Latent Heats of Vaporization of Hydrocarbons

MICHAEL L. BRADFORD and GEORGE THODOS
Northwestern University, Evanston, Ill.

Latent heats of vaporization for different types of hydrocarbons were calculated using the rigorous Clapeyron equation, the Frost-Kalkwarf vapor pressure relationship, and experimental saturated vapor and liquid densities obtained from the literature. The calculated values ranged in temperature up to and including the critical point and were used to develop the relationship, $\lambda = \lambda_0\,[1 - T_R]^{0.39}$ where λ_0 is a constant for each hydrocarbon and represents the hypothetical latent heat of vaporization at $T = 0°$ K. For the hydrocarbons investigated, λ_0 depended on molecular weight as follows: $\lambda_0 = 800\,M^{0.72}$ where λ_0 has the units B.t.u. per pound-mole. These relationships were used to calculate latent heats of vaporization, which, when compared with values obtained from the Clapeyron equation, produced an average deviation of 2.6% for 184 values representing 23 hydrocarbons. Values were also calculated and compared with calorimetric measurements presented in the literature for several hydrocarbons to produce an average deviation of 3.0% for 58 values representing nine hydrocarbons. Values for four of these hydrocarbons were not used in the development of the relationships of this study.

A NUMBER of methods are presented in the literature for the calculation of the latent heats of vaporization of substances in their saturated liquid state. In 1923, Kistiakowsky (*7*) presented the relationship

$$\lambda_b = T_b[8.75 + 4.576 \log T_b] \tag{1}$$

which permits the calculation of the latent heat of vaporization of nonpolar substances at their normal boiling point. Another relationship for establishing this value was proposed in 1954 by Riedel (*15*):

$$\lambda_b = T_b\,\frac{5 \log P_c - 2.17}{0.930 - T_b/T_c} \tag{2}$$

To predict heats of vaporization for temperatures below the normal boiling point, Othmer (*13*) utilizes water as a reference substance and presents the following relationship:

$$\frac{\lambda}{\lambda_w} = \frac{\log \dfrac{p_2}{p_1}}{\log \dfrac{p_{w_2}}{p_{w_1}}}\,\frac{\Delta z}{\Delta z_w} \tag{3}$$

where $\Delta z = z_v - z_l = [1 - P_R/T_R^3]^{1/2}$. To cover the entire temperature range up to the critical point, Watson (*20*) proposed the relationship

$$\frac{\lambda}{\lambda'} = \left[\frac{1 - T_R}{1 - T_R'}\right]^{0.38} \tag{4}$$

where λ' is the latent heat of vaporization at T_R'. Equation 4 has the advantage over Equation 3 in that it does not require any vapor pressure data but does require a knowledge of a single latent heat of vaporization value. This value can be readily obtained through the use of Equation 1 or 2. Although the use of Equations 1 and 4 allows the calculation of latent heats of vaporization, a single relationship capable of predicting these values directly would be advantageous.

LATENT HEATS OF VAPORIZATION

To obtain latent heats of vaporization over a wide range of temperatures, the thermodynamically exact Clapeyron relationship

$$\frac{dP}{dT} = \frac{\lambda}{T(v_v - v_l)} \tag{5}$$

can be applied using vapor pressure data and saturated vapor and liquid densities. In order to express λ in terms of reduced variables, Equation 5 has been transformed to the following:

$$\lambda = z_c R T_c T_R [v_{R_v} - v_{R_l}]\,\frac{dP_R}{dT_R} \tag{6}$$

In this investigation the vapor pressure equation of Frost and Kalkwarf (*4*) has been used in reduced form to obtain the slopes, dP_R/dT_R, for temperatures ranging from the triple point to the critical point of a number of hydrocarbons including normal paraffins, olefins, diolefins, naphthenes, and aromatics. This reduced vapor pressure equation can be expressed as follows:

$$\ln P_R = \alpha + \frac{\beta}{T_R} + \gamma \ln T_R + \frac{27}{64}\,\frac{P_R}{T_R^2} \tag{7}$$

Equation 7 possesses the unique boundary condition that $\alpha + \beta + 27/64 = 0$. Upon differentiation, Equation 7 produces the slope in reduced variables as follows:

$$\frac{dP_R}{dT_R} = \frac{\dfrac{1}{T_R}\left[\gamma - \dfrac{\beta}{T_R} - \dfrac{54}{64}\,\dfrac{P_R}{T_R^2}\right]}{\dfrac{1}{P_R} - \dfrac{27}{64}\,\dfrac{1}{T_R^2}} \tag{8}$$

Values of β and γ for the hydrocarbons considered in this investigation were obtained from the vapor pressure studies

Table I. Basic Constants for the Calculation of Latent Heats of Vaporization and the Resulting Deviations

		Critical Constants				Vapor Pressure Constants			
	M	z_c	T_c, ° K.	P_c, atm.	ρ_c, g./cc.	β	γ	λ_0, B.t.u./ Lb.-Mole	λ, Av. Dev. %
n-Paraffins									
Methane	16.04	0.289	191.1	45.8	0.162	−6.84018	−2.70212	5,400	3.93
Ethane	30.07	0.284	305.4	48.20	0.205	−8.07324	−3.60963	9,400	1.85
Propane	44.09	0.279	370.0	42.0	0.220	−8.88467	−4.24329	12,100	1.39
n-Butane	58.12	0.274	425.4	37.43	0.228	−9.57174	−4.80311	14,650	1.08
n-Pentane	72.15	0.269	469.8	33.31	0.232	−10.28884	−5.33564	16,900	2.23
n-Hexane	86.17	0.264	507.9	29.94	0.233	−11.01386	−5.90492	19,250	1.97
n-Heptane	100.20	0.260	540.6	26.95	0.235	−11.72872	−6.46159	21,600	1.07
n-Octane	114.22	0.255	569.4	24.64	0.233	−12.53570	−7.15220	22,700	5.27
n-Nonane	128.25	0.250	593.8	23.25	0.234	−13.18787	−7.59158	25,750	2.34
n-Decane	142.28	0.245	616.1	21.65	0.234	−13.95281	−8.21951	28,000	1.18
n-Undecane	156.30	0.240	636.0	20.27	0.233	−14.80003	−8.98351	30,200	0.83
n-Dodecane	170.33	0.235	653.9	19.06	0.232	−15.72640	−9.80767	32,800	2.53
Olefins									
Ethylene	28.05	0.284	283.1	50.5	0.215	−11.74860	−3.75709	8,600	4.85
Propylene	42.08	0.275	365.0	45.6	0.233	−9.99865	−4.26637	11,800	1.70
Diolefins									
1,3-Butadiene	54.09	0.270	425.2	42.7	0.245	−9.48450	−4.71334	14,400	2.82
Naphthenes									
Cyclohexane	84.16	0.272	553.0	40.0	0.273	−10.04415	−5.26151	19,350	0.64
Aromatics									
Benzene	78.11	0.270	562.2	48.60	0.304	−10.06536	−5.28840	19,350	5.92
Toluene	92.13	0.271	593.5	41.56	0.290	−10.44129	−5.45371	21,200	2.86
Ethylbenzene	106.16	0.266	616.1	36.51	0.288	−11.18362	−6.05908	23,100	2.72
o-Xylene	106.16	0.268	632.1	36.83	0.281	−11.07859	−5.94175	23,100	3.01
m-Xylene	106.16	0.268	625.1	35.91	0.277	−11.04194	−5.91474	23,100	3.01
p-Xylene	106.16	0.268	618.2	35.01	0.273	−11.09776	5.89868	23,100	3.30
n-Propylbenzene	120.19	0.262	638.8	32.0	0.28	−11.62240	−6.36370	24,700	2.63

of the saturated (*18*), unsaturated (*17*), naphthenic (*14*), and aromatic (*1*) hydrocarbons. These values with the critical constants of these hydrocarbons are summarized in Table I. The critical constants presented in Table I were obtained from the compilation of Kobe and Lynn (*8*) or were estimated by a group contribution method (*19*).

The use of Equations 7 and 8 at a fixed temperature T_R permits the calculation of dP_R/dT_R. The molar volumes of the saturated vapor and liquid states reported by Bradford (*2*) were used in Equation 6 to obtain values of λ ranging from the triple point to the critical temperature of each hydrocarbon. The resulting values of λ were related to the variable $1 - T_R$ on log-log coordinates to produce for each hydrocarbon the essentially linear relationships presented in Figure 1. These relationships are nearly parallel and have slopes of 0.39. This slope is in close agreement

Table II. Comparison of Latent Heats of Vaporization for *n*-Heptane Calculated with Clapeyron Equation and Equations 9 and 10

	λ, B.t.u./Lb.-Mole		
T_R	Clapeyron	Eq. 9, 10	Deviations, %
0.650	14,300	14,475	−1.23
0.700	13,400	13,631	−1.73
0.750	12,580	12,695	−0.92
0.800	11,460	11,637	−1.55
0.825	10,930	11,046	−1.07
0.850	10,290	10,402	−1.09
0.875	9,623	9,688	−0.68
0.900	8,802	8,880	−0.90
0.925	7,823	7,938	−1.48
0.950	6,718	6,777	−0.88
0.975	5,106	5,171	−1.29
1.000	0	0	0.00
			1.07

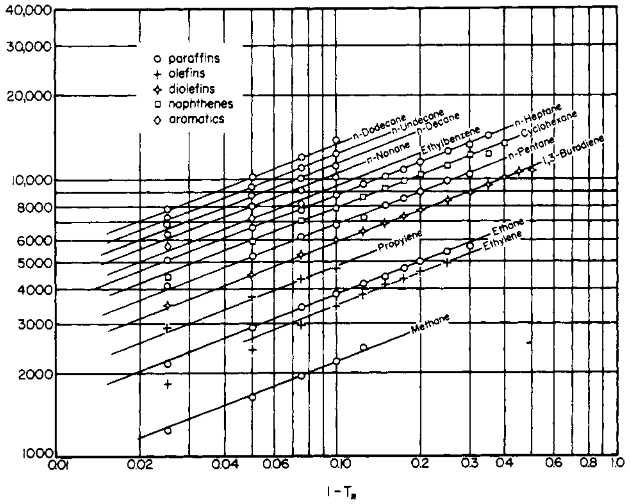

Figure 1. Linear relationships between log λ and log $(1 - T_R)$ for some of the hydrocarbons investigated

with the value of 0.38 reported by Watson (*20*). The straight lines of Figure 1 suggest a relationship of the form

$$\lambda = \lambda_0[1 - T_R]^{0.39} \tag{9}$$

where λ_0 is a hypothetical latent heat of vaporization at $T = 0°$ K. Values of λ_0 were obtained from Figure 1, are summarized in Table I, and are plotted against molecular weight in Figure 2 to produce the analytical expression

$$\lambda_0 = 800\, M^{0.72} \tag{10}$$

Equation 10 represents the behavior of hydrocarbons of all types including *n*-paraffins above methane, olefins, diolefins, naphthenes, and aromatics.

Equations 9 and 10 have been developed from basic physical data for hydrocarbons, and thus, their application should not be extended to other types of substances. Further work in this area should be carried out before any generalizations can be drawn.

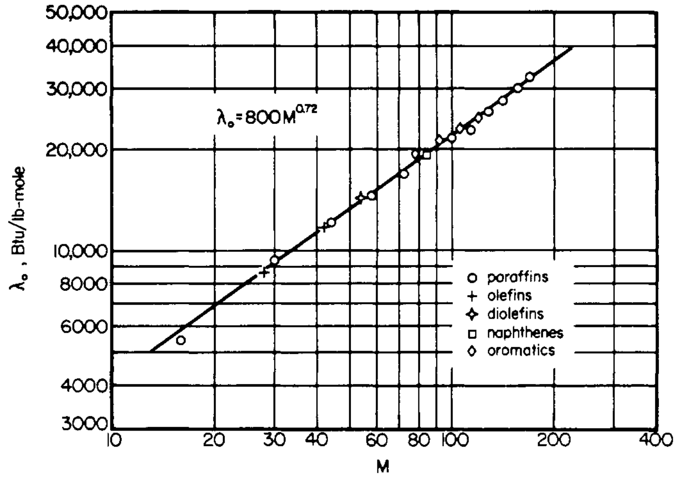

Figure 2. Linear relationship between log λ_0 and log *M* for the hydrocarbons investigated

Table III. Calculated and Experimental Latent Heats of Vaporization for Several Hydrocarbons

	λ, B.t.u./Lb.-Mole		
T, ° K.	Exptl.	Calcd.	Deviation, %
1-Butene (*9*); T_c = 419.6° K.			
311.0	8350	8590	−2.87
327.6	7857	8052	−2.48
344.3	7295	7455	−2.19
361.0	6593	6756	−2.47
377.6	5806	5926	−2.07
			2.42
2-Butene (*6*); T_c = 430.0° K.			
311.0	8834	8819	0.18
327.6	8368	8317	0.60
344.3	7815	7764	0.65
361.0	7230	7141	1.02
377.6	6478	6418	0.92
394.3	5483	5539	−1.02
			0.77
1-Pentene (*16*); T_c = 474° K.			
284.0	11,291	11,949	−5.83
298.2	10,958	11,593	−5.80
303.1	10,840	11,464	−5.76
			5.79
2-Methyl-2-butene (*16*); T_c = 470.0° K.			
289.9	11,835	11,740	0.80
298.2	11,642	11,527	0.99
311.7	11,317	11,163	1.36
			1.05
n-Pentane (*11*); T_c = 469.8° K.			
311.0	11,066	11,413	−3.14
327.6	10,595	10,930	−3.16
344.3	10,100	10,411	−3.08
361.0	9,584	9,848	−2.75
377.6	8,982	9,241	−2.78
394.3	8,316	8,540	−2.70
411.0	7,537	7,749	−2.81
444.3	6,571	6,805	−3.55
			3.00
Cyclohexane (*10*); T_c = 553.0° K.			
311.0	13,832	14,100	−1.94
327.6	13,462	13,713	−1.87
344.3	13,076	13,309	−1.78
361.0	12,585	12,883	−2.37
377.6	12,215	12,436	−1.81
394.3	11,721	11,960	−2.04
411.0	11,263	11,454	−1.70
444.3	10,673	10,909	−2.21
			1.96
n-Hexane (*5*); T_c = 507.9° K.			
311.0	13,191	13,681	−3.71
327.6	12,731	13,217	−3.82
344.3	12,315	12,727	−3.34
361.0	11,777	12,205	−3.63
377.6	11,262	11,644	−3.39
394.3	10,679	11,039	−3.37
411.0	10,067	10,377	−3.08
427.6	9,343	9,641	−3.19
444.3	8,535	8,805	−3.17
			3.41
n-Octane (*12*); T_c = 569.4° K			
311.0	17,456	17,820	−2.09
327.6	16,981	17,363	−2.25
344.3	16,415	16,885	−2.87
361.0	15,858	16,388	−3.34
377.6	15,368	15,863	−3.22
394.3	14,749	15,310	−3.81
411.0	14,361	14,726	−2.54
427.6	13,693	14,101	−2.98
444.3	13,029	13,429	−3.07
			2.91
n-Decane (*3*); T_c = 616.1° K.			
344.3	20,505	20,420	−2.13
361.0	19,933	20,138	−1.56
377.6	19,313	19,616	−1.57
394.3	18,775	19,068	−1.03
411.0	18,112	18,497	−0.67
427.6	17,426	17,895	−2.69
444.3	16,890	17,259	−2.19
			1.69

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES

Equations 9 and 10 were used to calculate latent heats of vaporization for the hydrocarbons used to develop these relationships. These calculated values were compared with the ones from the Clapeyron equation to obtain for each hydrocarbon the average deviation presented in Table I. Maximum deviations are encountered with ethylene, benzene, and *n*-octane, while minimum deviations occur with cyclohexane, *n*-heptane, and *n*-undecane. For *n*-heptane, the deviations are presented in Table II for the temperature range $0.65 \leqq T_R \leqq 1.00$. The average deviation for *n*-heptane was 1.07% and the over-all average deviation for the 23 hydrocarbons used in this study was 2.6%.

Calorimetric measurements presented in the literature for a number of hydrocarbons were compared with corresponding values obtained from Equations 9 and 10. Table III presents calculated and experimental latent heats of vaporization for nine hydrocarbons along with their resulting deviations. *n*-Pentane, cyclohexane, *n*-hexane, *n*-octane, and *n*-decane were five of the 23 original hydrocarbons used for the development of Equations 9 and 10. The average deviations for these five hydrocarbons ranged from 1.69% for *n*-decane to 3.41% for *n*-hexane. The remaining four hydrocarbons were butenes and pentenes which were not included in the development of the basic relationships. The average deviation for the nine hydrocarbons was 3.0%.

NOMENCLATURE

M = molecular weight
p = vapor pressure
P = pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
R = gas constant, 82.055 atm. cc./g.-mole ° K.
T = temperature, ° K.
T = normal boiling point, ° K.
T_c = critical temperature, ° K.
T_R = reduced temperature, T/T_c
v = molar volume, cc./g.-mole
v_c = critical volume, cc./g.-mole
v_l = molar volume for saturated liquid, cc./g.-mole
v_v = molar volume for saturated vapor, cc./g.-mole
v_{R_l} = reduced volume for saturated liquid state, v_l/v_c
v_{R_v} = reduced volume for saturated vapor state, v_v/v_c
z_c = critical compressibility factor, $P_c v_c/RT_c$
z_v = compressibility factor for saturated vapor, Pv/RT
z_l = compressibility factor for saturated liquid, Pv/RT

Greek Letters

α,β,γ = constants, Equation 7
λ = latent heat of vaporization, B.t.u./lb.-mole
λ_b = latent heat of vaporization at the normal boiling point, cal./g.-mole
λ_0 = hypothetical latent heat of vaporization at 0° K., B.t.u./lb.-mole
λ_w = latent heat of vaporization of water, Equation 3
ρ_c = critical density, g./cc.

Subscript

w = water

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