The Variation of Latent Heat with Temperature

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The Nutting equation for latent heat, $L = k\,(T_c - T)^n$, has been fitted to 44 substances. The average value of the exponent n was 0.378. This compares well with the 0.38 proposed for n by Watson in 1931. Values of n ranged from 0.237 for p-hydrogen to 0.389 for acetaldehyde. Tables of acentric factors and solubility parameters for these substances are also presented.

THE PROBLEM of predicting latent heats from a minimum of data has long been with us. The estimation of latent heat at a temperature different from an experimental point has been done by the empirical Watson (*58*) relation:

$$L_1 = L_2 \left(\frac{T_c - T_1}{T_c - T_2}\right)^{0.38} \qquad (1)$$

Equation 1 can be rearranged to a form:

$$L(T) = k(T_c - T)^n \qquad (2)$$

where k is a constant dependent upon the material and n is an exponent.

Various authors have examined this form and provided sets of constants. This form was first proposed by Thiesen (*56*) in 1897 with a universal exponent of $\frac{1}{3}$. Bowden (*4*), DeWijs (*8*), Jones and Bowden (*36*), Kendall (*39*), Nutting (*46*), Wilson, Silverberg, and Zellner (*60*), and Winter (*61*) have fitted various materials to this equation. Their results will be compared with results of the current study below.

The 0.38 value of the exponent was tested for 33 hydrocarbons by Thompson and Braun (*57*) and was reasonably good but slightly biased (about 1%) so that the calculated values were higher then the data. No attempt was made to fit better exponents to the data points.

This paper presents new calculated values of k and n for 44 materials and also tables of other properties with which n failed to correlate. The data were fitted to Equation 2 by a least squares routine on a digital computer.

DISCUSSION

Table I presents values taken from the literature, and where possible compares results from this study. It shows the divergence of opinion on the proper value of n. General exponents to be used for all compounds were proposed as follows by various authors: Bowden (*4*), n = 0.4; Jones and Bowden (*36*), n = 0.3889; Kendall (*39*), n = 0.386; Winter (*61*), n = 0.4; and Watson (*58*), n = 0.38. These also do not agree.

The authors of this paper believe that the values of n they have calculated are the most accurate since they are based on the most recent values for the substances studied and a machine procedure unavailable to earlier researchers. For many materials reported in Table I, neither the error or the data source are known, leaving the validity of the reported exponent seriously in doubt.

Table II gives the results of this study for 44 compounds. Also given are values of the constant k, as its logarithm (base 10) for easy computation; the critical temperature; the correlation error; the number of points fitted; the temperature range covered; and the literature source. The units of latent heat are expressed as B.t.u. per pound and temperature as degrees Rankine. Sample deviations of the data points from this simple equation are shown in Figure 1. The average value of n for all 44 substances is 0.378. The data input was from tables of thermodynamic functions and raw experimental points.

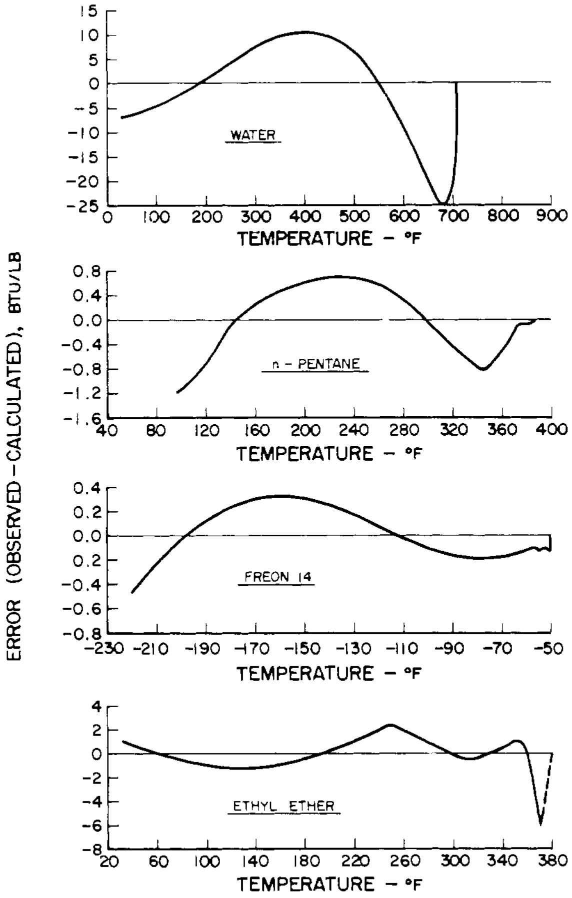

Figure 1. Sample deviation plots

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Table I. Comparative Values of Latent Heat Exponents

Compound	n	Reference	Compound	n	Reference
Ammonia	0.33301	(*36*)	n-Hexane	0.42461	(*36*)
	0.396	[a]		0.4	(*61*)
Argon	0.366	(*60*)		0.386	[a]
	0.370	[a]	n-Heptane	0.38293	(*36*)
Carbon dioxide	0.45251	(*36*)		0.4	(*61*)
	0.424	(*46*)	n-Octane	0.39095	(*36*)
	0.392	[a]		0.386	(*39*)
Carbon disulfide	0.40395	(*36*)		0.4	(*61*)
	0.395	[a]	2,3-Dimethylbutane	0.394	(*8*)
Carbon tetrachloride	0.37929	(*36*)		0.40198	(*36*)
	0.386	(*39*)	Isopentane	0.40035	(*36*)
	0.379	(*46*)		0.4	(*61*)
	0.4	(*61*)	Benzene	0.394	(*8*)
Nitrogen	0.355	(*60*)		0.38288	(*36*)
Oxygen	0.385	(*60*)		0.383	[a]
Sulfur dioxide	0.38327	(*36*)	Fluorobenzene	0.38989	(*36*)
	0.64	(*46*)		0.386	(*39*)
	0.399	[a]	Methyl acetate	0.40595	(*36*)
Stannic chloride	0.39882	(*36*)		0.4	(*61*)
	0.4	(*61*)	Ethyl acetate	0.421	(*8*)
Water	0.376	(*8*)		0.40744	(*36*)
	0.31820	(*36*)		0.4	(*61*)
	0.33357	(*46*)	Propyl acetate	0.40092	(*36*)
	0.360	[a]		0.4	(*61*)
Ethyl ether	0.3969	(*36*)	Methyl formate	0.41767	(*36*)
	0.4	(*61*)		0.4	(*61*)
	0.367	[a]	Ethyl formate	0.41493	(*36*)
Methanol	0.391	(*8*)		0.4	(*61*)
	0.38256	(*36*)	Propyl formate	0.39388	(*36*)
	0.4	(*61*)		0.4	(*61*)
	0.366	[a]	Methyl propionate	0.42452	(*36*)
Ethanol	0.40254	(*36*)		0.4	(*61*)
	0.36	(*46*)	Ethyl propionate	0.40234	(*36*)
	0.4	(*61*)		0.4	(*61*)
n-Pentane	0.40	(*8*)	Methyl butyrate	0.38950	(*36*)
	0.40035	(*36*)		0.386	(*39*)
	0.4	(*61*)		0.4	(*61*)
	0.383	[a]	Methyl isobutyrate	0.40460	(*36*)
				0.4	(*61*)

[a] This work, see Table II.

Table II. Calculated Values of Latent Heat Parameters

Compound	$\log_{10} k$	n	T_c, °R	T_R Range of Data Points	No. of Points	Latent Heat RMS Error	References
Acetaldehyde	0.91953	0.589	830.0	0.748–0.916	8	0.85	(*7, 33*)
Acetylene	1.68641	0.314	555.7	0.624–0.996	14	19.72	(*10*)
Ammonis	1.79055	0.396	730.1	0.480–0.985	22	7.21	(*9*)
Argon	1.08667	0.370	271.6	0.572–0.987	19	0.37	(*32*)
Benzene	1.23127	0.383	1012.8	0.533–0.997	47	0.75	(*48*)
1,3-Butadiene	1.34070	0.372	765.3	0.387–0.978	296	0.50	(*43*)
n-Butane	1.30141	0.378	765.3	0.601–0.999	62	1.28	(*33, 34*)
Carbon dioxide	1.31434	0.392	547.5	0.710–0.995	19	0.57	(*9*)
Carbon disulfide	1.14967	0.395	983.1	0.502–0.980	26	0.92	(*47*)
Carbon monoxide	1.82125	0.377	239.1	0.511–0.974	25	0.71	(*9*)
Chlorine	1.45010	0.259	718.9	0.585–0.988	14	3.25	(*11, 33*)
Ethane	1.47889	0.361	549.8	0.437–0.992	55	1.17	(*1*)
Ethyl ether	1.29104	0.367	840.2	0.586–0.988	35	1.49	(*51*)
Ethylene	1.42256	0.386	509.5	0.369–0.980	18	1.99	(*62*)
Ethylene oxide	1.20514	0.466	837.3	0.693–0.908	10	2.66	(*33, 44*)
Freon 11	0.97346	0.369	848.1	0.425–0.709	46	0.59	(*12, 13, 14*)
Freon 12	0.92274	0.386	693.3	0.445–0.999	385	0.42	(*15, 16*)
Freon 13	0.94353	0.375	540.6	0.481–0.999	34	0.33	(*17*)
Freon 13Bl	0.84984	0.365	612.3	0.490–0.999	313	0.33	(*18*)
Freon 14	0.95926	0.372	409.5	0.562–0.999	180	0.25	(*19*)
Freon 21	1.07794	0.378	813.0	0.517–0.762	102	0.11	(*2*)
Freon 22	1.07584	0.388	664.5	0.459–0.932	157	0.33	(*20, 21*)
Freon 113	0.80433	0.401	877.1	0.490–0.993	112	0.75	(*22, 23*)
Freon 114	0.84736	0.384	753.9	0.504–0.997	189	0.54	(*3, 24, 25*)
Freon 115	0.87985	0.366	635.6	0.702–0.992	36	0.53	(*26*)
Freon 116	0.99602	0.310	534.5	0.658–0.955	7	1.45	(*28, 29*)
Freon C318	0.77427	0.397	699.3	0.600–0.972	14	0.40	(*29, 30*)
Freon 502	0.79610	0.456	653.8	0.551–0.947	261	0.77	(*27*)

(*Continued on page 365*)

Table II. Calculated Values of Latent Heat Parameters *(Continued)*

Compound	$\log_{10} k$	n	T_c, °R	T_R Range of Data Points	No. of Points	Latent Heat RMS Error	References
n-Hexane	1.20203	0.385	914.3	0.558–0.888	31	0.22	(*33, 35*)
Hydrogen (*para*)	1.94813	0.237	59.37	0.394–0.949	21	6.78	(*31, 43*)
Hydrogen chloride	1.37362	0.383	584.2	0.582–0.959	12	2.35	(*11, 33*)
Hydrogen sulfide	1.46219	0.374	672.6	0.569–0.968	27	1.83	(*59*)
Isobutane	1.22322	0.403	734.3	0.600–0.994	59	1.03	(*33, 34*)
Methane	1.59688	0.347	343.9	0.523–0.988	33	1.96	(*42*)
Methanol	1.75706	0.366	923.7	0.531–0.998	44	5.64	(*52*)
Methyl chloride	1.38799	0.356	739.0	0.568–0.852	27	0.25	(*55*)
Neon	1.03396	0.363	79.9	0.563–0.992	20	0.66	(*41*)
Nitrogen	1.24393	0.355	226.9	0.500–0.999	72	0.79	(*60*)
Oxygen	1.17016	0.385	278.6	0.301–0.535	22	2.41	(*60*)
n-Pentane	1.24662	0.383	845.6	0.658–0.994	30	0.58	(*5*)
Propane	1.34523	0.384	666.0	0.503–0.975	18	0.18	(*10*)
Propylene	1.35202	0.386	656.8	0.617–0.990	26	1.28	(*6*)
Sulfur dioxide	1.23686	0.399	775.1	0.465–0.997	79	1.99	(*50*)
Water	2.02128	0.358	1165.1	0.422–0.999	332	7.59	(*38*)

Table III. New Calculated Acentric Factors and Solubility Factors

Compound	ω	$\delta \left(\frac{\text{B.T.U.}}{\text{Cu. Ft.}}\right)^{1/2}$	References
Acetaldehyde	No data	103.9	(*7, 33*)
Acetylene	0.196	192^a	(*10*)
Ammonia	0.252	151.0	(*9*)
Argon	−0.013	73.6	(*32*)
Benzene	0.215	88.3	(*48*)
1,3-Butadiene	0.184	80.2	(*43*)
n-Butane	0.201	74.4	(*33, 34*)
Carbon dioxide	0.225	98.6^a	(*9*)
Carbon disulfide	0.149	102.5	(*47*)
Carbon monoxide	0.034	63.7	(*9*)
Chlorine	0.235	149.3	(*33, 54*)
Ethane	0.105	80.1	(*1*)
Ethyl ether	0.286	78.8	(*51*)
Ethylene	0.099	81.3	(*62*)
Ethylene oxide	No data	112.2	(*33, 44*)
Freon 11	0.185	80.8	(*12, 13, 14*)
Freon 12	0.176	77.0	(*15, 16*)
Freon 13	0.194	73.8	(*17*)
Freon 13Bl	0.172	73.8	(*18*)
Freon 14	0.177	72.5	(*19*)
Freon 21	0.204	91.0	(*2*)
Freon 22	0.190	89.4	(*20, 21*)
Freon 113	0.254	73.2	(*22, 23*)
Freon 114	0.250	71.0	(*3, 24, 25*)
Freon 115	0.256	68.6	(*26*)
Freon 116	0.240	No data	(*29*)
Freon C318	0.361	65	(*29*)
Freon 502	0.147	80.7	(*27*)
n-Hexane	0.311	66.5	(*33, 37, 53*)
Para-hydrogen	−0.217	26.6	(*31, 45*)
Hydrogen chloride	0.136	113.0	(*33, 54*)
Hydrogen sulfide	0.100	110.6	(*59*)
Isobutane	0.192	72.9	(*33, 34*)
Methane	0.013	71.9	(*42*)
Methanol	0.162	142.6	(*52*)
Methyl chloride	0.221	104.2	(*55*)
Neon	−0.027	49.3	(*41*)
Nitrogen	0.031	61.9	(*60*)
Oxygen	0.017	76.2	(*60*)
n-Pentane	0.258	74.0	(*5*)
Propane	0.147	132.7	(*10*)
Propylene	0.144	80.5	(*6*)
Sulfur dioxide	0.254	118.4	(*50*)
Water	0.348	231.5	(*38*)

[a] At triple point.

Table IV. Acentric Factors Calculated by Various Authors

Compound	This Work	Lu (*40*)	Pitzer (*49*)	Thompson and Braun (*57*)
Ammonia	0.252	. . .	0.250	. . .
Argon	−0.013	. . .	−0.002	. . .
Benzene	0.215	. . .	0.215	. . .
1,3-Butadiene	0.184	. . .	. . .	0.190
n-Butane	0.201	0.210	0.201	. . .
Carbon dioxide	0.225	. . .	0.225	. . .
Carbon disulfide	0.149	0.115	. . .	. . .
Chlorine	0.235	0.047	. . .	. . .
Ethane	0.105	. . .	0.105	. . .
Ethyl ether	0.286	0.266	. . .	. . .
Ethylene	0.099	0.075	. . .	0.095
Freon 11	0.185	0.216	. . .	. . .
Freon 12	0.176	0.160	. . .	. . .
n-Hexane	0.311	. . .	. . .	0.290
Hydrogen sulfide	0.100	0.108	. . .	. . .
Isobutane	0.192	0.184	. . .	0.192
Methane	0.013	. . .	0.013	. . .
Methanol	0.162	0.560	. . .	. . .
Methyl chloride	0.221	0.144	. . .	. . .
Nitrogen	0.031	0.040	0.040	. . .
n-Pentane	0.258	0.252	0.252	0.252
Propane	0.147	0.152	0.152	. . .
Propylene	0.144	0.126	. . .	0.143
Water	0.348	. . .	0.398	. . .

It was thought that the exponent n might be expressible as a function of a thermodynamic variable. The values of n were graphically plotted against the following quantities: T_c (critical temperature), P_c (critical pressure), ω (Pitzer's acentric factor), δ (Hildebrand's solubility factor at the normal boiling point), ωT_c, $\omega T_c/P_c$, T_c/P_c, and liquid molar volume at the normal boiling point. For these ordinates no trend, except scatter around a constant value of 0.378, was found.

For most of these substances, the acentric factor and the solubility factor have not been evaluated previously. Therefore in this paper, values of these two quantities will be presented as Table III. All acentric factors were calculated from the definition:

$$\omega = -\log P_R - 1 \text{ at } T_R = 0.7 \tag{3}$$

The vapor pressure was interpolated directly from tabular data and was not estimated by any method. The solubility factor was calculated at the normal boiling point from the definition:

$$\delta = \left(\frac{L - RT}{V_{\text{liq}}}\right)^{1/2} \tag{4}$$

where V_{liq} is the liquid volume.

The values calculated by the authors agree well with those of Thompson and Braun (*57*) and of Pitzer (*49*) but are not often in agreement with Lu (*40*) as shown in Table IV. This is not surprising because, as Thompson and Braun have shown, methods of approximating the acentric factor do not always match the value calculated from the definition.

The exponents of $T_c - T$ do not correlate well because this simple formula is not exact. As can be seen from the figures, the latent heat varies in a manner slightly more complicated than $(T_c - T)^n$.

CONCLUSION

The latent heat equation $L = k\,(T_c - T)^n$ has been fitted for 44 substances with an average value of n of 0.378. This value is little different from 0.38 proposed by Watson (*58*) in 1931. The exponent was found to be a random variable against various parameters that might have been expected to correlate it.

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Application of Benedict-Webb-Rubin Equation of State to Ammonia

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THE BENEDICT-WEBB-RUBIN EQUATION of state (hereafter called BWR equation) has been used primarily in predicting the thermodynamic properties of light hydrocarbons and light hydrocarbon mixtures (*1–7, 13, 15, 18, 19, 21, 23*). Some effort has been extended towards investigation of the applicability of the BWR equation to polar compounds, and successful results have been achieved with nitrous oxide (*16*), carbon dioxide (*9*), sulfur dioxide (*14*), and nitrogen–carbon monoxide (*12*) systems. The objectives of this work are: to determine the coefficients for the BWR equation for ammonia from available pressure-volume-

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