On Latent Heat of Vaporization, Surface Tension, and Temperature

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A semitheoretical equation for latent heat of vaporization has been derived and tested. The average error in predicting the value at the normal boiling point in the case of about 90 compounds, which includes polar and nonpolar liquids, is about 1.8%. A relation between latent heat of vaporization and surface tension is also derived and is shown to lead to Watson's empirical relation which gives the change of latent heat of vaporization with temperature. This gives a physico-chemical justification for Watson's empirical relation and provides a rapid method of determining latent heats by measuring surface tension.

THE CHANGE of latent heat of vaporization with temperature has been a subject of many investigations. The exact method of evaluation using the rigorous Clausius-Clapeyron equation suffers from the disadvantage that the necessary data often are lacking. Several relations (*16, 24, 25, 28, 31*) for calculating the latent heat at a given temperature are available, but they need data such as compressibilities of vapor and liquid, the value of latent heat at a particular temperature, or the use of a reference substance.

Guggenheim (*15*) has shown that, in the region of temperature $T < 0.65\,T_c$, the vapor pressure–temperature variation follows the reaction

$$\ln P/P_c = A - BT_c/T \qquad (1)$$

with $A \cong B$ and equal 5.30. The relation was further tested and found valid, although A and B depend upon the class of substances investigated. Guggenheim also noted that $A \cong B$ (*15*). The values, for example, were 4.30 for alcohols, 2.92 for ethers, benzene, acetones, and 5.30 for spherical, nonpolar substances. However, the value of neither A nor B is needed for the present work.

PRESENT WORK

Differentiating Equation 1 gives

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} = \frac{BT_c}{T^2} \qquad (2)$$

Applying the relation $PV = Z\,RT$ for 1 mole of both the gas and the liquid phases, and rearranging, gives

$$(V_g - V_l) = (Z_g - Z_l)\frac{RT}{P} \qquad (3)$$

The quantity $(Z_g - Z_l)$ is a function of reduced pressure only, independent of the nature of the substances. The data(*16*) plotted as a function of $(1 - P_r)$ gave the relation

$$(Z_g - Z_l) = 0.95(1 - P_r)^{0.69} \qquad (4)$$

for $0.01 < P_r < 0.4$. Equations 2 and 1 give

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} = \frac{T_c}{T^2}\ln\frac{P}{P_c}\cdot\frac{1}{(1 - T_c/T)} \qquad (5)$$

The latent heat of vaporization at constant volume according to the Clausius-Clapeyron equation is given by

$$\lambda = T(\mathrm{d}P/\mathrm{d}T)(V_g - V_l) \qquad (6)$$

Substituting for $(V_g - V_l)$ from Equations 3 and 4, and using Equation 5 yields

$$\lambda = \frac{4.35T_c(1.0 - P_r)^{0.69}\log P_r}{(1 - 1/T_r)} \qquad (7)$$

Equation 7 is similar to the one derived by Meissner (*21*). Figure 1 shows $[\lambda\ (1 - 1/T_r)]/T_c$ plotted as a function of P_r and also experimental values for various substances. The experimental values are believed to fall within ± 5%. A calculation of λ values using Equation 7 at the normal boiling point indicated that the experimental and calculated values were in better agreement if the constant was changed from 4.35

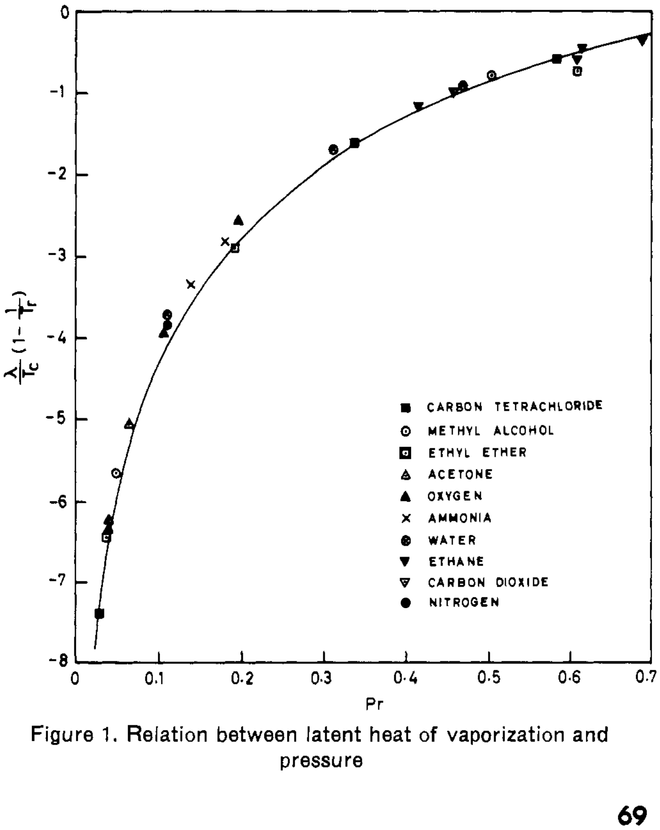

Figure 1. Relation between latent heat of vaporization and pressure

to 4.70. Table I shows λ values calculated using Equation 7 and a value of 4.7 for the constant. The average deviation of some 90 compounds tested is about 1.8%. The values are also compared with those calculated using Riedel's equation (*28*) and Giacalone's equation (*28*). The present relation is slightly superior to either Giacalone's relation or Riedel's relation and also correlates well substances such as ethylene. Experimental calorimetric values from primary sources are also listed in Table I along with the literature values from secondary sources. As the difference between these two values is negligible, the so-called literature values were used in calculating the per cent errors.

LATENT HEAT OF VAPORIZATION AND SURFACE TENSION

Latent heat of vaporization and surface tension are both surface phenomena and are defined by the relations

$$(\mathrm{d}P/\mathrm{d}T) = \frac{\lambda \rho_l \rho_g}{T(\rho_l - \rho_g)} \tag{8}$$

and

$$\gamma^{1/4} = \frac{[P](\rho_l - \rho_g)}{M} \tag{9}$$

Table I. Latent Heat of Vaporization at the

Substance	Literature Value	Experimental Value	% Error^{a}		
			1	2	3
		Inorganic			
Ammonia	5,580(*17*)		−1.2	−2.3	+1.6
Argon	1,590(*25*)	1,557.5(*6*)	−1.9		−1.9
Bromine	7,420(*17*)		+2.3		
Carbon disulfide	6,400(*17*)		−3.4	−4.9	−3.6
Carbon monoxide	1,444(*17*)	1,443.6(*4*)	−3.9		
Chlorine	4,880(*17*)	4,878.0(*9*)	−1.4	+1.2	−1.6
Hydrazine	9,637(*28*)		0.0	+2.7	−2.8
Hydrogen bromide	4,210(*17*)	4,210.0(*12*)	+2.6		
Hydrogen chloride	3,860(*17*)	3,860.0(*11*)	+1.0	−2.9	−1.5
Hydrogen iodide	4,720(*17*)	4,724.0(*13*)	+1.9	...	...
Hydrogen sulfide	4,460(*17*)	4,463.0(*7*)	+3.6	...	...
Neon	440(*25*)		−2.5	...	...
Nitric oxide	3,290(*17*)	3,292(*19*)	+1.5		
Nitrogen	1,330(*17*)		−5.2	...	...
Nitrous oxide	3,960(*17*)		−0.5		
Oxygen	1,630(*17*)	1,630.7(*6, 8*)	−4.3	...	...
Phosgene	5,830(*17*)		−3.3	−1.9	−1.2
Phosphine	3,490(*17*)	3,489.0(*30*)	−4.9	...	...
Sulfur dioxide	5,950(*17*)	5,960.0(*10*)	−1.0	−1.3	+1.3
Water	9,720(*17*)		−0.3	−3.7	+2.9
		Hydrocarbons			
Methane	1,960(*17*)	1,955.0(*17*)^{b}	−6.1	−1.5	−4.6
Ethylene	3,240(*17*)	3,237.0(*5*)	−4.0	+17.3	+11.7
Ethane	3,520(*17*)	3,514.0(*33*)	−4.5	...	...
Propene	4,400(*17*)	4,402.0(*27*)	−3.2	...	...
Isobutane	5,090(*17*)	5,089.0(*2*)	−3.3	...	...
n-Butane	5,350(*17*)	5,351.0(*3*)	−3.6	...	...
1-Butene	5,240(*17*)	5,239.0(*1*)^{c}	−4.0	−0.8	−2.5
n-Pentane	6,160(*17*)	6,262.0(*23*)	−2.6	...	...
Methyl cyclohexane	7,580(*17*)		−0.9	...	...
Benzene	7,350(*17*)	7,353 (*17*)^{b}	−0.8	+0.7	+0.7
Toluene	8,000(*17*)	8,000 (*17*)^{b}	−2.0	...	...
Hexane	6,921(*17*)		−2.6	...	...
n-Octane	8,343(*25*)	8,215 (*17*)^{b}	−1.3	...	...
o-Xylene	8,750(*24*)	8,800 (*24*)^{b}	−1.1	−0.6	−0.8
cis-2-Butene	5,580(*17*)		−4.8	...	...
n-Heptane	7,580(*17*)	7,660 (*26*)	−3.4	−0.9	−2.9
Cyclopentane	6,525(*17*)		−1.5	+0.4	−0.2
Cyclohexane	7,190(*17*)		−1.4	+1.0	−0.3
3-Methyl hexane	7,358(*28*)		−3.9	−1.2	−3.2
2,4-Dimethylpentane	7,050(*28*)		−2.3	−1.0	−3.3
2,2,3-Trimethylbutane	6,918(*28*)		−3.3	−0.8	−3.2
Methyl cyclopentane	7,002(*28*)		−0.6	+1.8	−0.7
trans-2-Butene	5,438(*28*)		−1.8	−0.5	−1.4
1,3-Butadiene	5,367(*28*)		−3.6	−2.9	−3.6
Ethyl benzene	8,599(*28*)		−1.7	−1.4	−1.5
m-Xylene	8,800(*25*)	8,700 (*24*)^{b}	0.0	+0.2	0.0
Naphthalene	10,240(*28*)		−0.8	−1.2	−1.3
Propane	4,490(*17*)	4,487.0(*20*)	−2.9	−0.4	−2.0

From Equations 8 and 9, noting that the logarithm of vapor pressure varies linearly with reciprocal absolute temperature, one derives the relation

$$\frac{\gamma^{1/4}}{\gamma_B{}^{1/4}} = \frac{\gamma}{\gamma_B}\frac{T}{T_B}\frac{P_B}{P}\frac{\rho_1\rho_g}{(\rho_1\rho_g)_B} \tag{10}$$

where B denotes the values at the boiling point. Assuming ideality of vapor and $\rho_1/\rho_{1B} \cong 1.0$, one derives the relation

$$\gamma/\gamma_B = (\gamma/\gamma_B)^4 \tag{11}$$

Figure 2 shows the validity of the relation $\gamma/\gamma_B = f(\gamma/\gamma_B)$ for compounds of different chemical nature. The values of surface tension were taken from the International Critical Tables (*18*). The values of γ_B were either read from a graph of surface tension *vs.* temperature or obtained from the relation $\gamma = \gamma_o\ (1 - T_r)\gamma$ after fitting the equation using the available experimental data. The exact relation from Figure 2 is

$$\gamma/\gamma_B = 1.02(\gamma/\gamma_B)^{3.16} \cong (\lambda/\lambda_B)^{3.16} \tag{12}$$

From the surface tension–temperature relation noted above, one can derive from Equation 11 that

$$\gamma/\gamma_B = \left(\frac{1 - T_r}{1 - T_{rB}}\right)^m = (\lambda/\lambda_B)^n \tag{13}$$

Boiling Point in Calories per Gram Mole

Substance	Literature Value	Experimental Value	% Error[a] 1	2	3
		Alcohols			
Methyl alcohol	8,430(*17*)		−3.8	−7.4	−1.5
Ethyl alcohol	9,220(*17*)		−0.2	...	...
Isopropyl alcohol	9,650(*17*)		+1.6	−2.8	+3.4
n-Propyl alcohol	9,890(*17*)		+3.0	+0.6	+5.7
Isobutyl alcohol	10,220(*25*)		0.0	...	...
		Hydrogenated Compounds			
Carbon tetrachloride	7,170(*17*)		−1.1	+0.8	+0.6
Methyl chloride	5,165(*25*)	5,147.0(*29*)[d] 5,138.0(*22*)	−1.6		
Chlorobenzene	8,736(*25*)		+1.0	+2.6	+2.5
Chloroform	7,400(*24*)		+1.3	+4.6	+5.0
Difluorodichloromethane	4,850(*17*)		−1.0	...	...
Methyl fluoride	4,230(*17*)		+1.9	...	...
Trichloromethane	7,020(*17*)		−2.6	...	...
Fluorobenzene	7,534(*28*)		−1.1	−0.6	−0.5
Bromobenzene	8,966(*28*)		−2.0	−0.6	−0.7
Iodobenzene	9,548(*28*)		−2.6	−1.6	−1.4
Ethyl bromide	6,349(*28*)		−6.3	−6.3	−5.0
		Esters			
Ethyl formate	7,191(*25*)		+0.1	...	...
Ethyl propionate	8,168(*25*)		+4.5	...	...
Methyl acetate	7,454(*25*)		+0.7	...	...
Methyl formate	6,738(*25*)		−0.1	+0.1	−1.9
Methyl isobutyrate	7,969(*25*)		+0.2	...	...
n-Propyl acetate	8,189(*25*)		+0.4	...	...
n-Propyl formate	7,756(*25*)		+0.5	...	...
Ethyl acetate	7,750(*24*)		+0.7	+1.0	+1.4
		Other Organic Compounds			
Acetaldehyde	6,500(*17*)		+3.1	...	...
Acetone	7,100(*17*)		−2.8	−1.0	0.0
Acetic acid	9,526(*28*)		+2.1	+1.7	+3.4
Ethyl ether	6,220(*17*)		−3.2	...	...
Ethylene oxide	6,100(*17*)		−2.0	...	...
Methyl amine	6,109(*24*)		−1.5	...	...
Ethyl amine	6,583(*25*)		+1.7	+1.9	+3.5
Methyl ether	5,141(*28*)		−1.6	−1.0	−0.6
Phenol	10,760(*28*)		−1.3	−4.5	−1.1
p-Cresol	11,250(*28*)		−2.4	−8.0	−3.0
Isobutyric acid	10,620(*28*)		−0.3	−3.0	+0.9
Diethyl amine	6,975(*28*)		−0.4	−0.1	−0.4
Triethyl amine	7,675(*28*)		+0.2	+0.7	−0.5
Aniline	10,360(*28*)		−1.7	−3.3	+0.6
Acetonitrile	7,500(*28*)		−3.4	−4.7	−3.3
Ethyl mercaptan	6,400(*28*)		−0.3	0.0	+0.3
Diethyl sulfide	7,591(*28*)		−1.4	−1.4	−1.6

[a] 1 refers to present correlation, 2 refers to Riedel's, and 3 to Giacalone's. The values according to Riedel's and Giacalone's method are taken from Tables IV–VI of Reid and Sherwood (*28*). % Error = 100 × (literature value − calculated value)/ literature value.

[b] Agrees with A.P.I. values.

[c] Corrected value from 5256.1 at 266.72° K. to boiling point.

[d] Calculated from vapor pressure values.

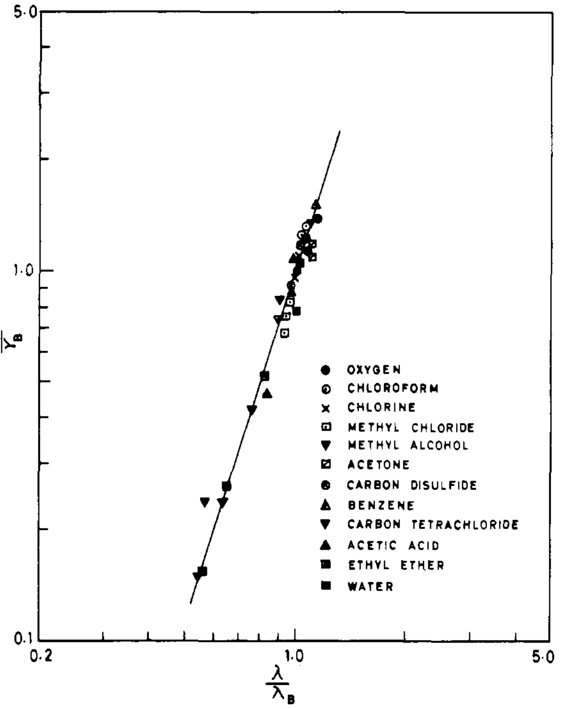

Figure 2. Surface tension–latent heat of vaporization

Table II. Calculated and Experimental Values of Surface Tension at Boiling Point

Compound	B^a Exptl.	B Calcd.	% Dev.
Ethyl ether	15.2	14.8	2.6
Benzene	21.2	20.8	1.9
Acetic acid	18.0	17.5	2.8
Chlorine	26.2	26.5	1.1
Oxygen	13.2	19.5	47.6
Water	58.9	54.0	8.3
Methyl alcohol	18.5	22.5	21.6

[a] Extrapolated or interpolated values using experimental data at other temperatures obtained from the International Critical Tables (*18*).

thus leading to the Watson's correlation (*32*). By using $n = 3.16$ from Equation 12, and $m = 1.2$ according to Guggenheim (*15*), one finds

$$\lambda/\lambda_B = \left(\frac{1 - T_r}{1 - T_{rB}}\right)^{0.37968} \cong \left(\frac{1 - T_r}{1 - T_{rB}}\right)^{0.38} \quad (14)$$

which is the empirical relation according to Watson (*32*).

Equation 12 shows that, if γ_B and λ_B are known, λ can be estimated from surface tension measurements. As noted earlier, λ_B can be evaluated using Equation 7. A reasonably good correlation (*14*) can be obtained for γ_B from Equation 9 by neglecting the vapor density, thus leading to

$$\gamma_B = \frac{[P]^4}{V_B^4} \quad (15)$$

Table II shows the validity of Equation 15. The parachor and molal volume values were calculated using the values given in the Chemical Engineers' Handbook (*25*).

The values of γ_B should be found by two measurements on surface tension. Surface tension measurements appear to provide a rapid way of finding latent heats of vaporization. The method is simple, rapid, and allows reasonable accuracy.

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NOMENCLATURE

A, B = constants in Equation 1
m, n = constants in Equation 13
P = vapor pressure
P_r = reduced vapor pressure, P/P_c
R = universal gas constants, cal./gram mole ° K.
T = temperature, ° K.
T_r = reduced temperature, T/T_c
V = volume
Z = compressibility factor
γ = surface tension, dynes/cm.
λ = molal latent heat of vaporization, cal./gram mole
ρ = density
$[P]$ = Sugden parachor

Subscripts

B = boiling point
C = critical point
g = gas
l = liquid

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