested the following Majer-Svoboda-Pick equation (MSP).

$$\Delta h = a(1 - T_r)^n \exp(- m T_r) \tag{3}$$

Torquato and Stell[6] suggested the following complicated equation having a semi-theoretical basis.

$$\frac{\Delta h}{RT_c} = a_0 \theta^\beta + a_1 \theta^{\beta + \Delta} + a_2 \theta^{1 - \alpha + \beta} + \sum_{i=1} a_i \theta^i \tag{4}$$

where $\theta = (1 - T_r)$, $\alpha = 0.11$, $\beta = 0.325$ and $\Delta = 0.51$. These are general exponents representing the non-analytic behavior near the critical point. Xiang[7] modified the Eq. (4) to give

$$\frac{\Delta h}{RT_c} = \frac{(a_0 \tau^\beta + a_1 \theta^{\beta + \Delta})}{(1 + n\theta)} \tag{5}$$

where $\tau = (1/T_r - 1)$. Xiang[7] claimed that Eq. (5) is the best equation among the three- or four- parameter equations available.

As a four-parameter equation, Guermouche

and Vergnaud[8] proposed the following correlation (GV).

$$\Delta h = a_0 \theta^{\alpha + \beta T_r + \gamma T_r^2} \qquad (6)$$

where α, β and γ are constants. Aerebrot equation[9] (A) has linear coefficients as follows.

$$\Delta h = a_0 \theta^{1/3} + a_1 \theta^{2/3} + a_2 \theta + a_3 \theta^{4/3} \qquad (7)$$

Radoz and Lydersen[10] proposed the four-parameter correlation (RL).

$$\Delta h = a_0 \theta^{1/3} + a_1 \theta^{2/3} + a_2 \theta^{5/3} + a_3 \theta^2 \qquad (8)$$

Somayajulu suggested the linear-parameter equations[11] (S3 and S4, respectively).

$$\Delta h = a_0 \tau + a_1 \theta^{3/8} + a_2 \theta^{9/4} \qquad (9)$$

$$\Delta h = a_0 \theta^{3/8} + a_1 \theta^{11/8} + a_2 \theta^{19/8} + a_3 \theta^{27/8} \qquad (10)$$

In this study, we introduce a new correlation (P4) as follows:

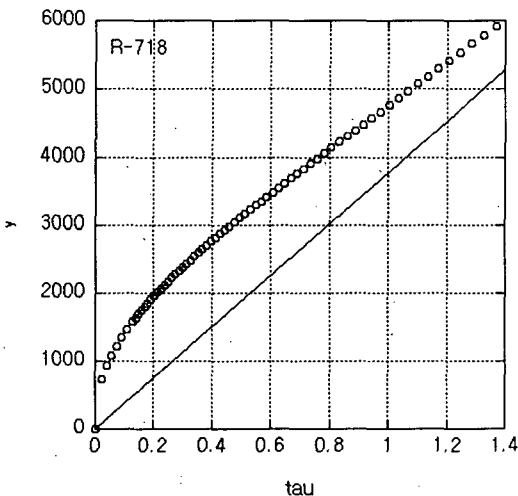$$\frac{\Delta h}{\Delta h_b} = a_0 \tau^{\beta} T_r^k + a_1 \theta \qquad (11)$$

Fig. 1   Plot of y vs. τ.

This equation originated from an assumption that, as in Fig. 1, $y (= \Delta h / T_r)$ can be represented with a linear term $a_1 \tau$ and an additional function $f(\tau)$, where $\tau = (1/T_r - 1)$; that is,

$$\frac{\Delta h}{T_r} = f(\tau) + a_1 \tau \qquad (12)$$

where $f(\tau)$ is proportional to τ^{β} near the critical point $(\beta \sim 1/3)$ and slowly decreases with temperature. Therefore, it is assumed $f(\tau) = a_0 \tau^{\beta} T_r^{k-1}$. This argument leads to the new correlation, Eq. (11).

In this study the four-parameter equation Eq. (11) will be tested and its performance will be examined comparing with existing equations.

3. Performance comparison

It is our aim to find a correlation which reproduces the pure substance enthalpies of vaporization accurately. Since the enthalpy of vaporization data are hardly measured by experiment, we used ASHRAE property tables[12] as a source of the enthalpy of vaporization data from the lowest temperature to the critical point for 22 substances. Table 1 shows critical temperatures, minimum temperatures, NBP's, and enthalpies of vaporization at NBP which are required to set up the correlations.

The average absolute deviation (AAD) and root mean squared deviation (RMS) used in this study are defined, respectively, as

$$AAD = \frac{1}{N} \sum_i |DEV_i| \ (\%) \qquad (13)$$

$$RMS = \sqrt{\frac{1}{N} \sum_i DEV_i^2} \ (\%) \qquad (14)$$

where N is the number of data points and deviation (DEV) is,

$$DEV = \frac{\Delta h_{cal} - \Delta h_{tbl}}{\Delta h_{tbl}} \times 100 \ (\%) \qquad (15)$$

Four-parameter correlations including P4 equation (11), proposed in this study are compared mutually. Therefore, exponents and/or coefficients in GV equation (6), A equation (7), RL equation (8), S4 equation (10), and P4 equation (11) are optimized for each substances.

For GV equation (6) and P4 equation (11) of which parameters are non-linear, the object function to be optimized is the value of RMS. For A equation (7), RL equation (8), and S4 equation (10) of which parameters are linear, least squares method is used to find values of the parameters.

During the optimization process, NBP is used as a constraint that every equation should pass

the NBP [R-744 (CO_2) is an exception since the constraint point is at $0°C$]. For this purpose, the forms of equations GV, A, RL, S4, and P4 are changed, respectively, as

$$\frac{\Delta h}{\Delta h_b} = (\theta/\theta_b)^{n+mT_r+lT_r^2} \tag{16}$$

$$\frac{\Delta h}{\Delta h_b} = n(\theta/\theta_b)^{1/3} + m(\theta/\theta_b)^{2/3} + l(\theta/\theta_b) + (1-n-m-l)(\theta/\theta_b)^{4/3} \tag{17}$$

$$\frac{\Delta h}{\Delta h_b} = n(\theta/\theta_b)^{1/3} + m(\theta/\theta_b)^{2/3} + l(\theta/\theta_b)^{5/3} + (1-n-m-l)(\theta/\theta_b)^2 \tag{18}$$

Table 1 Critical temperature, minimum temperature, NBP and corresponding enthalpy of vaporization

Subst.	T_c (K)	T_{min} (K)	T_b (K)	Δh_b (kJ/kg)
R-22	369.30	173.15	232.34	233.75
R-23	299.28	118.02*	191.09	238.68
R-32	351.26	136.34*	221.50	381.86
R-125	339.17	172.52*	225.02	163.78
R-134a	374.21	169.85*	247.08	216.97
R-152a	386.41	154.56*	249.13	329.91
R-143a	345.86	161.34*	225.91	226.63
R-245fa	427.20	223.15	288.05	196.69
R-717	405.40	195.50*	239.82	1369.50
R-718	647.10	273.16*	373.12	2256.47
R-744	304.13	216.59*	273.15	230.89
R-50	190.56	90.69*	111.67	510.83
R-170	305.33	98.15	184.55	489.47
R-290	369.85	123.15	231.07	425.43
R-600	425.16	173.15	272.62	385.79
R-600a	407.85	173.15	261.54	366.69
R-1150	282.35	103.99*	169.38	482.41
R-1270	365.57	133.15	225.46	439.17
R-704	5.20	2.18*	4.23	20.75
R-728	126.19	63.15*	77.35	198.84
R-732	154.58	54.36*	90.19	213.06
R-740	150.66	83.80*	87.29	160.99

*Triple point temperature.

Table 2 Numbers of data points and AAD's of GV, A, RL, S4 and P4 equation

Subst.	N^*	Correlation				
		GV	A	RL	S4	P4
R-22	68	0.10	0.13	0.09	0.04	0.05
R-23	69	0.08	0.10	0.05	0.06	0.02
R-32	67	0.10	0.17	0.09	0.10	0.05
R-125	68	0.14	0.13	0.08	0.05	0.04
R-134a	68	0.12	0.16	0.09	0.05	0.05
R-152a	68	0.09	0.14	0.09	0.01	0.06
R-143a	65	0.08	0.13	0.07	0.06	0.04
R-245fa	66	0.10	0.08	0.06	0.04	0.02
R-717	66	0.05	0.02	0.01	0.12	0.01
R-718	68	0.05	0.17	0.09	0.10	0.07
R-744	64	0.07	0.01	0.01	0.03	0.01
R-50	28	0.03	0.08	0.05	0.10	0.04
R-170	66	0.08	0.18	0.11	0.06	0.06
R-290	66	0.10	0.22	0.11	0.08	0.08
R-600	66	0.08	0.13	0.08	0.04	0.04
R-600a	63	0.01	0.10	0.02	0.17	0.05
R-1150	67	0.08	0.20	0.10	0.09	0.05
R-1270	68	0.06	0.17	0.08	0.12	0.05
R-704	32	0.35	0.30	0.31	0.30	0.29
R-728	25	0.01	0.05	0.02	0.04	0.01
R-732	22	0.07	0.19	0.12	0.08	0.08
R-740	26	0.01	0.03	0.01	0.07	0.00
AVE.		0.08	0.13	0.08	0.08	0.05

*Data from ASHRAE.[12]

$$\frac{\Delta h}{\Delta h_b} = n(\theta/\theta_b)^{3/8} + m(\theta/\theta_b)^{11/8}$$
$$+ l(\theta/\theta_b)^{19/8} + (1 - n - m - l)(\theta/\theta_b)^{27/8} \qquad (19)$$

$$\frac{\Delta h}{\Delta h_b} = n(\tau/\tau_b)^m (T_r/T_{br})^l + (1-n)(\theta/\theta_b) \qquad (20)$$

These equations have three parameters (n, m, l) that should be determined from the data. At NBP, $T = T_b$, $T_r = T_{br}$, $\tau = \tau_b$ and $\theta = \theta_b$, and thus the right-hand side becomes unity regardless of the values of n or m or l.

For all 22 substances, optimized correlations are used to calculate the enthalpies of vaporization. AAD's are calculated and shown in Table 2.

Comparing the equations by performance for individual substance, it is noted that the best equations are GV equation (6) for R-718, R-50, R-600a, and R-732, S4 equation (10) for R-22 and R-152a, P4 equation (11) for R-23, R-32, R-125, R-143a, R-245fa, R-1150, R-1270, R-704, R-740, respectively. For R-717, RL eqution (8) and P4 equation (11) seems to be equivalent, while for R-728 GV equation (6) and P4 equation (11) are equivalent. For R-134a, R-170,
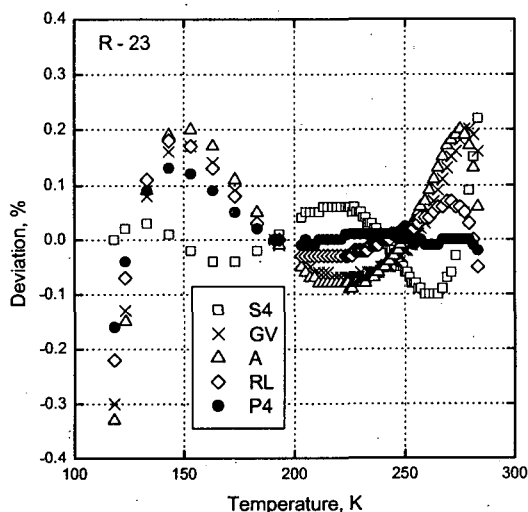
R-290, R-600, S4 equation (10) and P4 equation (11) gives essentially same performance and for R-744 A equation (7), RL equation (8), and P4 equation (11) are equivalent.

On the average, P4 equation (11) is the best among others yielding average AAD of 0.05% for 22 substances.

For R-23, Fig. 2 compares the values from ASHRAE Tables[12] with those calculated using the correlations. GV equation (6), A equation (7), and RL equation (8) give relatively larger deviations at both ends of the temperature range. S4 equation (10) yields small deviations at low temperatures while large deviations at high tempertures. P4 equation (11) gives smaller deviations over the whole temperature range than other correlations except at low temperatures.

Table 3 Values of the parameter in equation (20)

Subst.	Parameter		
	n	m	l
R-22	0.40426	0.35022	1.89103
R-23	0.41640	0.34840	1.81597
R-32	0.41310	0.35469	1.84878
R-125	0.42468	0.34639	1.92862
R-134a	0.40639	0.34790	2.00204
R-152a	0.41397	0.34676	1.89952
R-143a	0.42381	0.35181	1.92380
R-245fa	0.41013	0.32196	1.93811
R-717	0.44427	0.36428	1.55409
R-718	0.38756	0.37098	1.89113
R-744	0.71079	0.34754	1.96629
R-50	0.47765	0.36163	1.58447
R-170	0.42558	0.35553	1.76799
R-290	0.41641	0.35533	1.88279
R-600	0.43313	0.34892	1.84091
R-600a	0.40838	0.36295	2.00554
R-1150	0.39776	0.35606	1.86540
R-1270	0.40981	0.36834	1.88605
R-704	0.81467	0.38172	1.68084
R-728	0.44345	0.36234	1.78354
R-732	0.43087	0.36494	1.74270
R-740	0.40401	0.37151	1.87541

Fig. 2 Deviations of calculated R-23 enthalpies from the ASHRAE table values.

In Table 3 optimized values of (n, m, l) in P4 equation (20) suggested in this study are given.

4. Conclusions

Several commonly used correlations of the enthalpy of vaporization for pure substances are reviewed and a new four-parameter equation is proposed. Performances of some selected correlations are compared for 22 pure substance refrigerants.

The new four-parameter equation assumes that the enthalpy of vaporization could be represented with a linear term to the temperature and an additional function which slowly decreases as the temperature increases. The new equation reproduces the data from ASHRAE property tables with 0.05% of mean average absolute deviation which is smaller than those of other four-parameter equations, such as Guermouche-Vergnaud (0.08%), Aerebrot (0.13%), Radoz-Lydersen (0.08%), and Somayajulu four-parameter equation (0.08%).

The new correlation can be used to reproduce the enthalpy of vaporization for 22 refrigerants and is valid from the critical point to the lowest temperature where data point exists. Characteristic and optimal values of coefficients and exponents are given for the new four-parameter equation.

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