The Limiting Boiling Point and Homolog Boiling Point Equations

Sir:

Limiting properties (P_∞ for C_∞ and M_∞, where P, C, M, and ∞ are property, carbon, M.W., and infinity) are parameters in Equation 1 (1,2) and hence are helpful in developing equations correlating P with C or M:

$$P = P + m/(C + k) \qquad [1]$$

where P_∞ is intercept, m is slope, and k is an adjustable parameter.

Limiting values (P_∞) for many properties have been published (2), but there is wide disagreement about the proper limiting boiling point. Estimated values of $t_{b,\infty}$ range from 805°C to infinity (Eqs. 2–7 based on n-alkane normal boiling points). Huddle's 1190 K (Eq. 7) was used successfully in creating T_b(K) vs. C expressions (Eq. 8) for three homologous series (n-R acetates and Me and Et n-alkanoates) (3).

$$1/T = 0.000570 + 0.007753/C^{2/3} \qquad [2]$$
[Kurata and Isida (4); $T_\infty = 1754$ K; $t_\infty = 1481$°C]

$$\log (1{,}078 - T) = 3.03191 - 0.0499901 C^{2/3} \qquad [3]$$
[Kreglewski and Zwolinski (5); $T_\infty = 1078$ K; $t_\infty = 805$°C)]

$$T = 10^3 \, [1.209 - 1.163/(1 + 0.0742 C^{0.85})] \qquad [4]$$
[Stiel and Thodos (6); $T_\infty = 1209$ K; $t_\infty = 936$°C]

$$C/T = 0.015470 + 0.00086624\, C \qquad [5]$$
[Fisher (7); $T_\infty = 1154$ K; $t_\infty = 881$°C]

$$T = 138\, C^{1/2} \qquad [6]$$
[Partington (8); $T_\infty = \infty$]

$$(C + 2.355)/T,\ \text{K} = 0.01940 + 0.00084034\, C \qquad [7]$$
(Huddle, B.P., Jr., personal communication; $1/m = T_\infty = 1190$ K)

$$T_b,\ \text{K} = 1190 - m/(C + k) \qquad [8]$$

The work reported below, done in part to identify the proper $t_{b,\infty}$ (°C) value, supports Huddle's 1190 K (917°C) value. Best-fit equations [t_b, °C vs. $1/(C + k)$] were developed for many homologous series; the intercepts (indicating the $t_{b,\infty}$ value) were about 917°C. This value (917°C) was selected as $t_{b,\infty}$ and used successfully in developing equations (Eq. 9) for numerous homologous series. The equations were made with a computer or by plotting homolog carbons against $1/(t_b - 917)$ to derive Equation 10, which was rearranged to Equation 9:

$$T_b,\ ^\circ\text{C} = 917 - m/(C + k) \qquad [9]$$

$$C = -k - m/(t_b - 917) \qquad [10]$$

Equations similar to Equation 9 for 20 homologous series are presented in Table 1. Other unreported (in Table 1) homologous series (where R is n-alkyl) include RH, R cyclopentanes, R cyclohexanes, R benzenes, 1-alkenes, 1-alkynes, 1-R naphthalenes, 2-R naphthalenes, vinyl ethers, diethers, acetals, *tert*-Bu ethers, many aliphatic esters, R lactates, R acetyl lactates, esters of dibasic acids, cyclic ketones, R anilines, 2-thiols, R borates, R phosphates, R_4 Ge, R Si$(Me)_3$, and R Si$(Et)_3$.

The equations in Table 1 have important advantages. They are user-friendly and provide much information in little space. The boiling points of many additional homologs can be estimated by interpolation or by reasonable extrapolation. Significantly incorrect data can be identified. When the intercept (Eq. 9) is 917°C, the calculated boiling points are °C; when the intercept is 1190 K, the calculated boiling points are in K.

TABLE 1
Equations[a] Correlating Normal Boiling Points (t_b,°C) with Number of Homolog Carbons (C)[b]

	Carbons[c]	k	Slope (m)	Correlation coefficient[b] (r)	Reference
MeOR	4–7	23.28	–23,950	–6, 40	9
ROR	4–12	24.69	–25,342	–4, 50	10
RCOOMe	5–13	26.65	–25,771	–4, 80	3
RCOOEt	6–12	26.77	–26,053	–5, 00	3
MeCOOR	5–12	26.78	–25,932	–4, 80	3
RCHO	2–10	26.90	–25,964	–3, 87	11
MeCOR	5–11	26.48	–25,644	–4, 75	12
RCOR	4–15	28.06	–26,970	–4, 64	10
ROH	7–20	28.74	–26,538	–4, 34	13
2-ROH	6–12	24.44	–27,584	–3, 74	14
RCOOH	6–16	33.23	–27,933	–4, 20	15
$(RCO)_2O$	4–14	46.53	–39,236	–3, 73	16, 17
RCOCl	3–10	27.87	–25,893	–3, 74	18
RNH_2	8–40	26.07	–25,086	–4, 60	19
R_2NH	8–40	26.08	–25,789	–4, 42	19
R_3N	12–60	35.38	–33,534	–4, 50	19
RCN	6–21	27.39	–25,196	–4, 80	19
RCl	8–40	26.46	–26,293	–5, 00	19
RBr	6–30	26.24	–24,538	–5, 20	19
RSH	6–20	26.45	–24,737	–4, 20	20

[a] t_b,°C = 917 – $m/(C + k)$, where m is slope and k is an adjustable parameter.
[b] Correlation coefficient r of –0.99999940 is given as –6, 40.
[c] In addition to C_∞ = 917°C.

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