LETTER TO THE EDITOR

Estimating Vaporization Energies as One-Fourth of the Squared Boiling Points

Sir:

Molar vaporization energies (E_vM, J/mol, 25°C) of numerous organic and some inorganic compounds can be estimated as one-fourth of the squared b.p., $T^2/4$ (where T is the normal b.p., K):

$$E_vM \text{ (J/mol)} = T^2/k \qquad [1]$$

where k is 4. Equation 1 has the advantages of being simple, based on abundant and easily determined b.p., and related to the useful Equations 2–4.

Molar vaporization enthalpies (H_vM), from Equation 2, are needed in designing heat exchangers, reboilers, and distillation condensers (1):

$$H_vM \text{ (kJ/mol)} = E_vM \text{ (kJ/mol)} + 2.48 \qquad [2]$$

where 2.48 is RT (R, gas constant) at 298.2 K.

Solubility parameters (δ), from Equation 3, have many uses (2,3), i.e., in selecting solvents and plasticizers and for predicting polymer compatibilities:

$$\delta^2 = E_vM \text{ (J/mol)}/V \qquad [3]$$

where δ is the solubility parameter and V is the molar volume at 25°C.

Boiling points (T, K) can be calculated from E_vM (Eq. 4) where differences between E_vM and $T^2/4000$ are small:

$$T \text{ (K)} = 4000\ E_vM \text{ (kJ/mol)}^{1/2} \qquad [4]$$

Differences, Δ [E_vM (kJ/mol) less $T^2/4000$], are small for most of the lower homologs and functional groups (Table 1); oxygen compounds (Table 2); hydrocarbons and nitrogen, halogen, and sulfur compounds (Table 3); mixed halogen compounds (Table 4); and benzene derivatives (Table 5). (Sources of the E_vM and b.p. data are given in Tables 1–5.)

Differences, Δ (E_vM less $T^2/4000$), are relatively high for some compounds having hydrogen attached to oxygen or nitrogen (alcohols, glycols, hydroxy ethers, hydroxy esters, acids, primary amines, amides, and hydrazines). Differences (Δ) are greater than 2 kJ/mol for some benzene derivatives (4,6,8) but small for those listed in Table 5. Although the compounds

TABLE 1
Comparison of Molar Vaporization Energies (E_vM, kJ/mol) with $T^2/4000$: Functional Groups and Lower Homologs[a]

Compound	E_vM (kJ/mol)	Δ	Compound	E_vM (kJ/mol)	Δ
Propane	12.31	1.03	Hydrogen fluoride[b]	24.02	–2.56
Propene	11.76	0.95	1-Fluoropropane	19.33	–1.01
Cyclopropane	14.45	–0.01	Hydrogen chloride[b]	6.60	2.24
Propadiene	12.90	1.64	Chloromethane	16.44	–0.93
DiMe ether	16.03	–0.62	Hydrogen bromide[b]	10.21	0.48
DiEt ether	24.02	–0.35	Bromomethane	20.33	–1.20
Divinyl ether	23.72	–1.01	Hydrogen iodide[b]	14.87	–0.77
Ethylene oxide	22.27	–2.15	Iodomethane	25.49	–0.57
Me formate	25.87	–2.64	Hydrogen sulfide[b]	11.60	–0.19
DiEt carbonate	41.12	–1.32	Methanethiol	21.62	–0.21
Acetone	28.51	–1.42	DiMe sulfide	25.17	–1.07
Formaldehyde	17.42	–1.84	Thiacyclopropane	27.81	–0.90
Water[b]	41.50	–6.69	Hydrogen disulfide[b]	31.30	–1.73
Methanol	34.95	–6.44	DiMe disulfide	35.38	1.27
Glycol	65.32	–9.98	Carbon disulfide	25.03	0.41
Formic acid	17.62	17.4	DiMe sulfoxide	50.40	2.96
Acetyl chloride	27.82	–1.59	DiMe mercury	32.12	1.37
Acetyl bromide	30.52	0.07	Nitromethane	35.79	–0.76
Acetic anhydride	45.09	–2.61	Hydrogen cyanide[b]	23.72	–1.37
Ammonia[b]	17.38	–3.00	Acetonitrile	30.46	1.01
Me amine	20.89	–3.09	Ethanedinitrile	17.27	–1.39
DiMe amine	22.57	–2.97	TriMe amine	19.18	–0.13
Formamide	60.15	3.14	Me hydrazine	37.89	–5.38
N-Me formamide	53.71	2.14	*N*,*N*-DiMe formamide	44.41	0.96

[a] Data from References 4–6 except for propadiene, formaldehyde, formamide (1), and 1-fluoropropane (7). E_vM (kJ/mol) = H_vM (kJ/mol) – 2.48, where 2.48 is the gas constant at 298.2 K. Δ = E_vM (kJ/mol) less $T^2/4000$, where T is the normal b.p. (K).
[b] Functional group (G) of a homologous series, *n*-RG.

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TABLE 2
Comparison of Molar Vaporization Energies (E_vM, kJ/mol) with T^2/4000: Oxygen Compounds[a]

Compound	E_vM	Δ	Compound	E_vM	Δ
Bu Et ether	33.84	–0.46	Vinyl acetate	31.89	–1.94
DiPr ether	33.21	–0.25	IsoBu isobutanoate	43.92	0.56
Bu vinyl ether	33.69	0.00	Glycol diacetate	58.96	–5.37
Et isoBu ether	31.56	–0.18	Me trichloroacetate	45.85	–0.27
IsoPr pentyl ether	40.18	–0.34	2-Butoxyethyl acetate	56.90	–2.72
DiBu ether	44.97	0.24	Propionic anhydride	50.12	–1.70
Isopentyl Pr ether	40.42	–0.38	2-Hexanone	40.66	–0.52
Di(isoPr) ether	29.64	–0.46	3-Hexanone	39.99	–0.65
Epoxypropane	27.37	–1.64	4-Me-2-pentanone	38.15	–0.22
1,3-Dioxane	36.61	–0.66	2-Heptanone	44.76	0.27
1,4-Dioxane	36.12	–1.06	2,2-DiMe-3-pentanone	39.86	–0.12
Diethoxymethane	33.17	–0.57	Cyclopentanone	40.24	0.50
1,2-Dimethoxy ethane	33.91	–1.87	Cyclohexanone	42.58	3.34
1,2-Diethoxy ethane	40.72	–2.21	CycloPr Me ketone	36.93	0.01
1,3-Diethoxy propane	43.42	–0.63	2,4-Pentanedione	39.29	2.96
Paraldehyde	38.92	0.58	Mesityl oxide	40.92	–0.32
Furan	24.97	–1.79	IsoBu heptyl ketone	60.01	0.36
Tetrahydrofuran	29.51	–0.76	Pentanal	36.13	-0.79
Tetrahydropyran	32.10	0.48	Hexanal	41.13	-0.83
Et acetate	33.12	–2.44	2-Et butanal	38.17	-0.36
Me butanoate	36.80	–1.47	Heptanal	45.22	0.13
Et propionate	36.73	–2.10	Furfural	48.12	–0.84
IsoPr acetate	34.72	–1.81	Hexanol	59.12	–12.7
Et pentanoate	44.53	–0.60	1,4-Butanediol	74.12	–9.60
Me hexanoate	45.56	–0.91	Pentanoic acid	63.04	–10.30
Hexyl hexanoate[b]	67.13	–0.18	DiEt carbonate	41.12	–1.32
2-Ethoxyethyl acetate	50.21	–4.09	Me cyclobutanecarboxylate	42.24	–0.50
Diketene	39.84	–0.57	β-Propiolactone	44.55	2.76

[a] Data from References 4–6, except for vinyl acetate, hexyl hexanoate (2,8), and pentanoic acid (9). Δ = E_vM (kJ/mol) less T^2/4000, where T is the normal b.p. (K).
[b] Hoy's $\delta^2 V$ values were used as E_vM for hexyl hexanoate (2,8), where δ is the solubility parameter and V is the molar volume at 25°C.

TABLE 3
Comparison of Molar Vaporization Energies (E_vM, kJ/mol) with T^2/4000: Hydrocarbons and Nitrogen, Halogen, and Sulfur Compounds[a]

Compound	E_vM (kJ/mol)	Δ	Compound	E_vM (kJ/mol)	Δ
Hexane	29.08	0.14	1-Fluoropropane	19.33	–1.01
2-Me pentane	27.41	0.38	1-Fluoroctane	43.16	–0.33
1-Hexene	28.13	0.20	Perfluorooctane	36.85	–2.72
Cyclohexane	30.53	0.78	Octafluorocyclobutane	18.39	0.06
Me-cyclopentane	29.16	0.60	Fluorobenzene	32.10	–0.08
Benzene	31.35	–0.16	1-Chloropentane	35.76	0.51
Bu benzene	48.88	3.21	1-Chloroheptane	45.18	1.54
Hexylamine	42.62	–1.43	1,2 Dichloroethane	32.68	–0.89
Octylamine	51.44	–0.18	1,1,1-Trichloroethane	30.02	0.12
Cyclohexylamine	41.19	0.24	Chlorocyclohexane	41.02	2.04
DiBu amine	46.97	–0.04	Chloroacetyl chloride	36.42	–0.51
Dihexyl amine	68.42	–2.63	1-Bromopropane	29.53	–0.09
Di(2-ethylhexyl) amine[b]	76.75	–0.02	1-Bromobutane	34.16	0.94
Triethylamine	32.36	0.42	2-Bromobutane	31.93	1.29
Tributylamine	60.48	–0.05	1-Bromooctane	53.29	2.64
Pyridine	37.67	0.04	Allyl bromide	30.25	–0.80
2-Me pyridine	40.00	0.52	1-Iodopropane	33.77	1.52
2,4-DiMe pyridine	45.00	1.57	2-Iodopropane	31.58	1.29
Piperidine	36.81	–0.83	1-Iodobutane	38.15	2.59
Morpholine	41.48	–1.28	1-Iodo-2-Me-propane	36.35	2.50
N-Me formamide	53.71	2.14	2-Propanethiol	26.97	–0.45
N,*N*-DiMe formamide	44.41	0.96	1-Butanethiol	34.15	0.37
N,*N*-DiMe acetamide	47.76	0.20	2-Butanethiol	31.57	0.53
1-Nitropropane	40.91	–0.04	Pentanethiol	38.76	1.18
2-Nitropropane	38.86	–0.17	Cyclopentanethiol	38.94	2.13
1-Nitrobutane	44.52	0.88	DiPr sulfide	41.73	1.53
Butanenitrile	36.85	1.33			

(*Continued*)

TABLE 3 (continued)

Compound	E_vM (kJ/mol)	Δ	Compound	E_vM (kJ/mol)	Δ
Pentanenitrile	41.12	1.81	DiBu sulfide	50.48	2.88
3-Me butanenitrile	39.16	0.96	Et isoPr sulfide	35.30	0.91
Hexanenitrile	45.43	2.16	Et Pr sulfide	39.97	0.87
Dodecanenitrile	73.64	2.04	2-Me thiophene	36.39	–0.80
Iodoethane	29.45	0.41	DiMe disulfide	35.38	1.27

[a] Data from References 4–6, except for di(2-ethylhexyl) amine (2,8); 1-nitrobutane and octafluorocyclobutane (1); and 1-fluoropropane (7). $\Delta = E_vM$ (kJ/mol) less $T^2/4000$, where T is the normal b.p. (K).

[b] Hoy's $\delta^2 V$ values were used as E_vM for di(2-ethylhexyl) amine (2,8), where δ is the solubility parameter and V is the molar volume at 25°C.

TABLE 4
Comparison of Molar Vaporization Energies (E_vM, kJ/mol) with $T^2/4000$: Mixed Halogen Compounds[a]

Compound	E_vM	Δ
1,2-Dibromochlorotrifluoroethane	32.56	0.90
1,2-Dibromotetrafluoroethane	25.90	–0.26
1,1,1-Trichlorotrifluoroethane	25.60	–0.13
1,1,2-Trichlorotrifluoroethane	25.92	–0.21
1-Bromo-1-chloro-2,2,2-trifluoroethane	27.13	–1.00
1-Bromo-2-chloro-1,1,2-trifluoroethane	27.47	–0.97
1-Bromo-2-chloroethane	35.65	0.43
1,2-Dichlorohexafluoropropane	24.45	–0.84
1,1,1-Trichloro-3,3,3-trifluoropropane	34.21	–0.30
1,1-Dichloro-3,3,3-trifluoropropane	31.58	–1.74
1-Bromo-3-chloropropane	41.56	1.81
Chloropentafluorobenzene	38.59	–0.33
2-Chloro-1,1,2-trifluoroethyl ethyl ether	35.07	–2.31
1,1,1,5,5,5-Hexafluoro-2,4-pentanedione	28.10	1.35
Butyl 2-chloro-1,1,2-trifluoroethyl ether	42.62	–1.45

[a] Data from Reference 6. $\Delta = E_vM$ (kJ/mol) less $T^2/4000$, where T is the normal b.p. (K).

TABLE 5
Comparison of Molar Vaporization Energies (E_vM, kJ/mol) with $T^2/4000$: Benzene Derivatives[a]

Compound	E_vM (kJ/mol)	Δ	Compound	E_vM (kJ/mol)	Δ
Acetophenone	55.02	1.36	Ethoxybenzene	48.56	–0.50
Aniline	53.35	–1.14	Fluorobenzene	32.10	–0.08
Benzene	31.35	–0.14	4-Fluorotoluene	36.94	1.03
Benzonitrile	53.00	0.89	Hexafluorobenzene	33.23	–2.02
Benzyl alcohol	57.82	–0.59	Isopropylbenzene	40.41	1.87
Benzyl chloride	49.02	2.06	Isopropyl benzoate	58.50	2.07
Butyl benzoate	67.00	1.33	Methoxybenzene	44.22	1.12
Butyl salicylate	73.28	0.03	Methyl benzoate	54.73	1.04
Chlorobenzene	39.93	–0.11	α′-Methylbenzylamine	53.01	0.17
Chloropentafluorobenzene	38.59	–0.33	Pentafluorobenzene	33.79	–1.59
1,3-Diethylbenzene	49.21	1.93	Styrene	42.30	1.46
Diethyl phthalate	83.02	–2.05	Styrene oxide	53.11	1.46
p-Difluorobenzene	33.06	–0.30	Toluene	35.53	1.30
Di (α′-methylbenzyl) ether	78.56	–0.27	*o*-Vinyl toluene	46.54	2.06
N-Ethylaniline	58.36	–1.22	*m*-Xylene	40.77	1.73
Ethylbenzene	40.29	1.61	*p*-Xylene	40.49	1.86
Ethyl benzoate	57.39	1.61	*o*-Xylene	41.67	1.93
N-Ethyl α′-methylbenzylamine	54.72	1.49			

[a] $\Delta = E_vM$ (kJ/mol) less $T^2/4000$, where T is the normal b.p. (K). Data from References 4, 6, and 8.

included in Tables 1–5 differ greatly in structure and M.W., the agreement between E_vM (kJ/mol) and $T^2/4000$ is good or excellent in most instances.

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Charles H. Fisher*
Chemistry Department,
Roanoke College,
Salem, Virginia 24153

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*Address correspondence at Chemistry Department, Roanoke College, 221 College Lane, Salem, VA 24153. E-mail: fisher@roanoke.edu