Estimating Vaporization Heats from Boiling Points

Sir:

The Trouton ratio (HvM/T) has long been used (Eq. 1) to estimate molar vaporization heats (HvM, J/mol at boiling points) from normal boiling points (T,K) (1). A similar ratio [(HvM, J/mol, 25°C)/T] can be used to estimate vaporization heats at 25°C (Eq. 2).

$$\text{HvM (bp)}/T = \text{approx. } 88 \quad [1]$$

$$\text{HvM (25°C)}/T = \text{ratio (R)} \quad [2]$$

Equations correlating the Equation 2 R with total homolog carbons, C, for six homologous series are in Table 1. The R values from the Table 1 equations can be used conveniently to estimate vaporization heats at 25°C: [(HvM, J/mol) = RT].

The use of the Table 1 equations is illustrated with methyl n-octanoate (total carbons, 9). The calculated R from Equation 3 (from Table 1) is 121.27. This ratio times the methyl n-octanoate boiling point (466 K) is 56,510. This calculated HvM value agrees well with the published HvM of 56,410 J/mol (2,3).

TABLE 1
Equations[a] Correlating the Ratio (HvM/T) with Total Homolog Carbons (C)[b]

	Carbons[c]	b	m	r	Reference
RCOOMe	8–16	71.38	5.543	3,34	2,3
$(R)_2O$	4–12	68.18	5.029	3,73	2,3
ROH	4–14	115.7	4.589	3,47	2,4
$(R)_2NH$	4–8	75.90	4.800	9,99	2,5
RCN	4–14	81.65	4.699	3,61	2,5
RCl	5–16	75.94	4.868	3,65	2,5

[a]HvM/T = b + mC: where HvM is molar vaporization heat (J/mol) at 25°C, T is normal boiling point (K), b is intercept, m is slope, and C is total homolog carbon.
[b]Correlation coefficient (r) of 0.99934 given as 3, 34. r, n-alkyl.
[c]Total carbons in homologs, e.g., methyl n-octanolate has nine carbons.

TABLE 2
Equations [$(\text{HvM})^{1/2} = b + mT$] Correlating Vaporization Heats (HvM, J/mol) 25°C with Normal Boiling Points (T,K)[a]

	Carbons[b]	b	m	r	Reference
Ethers, EtOR	4–12	17.57	0.4745	3,74	2,3
Ethers, ROR	2–12	22.32	0.4596	4,27	2,3
Esters, RCOOMe	2–8	40.86	0.4194	3,39	2,3
Esters, RCOOMe	8–14	−10.79	0.5344	3,57	2,3
Me ketones	3–12	19.26	0.4717	3,00	2,3
n-Alkanals	2–10	24.25	0.4592	3,64	2,3
n-Alkanols	2–14	20.39	0.5299	3,34	2,4
Amines, RNH_2	1–10	37.90	0.4314	3,79	2,3
Amines, R_2NH	2–12	35.86	0.4325	3,05	2,3
Amines, R_3N	3–12	24.80	0.4451	4,11	2,3
Nitriles, RCN	4–14	4.029	0.4935	3,53	2,5
n-RF	4–12	14.83	0.4820	3,70	2,5
n-RCl	3–16	11.60	0.4827	2,85	2,5
n-RBr	6–16	−7.329	0.5144	3,49	2,5
n-RI	4–10	5.145	0.4830	3,01	2,5

[a]Correlation coefficient, r of 0.99974 given as 3,74.
[b]Total carbons in homologs. See Table 1 for abbreviations.

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$$\text{HvM (J/mol)}/T\text{,K} = R = 71.38 + 5.543\ \text{C} \qquad [3]$$

Equation 4 provides a simple method for estimating vaporization heats at 25°C directly from normal boiling points. Equations of this type for 15 homologous series are in Table 2.

$$(\text{HvM, J/mol})^{1/2} = b + mT \qquad [4]$$

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