

Comparative Study on the Performance of Correlations of the Enthalpy of Vaporization for Pure Substance Refrigerants

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ABSTRACT: A few commonly used correlation equations of the enthalpy of vaporization are reviewed and a new three-parameter correlation equation is proposed. Performance of the proposed equation is examined using the data listed in the ASHRAE table for 22 pure substance refrigerants. The new equation yields an average absolute deviation of 0.14% for 22 refrigerants, which is better than those of other equations, such as Xiang (0.18%), Majer-Svoboda-Pick (0.18%), and Somayajulu equation (0.23%).

Nomenclature

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

Greek symbols

α	: critical exponent
β	: critical exponent
θ	: function of temperature($= 1 - T_r$)
τ	: function of temperature($= 1/T_r - 1$)
ω	: acentric factor
Δ	: critical exponent

Subscripts

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

1. Introduction

Enthalpy of vaporization or latent heat of vaporization is the difference in enthalpies of saturated vapor and saturated liquid at the same temperature. 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. Since the enthalpy of vaporization is involved in most of the correlations for prediction of phase change heat transfer, calculation of the enthalpy also affects the evaluation of the heat transfer coefficients.

It is not a common practice to measure the enthalpy of vaporization by experiment. Most

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of the so-called experimental values comes from the Clapeyron equation or the saturation condition determined by an equation of state. If there are not much data for saturation state, the enthalpy of vaporization may be estimated from the corresponding-states principle.⁽¹⁾ 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⁽²⁾ is the one while there are several others found in the literature.⁽³⁻⁹⁾

In this study, (1) some of independent correlations of the enthalpy of vaporization are reviewed, (2) a new correlation is proposed, and (3) the performances of selected three-parameter correlations are compared based on the ASHRAE data⁽¹⁰⁾ which is considered to be reliable. It is our aim to improve the method of simple yet accurate calculation and reproduction of enthalpy of vaporization for each pure substance refrigerants.

2. Vaporization enthalpy correlations

Reid et al.⁽³⁾ suggested the following correlation based on the corresponding-states principle.

$$\frac{\Delta h}{RT_c} = 7.08(1 - T_r)^{0.354} + 10.94\omega(1 - T_r)^{0.456} \quad (1)$$

where R is a gas constant, T_r is a reduced temperature ($= T/T_c$), T_c is a critical temperature and ω is an acentric factor. The correlation may be used within the temperature range of $0.6 < T_r < 1.0$. Equation (1) is used when there are not sufficient experimental data. Its accuracy depends on the validity of the corresponding-states principle.

When there are some data available, it is desirable to have an independent correlation which expresses the enthalpy of vaporization as a function of temperature. For this purpose,

we have Watson equation.⁽²⁾

$$\frac{\Delta h}{\Delta h_b} = \left(\frac{1 - T_r}{1 - T_{br}} \right)^n \quad (2)$$

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 on the range of 0.23~0.41 depending on the refrigerant.⁽⁴⁾ Fish-Lielmezs⁽⁵⁾ (FL) correlation is more complicated and gives better performance than Watson.

$$\frac{\Delta h}{\Delta h_b} = \frac{T_r}{T_{br}} \frac{X^n + X}{1 + X^m} \quad (3)$$

where $X = T_{br}(1 - T_r)/T_r(1 - T_{br})$ and the optimal values of exponents, n and m vary depending on the group of substances. Park⁽⁴⁾ suggested the following equation (P1) which simplified the FL equation improving performance.

$$\frac{\Delta h}{\Delta h_b} = \left(\frac{1 - T_r}{1 - T_{br}} \right)^n \left(\frac{T_r}{T_{br}} \right)^m \quad (4)$$

Figure 1 shows behavior of the enthalpy of vaporization for R-718(H₂O).⁽¹⁰⁾ In Eq. (4), n represents the behavior mainly at higher temperatures including the critical point, while m corrects the low temperature behavior. Majer et al.⁽⁶⁾ used the Majer-Svoboda-Pick equation (MSP).

$$\Delta h = a(1 - T_r)^n \exp(-mT_r) \quad (5)$$

This equation also uses $(1 - T_r)^n$ to represent the behavior at higher temperatures and the exponential function is multiplied to correct the low temperature behavior. Torquato and Stell⁽⁷⁾ suggested the following complicated equation having a semi-theoretical basis.

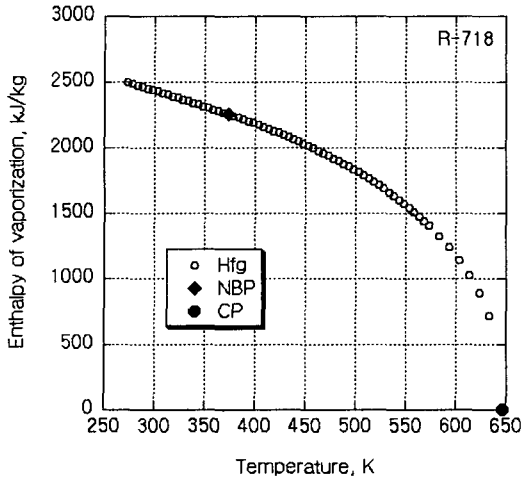


Fig. 1 Enthalpies of vaporization for R-718.

$$\frac{\Delta h}{RT_c} = a_0 \theta^\beta + a_1 \theta^{\beta+\Delta} + a_2 \theta^{1-\alpha+\beta} + \sum_{i=1}^4 a_i \theta^i \quad (6)$$

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⁽⁸⁾ modified the Eq. (6) to give

$$\frac{\Delta h}{RT_c} = \frac{(a_0 \tau^\beta + a_1 \theta^{\beta+\Delta})}{(1+n\theta)} \quad (7)$$

where $\tau = (1/T_r - 1)$. Xiang⁽⁸⁾ claimed that Eq. (7) was the best equation among the three- or four-parameter equations available.

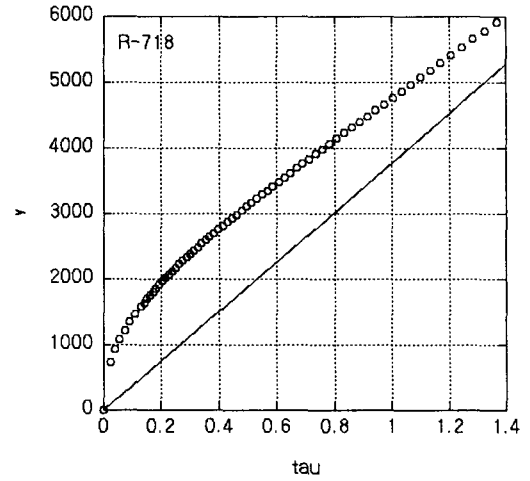
Some equations have linear coefficients. These are Eq. (6) and the following Somayajulu Eq. (9) (S).

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

In this study, we introduce a new correlation (P2) as follows:

$$\frac{\Delta h}{\Delta h_b} = a_0 \tau^\beta T_r^2 + a_1 \theta \quad (9)$$

This equation was made up from an assump-

Fig. 2 y vs. τ plot.

tion that, as in Fig. 2, $y (= \Delta h/T_r)$ can be represented with a linear term $a_1 \tau$ and an additional function $f(\tau)$, where $\tau = (1/T_r - 1)$; that is,

$$\frac{\Delta h}{T_r} = f(\tau) + a_1 \tau \quad (10)$$

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 a new correlation.

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

Equation (11) was fitted to the enthalpy of vaporization data for some substances, which found that the exponent, k was closed to 2 and that setting $k=2$ was good enough for our calculations. Therefore, we will test Eq. (9), which has three adjustable parameters and is relatively simple.

3. Performance comparison

Our concern in this study is not predict-

ability but reproducibility of the enthalpy of vaporization data available. It is our aim to find a simple correlation which reproduces the pure substance enthalpies of vaporization accurately. The independent equations compared are the three-parameter correlations; P1 Eq. (4), MSP Eq. (5), X Eq. (7), S Eq. (8) and P2 Eq. (9). The Watson Eq. (2) and FL Eq. (3) are excluded because they are not better than P1 Eq. (4) in terms of their performances.⁽⁴⁾ Torquato-Stell⁽⁷⁾ Eq. (6) is also excluded because it has at least six adjustable parameters making the equation itself fairly complicated.

Since the enthalpy of vaporization data are hardly measured by experiment, for the purpose of comparison of correlations, we use ASHRAE property tables⁽¹⁰⁾ 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.

First, the selected equations are optimized by adjusting coefficients and/or exponents for each refrigerant and then performances of correlations are compared. The object function for optimization is a root mean squared deviation (RMS) defined as

$$RMS = \sqrt{\frac{1}{N} \sum_i DEV_i^2} \quad (\%) \quad (12)$$

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

$$DEV = \frac{\Delta h_{cal} - \Delta h_{tbl}}{\Delta h_{tbl}} \times 100 \quad (\%) \quad (13)$$

During the optimization process, NBP is used as a constraint so that every equation should pass the NBP [R-744 (CO₂) is an exception since the constraint point is the one at 0°C]. For this purpose, the forms of equations P1, MSP, X,

P2 and S are changed, respectively, as

$$\frac{\Delta h}{\Delta h_b} = (\theta/\theta_b)^n (T_r/T_{br})^m \quad (14)$$

$$\frac{\Delta h}{\Delta h_b} = \left(\frac{\theta}{\theta_b}\right)^n \exp[-m(T_r - T_{br})] \quad (15)$$

$$\frac{\Delta h}{\Delta h_b} = \frac{n(\tau/\tau_b)^\beta + m(\theta/\theta_b)^{\beta+\Delta}}{1 + (n+m-1)(\theta/\theta_b)} \quad (16)$$

$$\frac{\Delta h}{\Delta h_b} = n\left(\frac{\tau}{\tau_b}\right)^m \left(\frac{T_r}{T_{br}}\right)^2 + (1-n)\left(\frac{\theta}{\theta_b}\right) \quad (17)$$

$$\frac{\Delta h}{\Delta h_b} = n\left(\frac{\tau}{\tau_b}\right) + m\left(\frac{\theta}{\theta_b}\right)^{3/8} + (1-n-m)\left(\frac{\theta}{\theta_b}\right)^{9/4} \quad (18)$$

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	221.5	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	90.690	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

These equations have two parameters (n , m) of which values are to be determined from the data. At NBP, $T = T_b$, $T_r = T_{br}$, $\tau = \tau_b$ and $\theta = \theta_b$ so that we can find that the right-hand side becomes 1 regardless of the values of n or m .

For all 22 refrigerants, optimized correlations are used to calculate the enthalpies of vaporization. Average absolute deviations (AAD) are calculated and shown in Table 2. The AAD is defined as

$$\text{AAD} = \frac{1}{N} \sum_i |\text{DEV}_i| (\%) \quad (19)$$

Table 2 Numbers of data points and AAD's of P1, MSP, X, P2 and S equation

Subst.	N^*	Correlation				
		P1	MSP	X	P2	S
R-22	68	0.14	0.13	0.04	0.08	0.03
R-23	69	0.15	0.13	0.10	0.12	0.35
R-32	67	0.24	0.18	0.08	0.13	0.35
R-125	68	0.16	0.16	0.02	0.06	0.05
R-134a	68	0.19	0.18	0.05	0.05	0.05
R-152a	68	0.20	0.17	0.06	0.08	0.13
R-143a	65	0.17	0.14	0.02	0.06	0.05
R-245fa	66	0.08	0.09	0.03	0.03	0.06
R-717	66	0.09	0.15	0.12	0.18	0.13
R-718	68	0.36	0.20	0.10	0.11	0.16
R-744	64	0.12	0.12	0.04	0.01	0.03
R-50	28	0.17	0.24	0.28	0.29	0.09
R-170	66	0.39	0.21	0.32	0.30	0.26
R-290	66	0.42	0.29	0.11	0.14	0.20
R-600	66	0.21	0.15	0.12	0.15	0.11
R-600a	63	0.27	0.18	0.11	0.05	0.25
R-1150	67	0.37	0.24	0.12	0.15	0.18
R-1270	68	0.33	0.19	0.08	0.11	0.38
R-704	32	0.55	0.44	1.58	0.49	1.65
R-728	25	0.14	0.05	0.10	0.10	0.06
R-732	22	0.47	0.20	0.42	0.36	0.34
R-740	26	0.11	0.04	0.06	0.05	0.14
AVE.		0.24	0.18	0.18	0.14	0.23

*Data from ASHRAE.⁽¹⁰⁾

Comparing the equations by performance for individual refrigerant, it is noted that the best equations are P1 Eq. (4) for R-717, MSP Eq. (5) for R-170, R-704, R-728, R-732 and R-740, S Eq. (8) for R-22, R-50 and R-600, P2 Eq. (9) for R-134a, R-744, R-600a and R-245fa, X Eq. (7) for the rest of 11 refrigerants, respectively. Comparing the equations by overall performance, it is observed that P2 Eq. (9) is the best among others yielding average AAD of 0.14% for 22 refrigerants. Excluding R-704 (Helium) for which deviations are always large regardless of the correlations, average AAD's are 0.12% in case of P2 Eq. (9), while X Eq. (7) has the smallest, 0.11%. The difference is marginal which makes it hard to tell a better one. Table 3 gives the optimized values of the coefficient, n and the exponent, m for the Eq.

Table 3 Values of the parameters in Eq. (17)

Subst.	Parameters	
	n	m
R-22	0.38706	0.35319
R-23	0.39081	0.35716
R-32	0.39161	0.36161
R-125	0.41356	0.34768
R-134a	0.40667	0.34783
R-152a	0.40201	0.35377
R-143a	0.41283	0.35465
R-245fa	0.40172	0.32361
R-717	0.35971	0.37474
R-718	0.37041	0.37660
R-744	0.70766	0.34748
R-50	0.38826	0.36844
R-170	0.39603	0.37413
R-290	0.40105	0.36242
R-600	0.41254	0.35755
R-600a	0.40912	0.36271
R-1150	0.37805	0.36301
R-1270	0.39342	0.37428
R-704	0.77480	0.39343
R-728	0.40968	0.37427
R-732	0.39676	0.38633
R-740	0.38227	0.37658

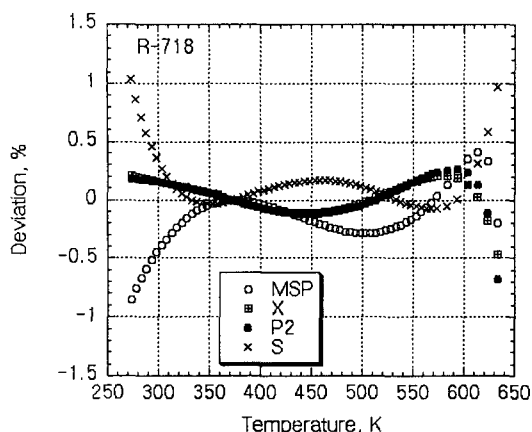


Fig. 3 Deviations of calculated R-718 enthalpies from the ASHRAE table values.

(17) which is equivalent to the P2 Eq. (9) proposed in this study. Figure 3 illustrates, for R-718, the differences between ASHRAE property table⁽¹⁰⁾ values and the ones calculated using the four correlations compared. MSP Eq. (5) and S Eq. (8) gives relatively larger deviations at low temperatures while X Eq. (7) and P2 Eq. (9) produce smaller deviations and show almost identical performance over a wide range excluding the critical point.

4. Conclusions

A few commonly used correlations of the enthalpy of vaporization for pure substance refrigerant are reviewed and a new correlation equation is proposed. Performances of some selected three-parameter correlations are compared for 22 refrigerants. The new equation reproduces the data from ASHRAE property tables with 0.14% of mean average absolute deviation so that the equation is better than or equivalent to Xiang equation and is better than Majer-Svoboda-Pick equation and Somayajulu equation. The new correlation can be used to reproduce the enthalpies of vaporization for 22

refrigerants and is valid from the critical point to the lowest temperature where data point exists. Characteristic values, optimal values of coefficients and exponents are given for the new equation.

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