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New Equations for Enthalpy of Vaporization from the Triple Point to the Critical Point

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Two new equations are proposed for the enthalpy of vaporization from the triple point to the critical point. One of these equations containing four parameters is exceptionally good for fitting the data. The other equation containing three parameters is quite adequate for fitting the data but it is exceptionally suited for interpolation when the data do not cover the entire range. These equations have been tested using the enthalpy of vaporization of water from the triple point to the critical point and are compared with other equations.

KEY WORDS: alcohols; alkanes; carbon dioxide; nitrogen; propylene; water.

1. INTRODUCTION

The calculation of the enthalpy of vaporization from the triple point to the critical point has been reviewed by Reid and Sherwood [1] and Reid et al. [2]. The purpose of this investigation is to propose several new procedures and to examine which of these procedures are reliable for fitting the data and which of these procedures are good for prediction and interpolation. Some of the commonly used equations are reviewed here.

The enthalpy of vaporization according to Watson [3] is represented by the following equation:[2]

$$\Delta H_{\mathrm{v}} = \Delta H_{\mathrm{vx}} X_{\mathrm{x}}^{0.375} \tag{1}$$

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[2] Explanation of symbols and the associated units are given under Nomenclature, at the end of the paper.

For the purpose of this paper, we write the Watson equation as follows:

$$\Delta H_{\mathrm{v}} = \Delta H_{\mathrm{vt}} X_{\mathrm{t}}^{0.375} \tag{2}$$

For fitting the data, we now propose the following four-parameter equation:

$$\Delta H_{\mathrm{v}} = aX_{\mathrm{t}}^{\mathrm{m}} + bX_{\mathrm{t}}^{1+\mathrm{m}} + cX_{t}^{2+\mathrm{m}} + dX_{\mathrm{t}}^{3+\mathrm{m}} \tag{3}$$

The constant m has the value of 3/8.

The Goodwin [4] equation for the enthalpy of vaporization is the following:

$$\Delta H_{\mathrm{v}} = \mathrm{a}X_{\mathrm{t}} + (X_{\mathrm{t}}^{0.35} - X_{\mathrm{t}})(b + cX_{\mathrm{t}} + dX_{\mathrm{t}}^{2}) \tag{4}$$

We also propose the following equation for the enthalpy of vaporization as an alternative to the Watson equation (2).

$$\Delta H_{\mathrm{v}} = aY + bX^{\mathrm{m}} + cX^{6\mathrm{m}} \tag{5}$$

where m has the value of 3/8.

2. RESULTS AND DISCUSSION

In order to compare the above equations, we have selected the enthalpies of vaporization of water compiled by Osborne et al. [5]. We have converted the temperatures to the IPTS-68. The data used for the triple point and critical point are from the NBS Steam Tables [6]. The values reported in the NBS Steam Tables agree in general with the values selected by Osborne et al. but disagree slightly very close to the critical temperature. We have selected for comparison the following four equations: Eqs. (2), (3), (4), and (5). The results obtained on the basis of these four equations are shown in Table I and Figs. 1 to 3. In the first regression we used 83 data points which extend over the entire liquid range. In this test the results indicate that the Eq. (3) is the best, followed by Eqs. (4), (5), and (2). In the second test we used six data points close to the triple point and an additional point at the critical point. We limited this test to Eqs. (2) and (5) and Eq. (3) truncated after the second and third terms. In this test only Eq. (5) came out successful. Equation (3) truncated after the third term fared worse than Eq. (3). However, when we truncated Eq. (3) after the second term, the result is slightly better than with the Watson equation. In the third test, we added one additional point at the reduced temperature, $T_{\mathrm{r}} = 0.9$. The normal order is once again restored and Eq. (3) takes the lead. These tests clearly indicate the supremacy of Eq. (3)

for fitting the data and Eq. (5) for interpolation. The results of these tests for the truncated equations are also shown in Table I.

We have also tested various equations reviewed by Reid and Sherwood [1] and by Reid et al. [2] and they failed to beat Eq. (3) in fitting the data and Eq. (5) in interpolation.

Similar tests were run for various compounds besides water and they lead to the same conclusions as with water except in the case of alcohols. In the case of alcohols, the three-parameter equation proved to be inferior to the four-parameter equations. The calorimetric data do not often extend to

Table I. Values of the Constants of Eqs. (2), (3), (4), and (5) for the Enthalpy of Vaporization of Water[a]

Equation No.	*a*	*b*	*c*	*d*	SD	Av. dev.
			Results of 1st regression with 83 data points			
(2)	45.867317				0.440	0.379
(3)	44.457979	14.635863	−27.945633	13.985176	0.050	0.037
(3)[b]	45.445181	7.018465	−7.768938		0.165	0.139
(3)[c]	46.984819	−1.754147			0.297	0.238
(4)	45.173464	39.883995	26.081034	−24.442823	0.069	0.055
(5)	13.405538	54.188028	−58.822461		0.052	0.052
			Results of 1st regression with 7 data points[d]			
(2)	45.101005				0.034	0.575
(3)[b]	53.816706	−21.229749	12.472012			0.987
(3)[c]	46.442705	−1.387485			0.003	0.313
(5)	3.531965	56.328732	−19.352771			0.155
			Results of 1st regression with 8 data points[d]			
(2)	45.154126				0.253	0.548
(3)	45.362607	8.169244	−16.307411	7.834589		0.086
(3)[b]	46.627224	−1.888158	0.316332		0.003	0.306
(3)[c]	46.582047	−1.531485			0.005	0.292
(4)	45.059024	41.526386	16.625343	−13.374091		0.109
(5)	3.066511	56.320631	−17.143303		0.001	0.179

[a] T_t and T_c of water are 273.16 and 647.126 K.

[b] Truncated after the third term.

[c] Truncated after the second term.

[d] The average deviation is for all the 83 data points but the standard deviation is for the number of data points used in the regression. For a few of these regressions the standard deviation is negligible and was not shown.

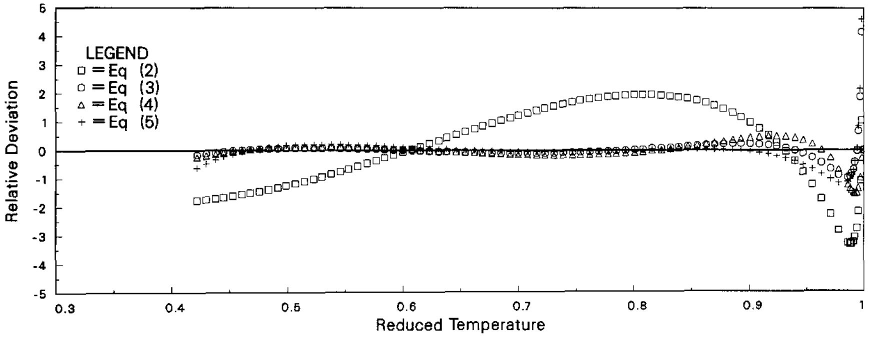

Fig. 1. Plot of relative deviation in enthalpy of vaporization of water versus reduced temperature. The results of the first regression with 83 data points.

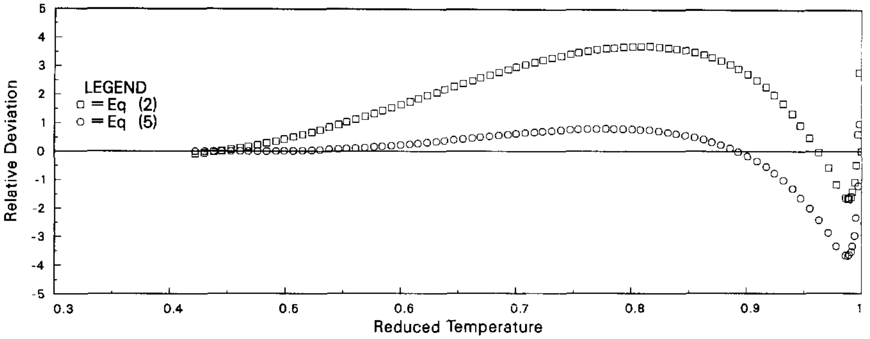

Fig. 2. Plot of relative deviation in enthalpy of vaporization of water versus reduced temperature. The results of the second regression with seven data points.

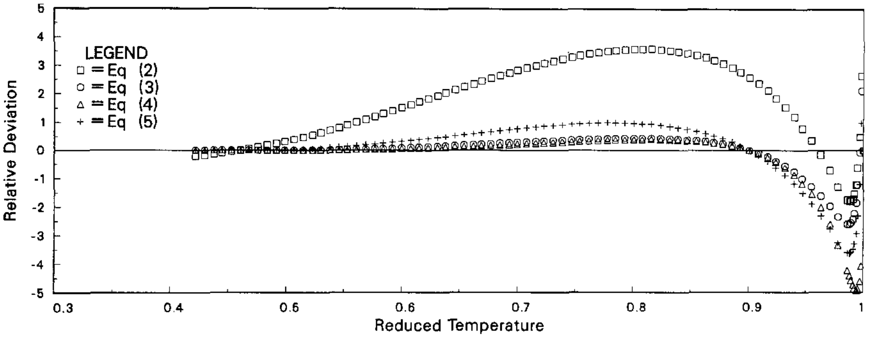

Fig. 3. Plot of relative deviation in enthalpy of vaporization of water versus reduced temperature. The results of the third regression with eight data points.

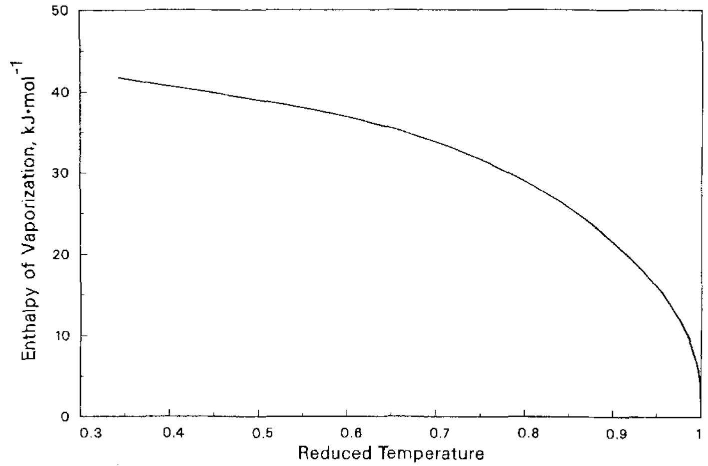

Fig. 4. Plot of enthalpy of vaporization of methanol versus reduced temperature.

Table II. Values of the Constants of Eq. (3) for the Enthalpy of Vaporization of Some Compounds

Compound	T_m(K)	T_c(K)	a	b	c	d	SD	Av. dev.
Methanol	175.59	512.60	40.38384	30.09167	−53.39520	24.67660	0.048	0.025
Ethanol	159.00	513.92	44.04282	37.57678	−61.47456	27.31003	0.094	0.062
1-Propanol	147.00	536.78	43.84980	62.58408	−94.40090	45.44930	0.131	0.097
2-Propanol	184.65	508.30	40.15367	50.67680	−60.84775	22.00139	0.113	0.084
1-Butanol	184.51	563.05	43.01045	55.48347	−56.86091	17.33482	0.152	0.099
2-Butanol	158.45	536.05	48.11093	7.47268	38.18325	−33.81230	0.396	0.257
iso-Butanol	165.00	547.78	42.72773	52.80624	−50.03555	14.46768	0.231	0.161
t-Butanol	298.81	505.59	35.59111	0.48094	27.79435	−17.15370	0.183	0.123
1-Pentanol	195.00	588.15	49.85791	19.62522	14.61201	−19.95579	0.280	0.183
Propylene	187.66	373.40	19.79362	−0.29145	1.16994	−1.06765	0.028	0.015
Nitrogen	63.15	126.20	6.15835	0.77101	−1.59378	0.69579	0.009	0.003
Carbon dioxide	216.58	304.21	14.12640	3.23842	−2.48485	0.30581	0.024	0.017
Benzene	278.68	562.16	32.10881	10.88635	−17.31814	9.31721	0.102	0.055
Methane	90.68	190.555	9.06452	1.52000	−3.05190	1.18854	0.011	0.006
Ethane	90.348	305.33	18.00355	4.43633	−10.23662	5.66822	0.030	0.022
Propane	85.47	369.80	23.97875	5.87352	−13.78513	8.79046	0.014	0.011
Butane	134.86	425.16	27.75109	6.80611	−14.86852	9.12374	0.047	0.026
Isobutane	113.55	407.85	26.43866	7.48086	−14.19413	8.46077	0.084	0.053
Pentane	143.47	469.69	31.99268	10.49111	−21.12261	13.43919	0.025	0.015
Isopentane	113.25	460.43	32.44833	2.66071	−2.77906	−0.45275	0.016	0.008
Neopentane	256.58	433.75	18.71625	17.47940	−18.58812	6.55435	0.018	0.009
Hexane	177.83	507.50	34.68597	13.26302	−22.50859	13.05969	0.082	0.046
Heptane	182.55	540.30	58.10158	−72.53145	106.39644	−49.66728	0.078	0.036
Octane	216.37	568.80	44.12174	3.16533	−3.61431	2.89551	0.142	0.098
Nonane	244.63	594.60	44.00980	17.64311	−25.45160	14.35835	0.012	0.005
Decane	243.49	617.70	42.82884	8.62937	−5.02164	3.12349	0.077	0.038

the triple point and all the equations except the one-parameter Watson equation fail to extrapolate the value well to the triple point. We have found it necessary to provide even an approximate value at the triple point so that these equations behave normally. The enthalpy of vaporization varies almost linearly with temperature from the triple point to the normal boiling point as shown with respect to methanol in Fig. 4. In most cases we have determined the enthalpy of vaporization at the triple point by graphical extrapolation and used that value in the regression. Results obtained by such a procedure are shown in Table II for a number of alcohols. We have also recorded in Table II the coefficients obtained on the basis of Eq. (3) for a number of compounds for which the data extend from the triple point to the critical point. For 23 compounds listed in Table II, Eq. (3) is the best of all the equations. For methanol, methane, and butane, Eq. (4) gave better results than Eq. (3). The data for methanol, methane, ethane, propane, butane, isobutane, propylene, nitrogen, and carbon dioxide are taken from Refs. 4 and 9 to 16. Data for the rest of the compounds are from Mejer and Svoboda [8].

Table III. Values of the Constants of Eq. (5) for the Enthalpy of Vaporization of Some Alkanes

Alkane	T_m(K)	T_c(K)	a	b	c	SD[a]	Av. dev.[a]
Methane	90.68	190.555	1.80340	11.45176	−3.05190	0.013	0.008
Ethane	90.348	305.33	0.91214	21.00711	−5.95346	0.059	0.039
Propane	85.47	369.80	0.86882	27.05338	−4.54116	0.059	0.041
Butane	134.80	425.16	2.52146	32.44967	−11.02822	0.068	0.047
Pentane	143.47	469.69	2.73539	37.70081	−9.71302	0.063	0.038
Hexane	177.83	507.50	3.08617	42.72930	−9.41540	0.080	0.047
Heptane	182.55	540.30	−0.65134	49.32424	3.33555	0.105	0.057
Octane	216.37	568.80	1.19184	53.13713	0.64112	0.139	0.098
Nonane	244.63	594.60	6.83422	56.14841	−17.28324	0.010	0.004
Decane	243.49	617.70	−1.73127	62.07339	20.90878	0.079	0.050
Undecane	247.57	639.00	10.07226	64.18966	−23.82227		
Dodecane	263.57	658.20	−24.85976	78.22870	112.38073	0.015	0.006
Tridecane	267.76	676.00	0.502164	75.12087	20.02263	0.141	0.079
Tetradecane	279.01	691.90	−16.63561	84.44142	88.64433	0.212	0.136
Pentadecane	283.07	706.80	0.56176	83.98691	23.78540	0.162	0.098
Hexadecane	291.31	720.60	−6.90733	89.91776	58.03636	0.150	0.057
Heptadecane	295.13	733.30	−12.89250	95.49127	85.75110		
Octadecane	301.31	745.20	−17.68159	100.59545	109.12376		
Nonadecane	305.05	756.20	−24.24375	106.09238	141.43467		
Icosane	309.58	766.50	−29.33513	111.50464	165.75354		

[a] The standard deviation and the average deviation are not shown when the number of data points equaled the number of parameters.

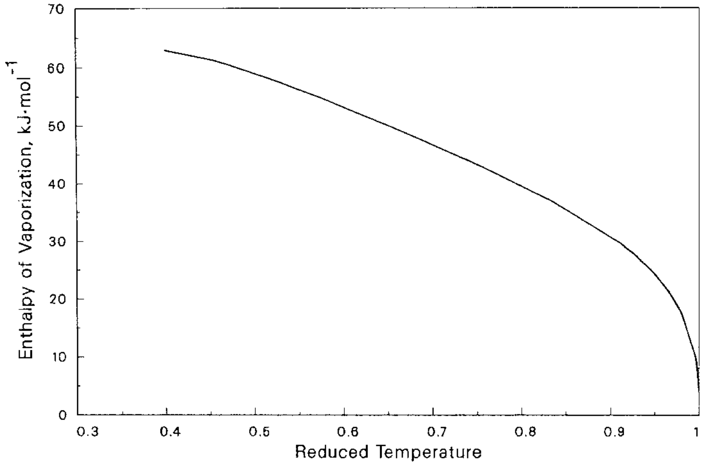

Fig. 5. Plot of enthalpy of vaporization of dodecane versus reduced temperature.

When the data are sparse as in the case of alkanes from undecane to icosane, we have taken the enthalpy of vaporization at the normal boiling point from Zwolinski and Wilhoit [17]. We have also resorted in such cases to the use of Eq. (5). The coefficients obtained by such a procedure are recorded in Table III. A typical plot illustrating the results of Eq. (5) with respect to dodecane is shown in Fig. 5.

When the experimental enthalpies of vaporization are very scarce, one may use the vapor pressure data to determine the enthalpies of vaporization using the Clapeyron equation.

$$\Delta H_v = RT^2(d\ln P/dT)/\Delta Z \tag{6}$$

where

$$\Delta Z = Z_v - Z_l \tag{7}$$

ΔZ is usually set equal to 1 at low pressures but may also be calculated using the Haggenmacher [7] relation,

$$Z_v - Z_l = (1 - P_r/T_r^3)^{\frac{1}{2}} \tag{8}$$

Thus one can obtain the enthalpies of vaporization at low pressures using Eq. (6). The enthalpy of vaporization at the critical temperature is zero. With this data set, one can then use Eq. (5) to determine the enthalpies of vaporization at other temperatures.

NOMENCLATURE

T_c = Critical temperature, K
T_t = Triple point, K
T_x = Any particular temperature, K
T_r = Reduced temperature
P_r = Reduced pressure
R = Gas constant
P = Vapor pressure
$X = (T_c - T)/T_c$
$Y = (T_c - T)/T$
$X_x = (T_c - T)/(T_c - T_x)$
$X_t = (T_c - T)/(T_c - T_t)$
ΔH_{vt} = Enthalpy of vaporization at the triple point, $kJ \cdot mol^{-1}$
ΔH_{vx} = Enthalpy of vaporization at any temperature x, $kJ \cdot mol^{-1}$
Z_v = Compressibilty factor of the saturated vapor
Z_l = Compressibilty factor of the saturated liquid
Relative deviation = $100[\Delta H_v(\text{obs}) - \Delta H_v(\text{cal})]/\Delta H_v(\text{obsd})$
Standard deviation = $\{\sum [\Delta H_v(\text{obs}) - \Delta H_v(\text{cal})]^2/(\text{No. points} - \text{No. parameters})\}^{0.5}$

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