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Calculation of programmed temperature gas chromatographic characteristics from isothermal data

III. Predicted retention indices and equivalent temperatures

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SUMMARY

Theoretical procedures, described in Part I [*J. Chromatogr.*, 405 (1987) 67], for predicting retention indices in programmed temperature gas chromatography from isothermal data are experimentally tested for a number of compounds under a range of experimental conditions. In general, and taking into full consideration random error predictions, agreement is reasonably satisfactory. Also calculated by procedures of Part I are two distinct kinds of equivalent temperature, these being the temperatures of isothermal chromatographic experiments giving the same calculated retention time (a) or index (b) as a corresponding programmed temperature experiment. These temperatures are compared with various simple functions of initial and calculated final temperatures in such an experiment.

INTRODUCTION

Part I[1] describes theoretical and computational procedures for predicting programmed-temperature gas chromatography (PTGC) characteristics using, as input information, experimental data for the same column and carrier gas pressure differential, but obtained under isothermal conditions (isothermal gas chromatography, IGC). Part II[2] describes the calculation (with due consideration of random errors), and comparison with experiment, of retention times and elution temperatures for a range of organic compounds (*n*-alkanes, monocyclic aromatic hydrocarbons and ketones) on a capillary column under a variety of programmed-temperature conditions; the temperature programme corresponded in each case to a linear increase of temperature with time ("single linear ramp"). The present paper extends the comparison to PTGC retention indices and also calculates two kinds of equivalent

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temperature[1]. These are the temperatures of IGC experiments for which, on the one hand, retention times are the same as calculated PTGC values, and on the other hand, retention indices are the same. The equivalent temperatures are then compared with various averages of initial and elution temperatures and with the Giddings significant temperature[3].

EXPERIMENTAL

The experimental procedure is fully described in Part II[2], which also lists the compounds studied. The list is repeated in the first column of Tables I and II. For the present purpose, it should be noted that it includes a contiguous set of *n*-alkanes, to be used as retention index standards for the remaining compounds.

PREDICTED EQUIVALENT TEMPERATURES (RETENTION TIME TYPE)

Part II[2] presents (a) experimental isothermal retention times for the compounds studied, (b) two simple alternative relationships between column dead time and

TABLE I

PREDICTED EQUIVALENT TEMPERATURES (RETENTION TIME TYPE) AND VARIOUS TRADI

Values in parentheses are estimated standard deviations.

Compound	*Heating rate = 2.00 K min^{-1}*							
	Initial temperature = 333.16 K				*Initial temperature = 393.16 K*			
	Equivalent temperature/K	*Comparison temperatures/K*[a]			*Equivalent temperature/K*	*Comparison temperatures/K*[a]		
		(a)	*(b)*	*(c)*		*(a)*	*(b)*	*(c)*
n-Nonane	338.7(0.2)	338.7	338.6	316.7	395.4(0.0)	395.4	395.4	365.8
n-Decane	342.9(0.0)	342.6	342.3	323.8	396.0(0.1)	396.0	396.0	367.0
n-Undecane	348.6(0.1)	347.7	347.1	333.3	397.0(0.0)	397.0	397.0	368.8
n-Dodecane	356.6(0.1)	354.3	353.0	345.0	398.7(0.1)	398.6	398.6	371.8
n-Tridecane	365.1(0.5)	360.9	358.8	357.6	401.1(0.1)	401.0	400.8	376.1
n-Tetradecane	376.7(0.9)	369.0	365.5	372.5	405.0(0.8)	404.5	404.2	382.5
n-Pentadecane	384.5(0.1)	374.5	370.0	382.7	409.4(0.1)	408.3	407.8	389.6
Nonan-5-one	347.7(0.1)	346.9	346.3	331.7	396.9(0.0)	396.9	396.8	368.6
Propiophenone	353.5(0.2)	351.9	350.9	340.9	398.3(0.1)	398.2	398.2	371.0
Butyrophenone	360.6(0.2)	357.7	356.0	351.6	400.2(0.1)	400.0	399.9	374.4
Valerophenone	370.2(0.2)	364.9	362.1	364.9	403.4(0.1)	403.0	402.8	379.9
Hexanophenone	380.0(0.1)	371.8	367.8	377.6	407.5(0.1)	406.8	406.3	386.8
Isopropyl benzoate	356.8(0.1)	354.6	353.5	345.9	399.0(0.1)	398.9	398.8	372.3
2-Phenylpropane	339.8(0.1)	339.7	339.6	318.5	395.6(0.1)	395.6	395.6	366.2
1-Phenylpropane	340.8(0.1)	340.6	340.4	320.2	395.8(0.1)	395.8	395.8	366.5
1-Phenylbutane	345.8(0.1)	345.3	344.9	328.8	396.7(0.1)	396.7	396.6	368.2
1-Phenylpentane	352.8(0.1)	351.3	350.3	339.8	398.1(0.1)	398.0	398.0	370.7
1-Phenyloctane	380.3(0.1)	372.0	367.9	378.0	407.7(0.1)	407.0	406.5	387.1

[a] Values are given in the order (a) arithmetic mean of initial and calculated elution temperature, (b) corresponding harmonic mean, (c) Giddings significant temperature, *i.e.*, 0.92 × calculated elution temperature.

temperature derived from the values of (a) for *n*-alkanes, (c) least squares linear regression coefficients for plots of ln(capacity factor) against reciprocal absolute temperature, and (d) a selection of predicted PTGC retention times and elution temperatures for a variety of single-linear-ramp programmed conditions using the theoretical/computational procedures described in Part I[1]. From this starting point, one can calculate[1] the temperatures of corresponding IGC experiments predicted to have the same retention times as the PTGC experiments; in Part I, such an "equivalent temperature" has been symbolised $T_{eq(1)}$. Tables I and II give a selection of these, together with estimates of standard deviations derived from a numerical application of error propagation theory[1,2].

Because of the close similarity in predictions using two alternative column dead time formulae[2] (and this is also the case in the predictions of Part II), these and subsequent tables in this paper have been restricted to predictions from one of the formulae, *viz.*,

$$t/\mathrm{s} = -46.4(3.6) + 6.54(0.179)\sqrt{T/\mathrm{K}}; \text{covariance } -0.64 \qquad (1)$$

where t is the column dead time at absolute temperature T (in this paper standard

TIONAL EQUIVALENT TEMPERATURES FOR HEATING RATE OF 2.00 AND 7.00 K min^{-1}

Heating rate = 7.00 K min^{-1}							
Initial temperature = 333.16 K				*Initial temperature = 393.16 K*			
Equivalent temperature/K	*Comparison temperatures/K*[a]			*Equivalent temperature/K*	*Comparison temperature/K*[a]		
	(a)	*(b)*	*(c)*		*(a)*	*(b)*	*(c)*
348.6(0.5)	348.4	347.8	334.6	400.5(0.1)	400.6	400.5	375.5
356.3(0.0)	355.2	353.9	347.1	402.2(0.1)	402.4	402.2	378.7
365.1(0.1)	362.5	360.1	360.5	404.8(0.0)	404.9	404.5	383.3
375.5(0.1)	370.5	366.7	375.2	408.6(0.0)	408.5	407.9	389.9
385.6(0.5)	377.8	372.5	388.7	413.4(0.2)	412.8	411.9	397.9
397.6(1.6)	385.4	378.3	402.6	419.5(1.6)	417.8	416.4	407.1
406.7(0.1)	391.8	393.0	414.4	426.2(0.1)	423.4	421.2	417.3
363.9(0.1)	361.6	359.3	358.8	404.5(0.0)	404.6	404.3	382.8
372.1(0.2)	368.2	364.9	371.0	407.8(0.1)	407.8	407.3	388.6
381.2(0.2)	374.9	370.3	383.3	411.8(0.1)	411.4	410.6	395.3
392.1(0.2)	382.7	376.3	397.6	417.6(0.1)	416.5	415.2	404.6
402.6(0.0)	389.6	381.4	410.4	424.0(0.1)	421.8	419.9	414.4
376.2(0.1)	371.2	367.3	376.5	409.3(0.0)	409.1	408.5	391.1
350.9(0.2)	350.5	349.6	338.4	401.2(0.1)	401.4	401.2	376.8
352.8(0.2)	352.2	351.2	341.6	401.6(0.1)	401.8	401.6	377.6
361.4(0.1)	359.6	357.7	355.2	404.0(0.2)	404.2	403.9	382.0
371.2(0.1)	367.4	364.2	369.5	407.4(0.1)	407.3	406.8	387.8
403.0(0.0)	389.9	381.6	410.9	424.3(0.0)	422.0	420.1	414.9

TABLE II

PREDICTED EQUIVALENT TEMPERATURES (RETENTION TIME TYPE) AND VARIOUS TRADITIONAL EQUIVALENT TEMPERATURES FOR HEATING RATE OF 15.00 K min^{-1}

Values in parentheses are estimated standard deviations.

Compound	*Initial temperature = 333.16 K*				*Initial temperature = 393.16 K*			
	Equivalent temperature/K	*Comparison temperatures/K*[a]			*Equivalent temperature/K*	*Comparison temperatures/K*[a]		
		(a)	*(b)*	*(c)*		*(a)*	*(b)*	*(c)*
n-Nonane	359.4(0.6)	359.5	357.6	354.9	407.6(0.2)	408.5	407.9	389.9
n-Decane	368.9(0.1)	367.7	364.5	370.1	410.5(0.1)	411.3	410.5	395.1
n-Undecane	379.1(0.1)	375.9	371.0	385.1	414.3(0.1)	415.0	413.9	401.9
n-Dodecane	390.3(0.1)	384.3	377.5	400.5	419.6(0.0)	419.8	418.1	410.8
n-Tridecane	401.0(0.5)	391.9	383.1	414.5	425.7(0.3)	425.2	422.8	420.7
n-Tetradecane	412.5(2.1)	398.9	388.1	427.4	432.3(2.1)	430.5	427.2	430.3
n-Pentadecane	422.5(0.2)	405.9	392.9	440.4	440.2(0.2)	436.9	432.5	442.2
Nonan-5-one	377.8(0.1)	374.9	370.3	383.4	414.0(0.1)	414.7	413.6	401.3
Propiophenone	387.3(0.2)	382.4	376.1	397.1	418.8(0.2)	419.2	417.6	409.6
Butyrophenone	396.9(0.2)	389.4	381.3	410.0	424.0(0.1)	423.8	421.6	418.2
Valerophenone	408.3(0.2)	397.3	386.9	424.5	431.0(0.1)	429.8	426.7	429.1
Hexanophenone	419.0(0.0)	404.2	391.7	437.3	438.3(0.1)	435.6	431.5	439.8
Isopropyl benzoate	391.4(0.1)	385.3	378.3	402.5	420.7(0.0)	420.9	419.0	412.7
2-Phenylpropane	362.5(0.2)	362.0	360.0	360.2	408.9(0.3)	409.7	409.1	392.2
1-Phenylpropane	364.9(0.2)	364.5	361.8	364.1	409.6(0.1)	410.5	409.8	393.6
1-Phenylbutane	375.3(0.0)	373.1	368.8	379.9	413.4(0.1)	414.1	413.1	400.3
1-Phenylpentane	386.1(0.2)	381.5	375.4	395.4	418.1(0.2)	418.6	417.0	408.4
1-Phenyloctane	419.4(0.0)	404.5	391.9	437.8	438.6(0.1)	435.9	431.7	440.4

[a] Values are given in the order (a) arithmetic mean of initial and calculated elution temperature, (b) corresponding harmonic mean, (c) Giddings significant temperature, *i.e.*, 0.92 × calculated elution temperature.

deviations are given in parentheses). A full set of data covering both formulae and 32 combinations (listed in Part II) of initial oven temperature and heating rate is available from the authors on request. Also included in Tables I and II, for comparison purposes, are the arithmetic and harmonic means of initial and *calculated* elution temperatures and the *calculated* Giddings significant temperature (0.92 × calculated elution temperature)[3], all three of which have been used in the past as "equivalent temperatures".

PREDICTED PTGC RETENTION INDICES AND EQUIVALENT TEMPERATURES (RETENTION INDEX TYPE)

For the same selection of experimental conditions, Tables III–V give calculated retention indices by two alternative procedures, (a) by linear interpolation between adjacent points on a plot of programmed temperature retention time against carbon number for *n*-alkanes, and (b) by cubic spline interpolation for the same plot (the two methods are detailed in Part I[1]). Observed values corresponding to the calculated values of method (b) are included for comparison. The tables also present calculated

TABLE III

PREDICTED AND OBSERVED RETENTION INDICES AND EQUIVALENT TEMPERATURES (RETENTION INDEX TYPE) FOR INITIAL TEMPERATURES OF 333.16 AND 393.16 K AND A HEATING RATE OF 2.00 K min^{-1}

For each compound, the first and second lines correspond to initial temperatures of 333.16 and 393.16 K, respectively.

Compound	*Retention index*			*Equivalent temperature/K*[a]	
	Predicted[a]		*Observed*[b]	*(a)*	*(b)*
	(a)	*(b)*			
(1) Nonan-5-one	1084 (2)	1086 (1)	1073.1(0.1)	330(4)	371(17)
	1088 (2)	1091 (1)	1076.2(0.1)	376(6)	405(15)
(2) Propiophenone	1163 (3)	1164 (3)	1165.3(0.1)	351(0)	361 (6)
	1175 (2)	1179 (2)	1180.3(0.1)	388(2)	400(12)
(3) Butyrophenone	1251 (4)	1252 (4)	1252.2(0.1)	363(0)	378 (7)
	1261 (4)	1264 (4)	1265.3(0.0)	390(1)	404(11)
(4) Valerophenone	1349 (6)	1349 (7)	1355.6(0.2)	380(1)	372(11)
	1359(12)	1364(10)	1366.2(0.0)	399(5)	405(12)
(5) Hexanophenone	1450 (8)	1443(10)	1459.9(0.1)	388(1)	365(20)
	1460 (8)	1456(18)	1467.7(0.1)	404(1)	395(24)
(6) Isopropyl benzoate	1204 (2)	1204 (2)	1207.2(0.0)	359(1)	368(10)
	1212 (1)	1213 (1)	1216.7(0.0)	391(2)	399(15)
(7) 2-Phenylpropane	926 (5)	928 (5)	929.2(0.1)	315(8)	319 (6)
	938 (4)	942 (3)	941.6(0.1)	371(6)	385 (4)
(8) 1-Phenylpropane	950 (4)	953 (3)	958.2(0.1)	314(5)	319 (9)
	964 (3)	968 (3)	971.5(0.1)	375(4)	385 (9)
(9) 1-Phenylbutane	1053 (1)	1057 (1)	1056.4(0.1)	334(2)	351(13)
	1067 (1)	1072 (2)	1071.8(0.1)	382(3)	399(16)
(10) 1-Phenylpentane	1154 (1)	1155 (1)	1157.3(0.1)	349(2)	362 (7)
	1163 (3)	1169 (3)	1169.9(0.1)	382(4)	400 (9)
(11) 1-Phenyloctane	1454 (7)	1448(10)	1465.1(0.1)	388(1)	368 (9)
	1464 (7)	1460(17)	1471.7(0.1)	405(1)	396(29)

[a] Values in parentheses are estimated standard deviations. Retention index (a)[1] is obtained by linear interpolation between adjacent points on a plot of programmed temperature retention time against carbon number for *n*-alkanes. Retention index (b)[1] is obtained by cubic spline interpolation for the same plot. Equivalent temperature (a)[1] uses retention index (a) in conjunction with a linear interpolation between adjacent points on a plot of log(isothermal capacity factor) against carbon number for *n*-alkanes. Equivalent temperature (b)[1] uses retention index (b) in conjunction with a least squares linear fit to the points of the same plot.

[b] Values in parentheses are 95% confidence deviations. Experimental values are analogues of the predicted indices (b).

temperatures of IGC experiments for which Kováts retention indices are the same as calculated PTGC indices; in Part I, such an "equivalent temperature" has been symbolised $T_{eq(2)}$. Again two different methods have been used to calculate these: method (a) uses retention index (a) in conjunction with a linear interpolation between adjacent points of a plot of log(isothermal capacity factor) against carbon number for *n*-alkanes; method (b) uses retention index (b) in conjunction with a least squares linear fit to the points of the same plot. Standard deviation estimates (see Part I[1]) are included for all calculated values.

TABLE IV

PREDICTED AND OBSERVED RETENTION INDICES AND EQUIVALENT TEMPERATURES (RETENTION INDEX TYPE) FOR INITIAL TEMPERATURES OF 333.16 AND 339.16 K AND A HEATING RATE OF 7.00 K min^{-1}

For each compound, the first and second lines correspond to initial temperatures of 333.16 and 393.16 K, respectively.

Compound	*Retention index*			*Equivalent temperature/K*[a]	
	Predicted[a]		*Observed*[b]	*(a)*	*(b)*
	(a)	*(b)*			
Nonan-5-one	1087 (1)	1088 (1)	1074.5(0.1)	363(1)	384(23)
	1089 (2)	1091 (1)	1076.9(0.0)	392(4)	410(18)
Propiophenone	1174 (2)	1171 (3)	1172.8(0.1)	378(0)	380 (5)
	1181 (2)	1183 (2)	1183.0(0.0)	403(0)	408 (8)
Butyrophenone	1260 (4)	1260 (5)	1261.0(0.1)	390(1)	396 (8)
	1268 (4)	1269 (4)	1270.2(0.0)	408(1)	414(12)
Valerophenone	1364(12)	1363(13)	1365.7(0.1)	407(1)	403(15)
	1373(19)	1374(18)	1372.6(0.1)	419(1)	423(21)
Hexanophenone	1466 (8)	1463(14)	1470.8(0.1)	415(2)	409(16)
	1471 (7)	1472(20)	1475.7(0.1)	425(2)	426(18)
Isopropyl benzoate	1210 (2)	1209 (2)	1212.7(0.1)	383(2)	387 (5)
	1215 (1)	1216 (2)	1219.7(0.0)	405(1)	408(16)
2-Phenylpropane	931 (5)	931 (4)	931.6(0.0)	340(3)	334(15)
	940 (4)	944 (3)	944.9(0.1)	381(5)	392 (4)
1-Phenylpropane	956 (4)	956 (3)	960.8(0.1)	343(3)	336(12)
	976 (3)	970 (3)	974.4(0.1)	386(3)	392 (8)
1-Phenylbutane	1060 (1)	1062 (1)	1062.2(0.1)	361(1)	368 (8)
	1071 (2)	1075 (2)	1074.5(0.0)	394(4)	406 (7)
1-Phenylpentane	1162 (2)	1161 (2)	1163.5(0.1)	377(1)	380 (8)
	1169 (3)	1172 (3)	1173.5(0.1)	399(2)	408 (8)
1-Phenyloctane	1470 (7)	1467(13)	1474.2(0.1)	416(3)	410(14)
	1476 (6)	1476(18)	1478.3(0.1)	426(1)	426(20)

[a,b] See corresponding footnotes for Table III.

DISCUSSION

Corresponding PTGC retention indices calculated by the two methods are very similar; in the main, bearing in mind the estimated standard deviations, they may indeed be regarded as indistinguishable. Agreement between predicted and observed is generally good, again in the light of the stated uncertainties, although there is certainly a tendency for observed values to be higher. The situation is shown graphically in Fig. 1, which excludes any error considerations; the compound to box number correspondence is given in Table III. It will be seen that for four compounds predictions are less satisfactory than for the others. These four are nonan-5-one (compound 1) where predictions are *consistently* high, and valerophenone, hexanophenone and 1-phenyloctane (compounds 4, 5 and 11) where there is significant spread of predictions around the observations. Possible reasons for imperfect prediction have been presented in Part

TABLE V

PREDICTED AND OBSERVED RETENTION INDICES AND EQUIVALENT TEMPERATURES (RETENTION INDEX TYPE) FOR INITIAL TEMPERATURES OF 333.16 AND 393.16 K AND A HEATING RATE OF 15.00 K min^{-1}

For each compound, the first and second lines correspond to initial temperatures of 333.16 and 393.16 K, respectively.

Compound	*Retention index*			*Equivalent temperature/K*[a]	
	Predicted[a]		*Observed*[b]	*(a)*	*(b)*
	(a)	*(b)*			
Nonan-5-one	1089 (1)	1089 (1)	1075.3(0.0)	382(4)	394(22)
	1091 (2)	1092 (1)	1077.6(0.1)	406(5)	417(16)
Propiophenone	1178 (2)	1177 (3)	1179.0(0.0)	396(1)	396(10)
	1187 (3)	1188 (3)	1188.6(0.1)	417(3)	418 (7)
Butyrophenone	1268 (4)	1267 (5)	1267.9(0.0)	408(1)	409(17)
	1275 (3)	1274 (5)	1275.6(0.1)	423(1)	423(16)
Valerophenone	1377(20)	1377(21)	1373.2(0.1)	424(2)	428(22)
	1387(28)	1388(28)	1378.7(0.1)	434(1)	444(23)
Hexanophenone	1476 (7)	1477(17)	1478.7(0.1)	434(1)	434(10)
	1480 (6)	1484(21)	1482.4(0.1)	441(2)	445(11)
Isopropyl benzoate	1214 (2)	1214 (2)	1217.0(0.1)	401(1)	400 (5)
	1219 (1)	1219 (2)	1223.0(0.1)	419(1)	417 (8)
2-Phenylpropane	935 (5)	934 (4)	934.3(0.1)	358(2)	349 (6)
	944 (4)	946 (3)	946.5(0.1)	393(6)	401 (6)
1-Phenylpropane	960 (4)	960 (3)	963.9(0.1)	362(1)	352(16)
	970 (3)	973 (3)	976.6(0.0)	398(3)	402 (8)
1-Phenylbutane	1066 (1)	1066 (1)	1066.4(0.1)	379(0)	382 (7)
	1076 (2)	1078 (2)	1078.0(0.1)	407(2)	414 (7)
1-Phenylpentane	1167 (3)	1167 (3)	1168.2(0.2)	395(0)	395 (7)
	1174 (4)	1176 (4)	1177.0(0.1)	414(1)	418 (7)
1-Phenyloctane	1481 (6)	1481(14)	1480.3(0.0)	435(1)	433 (4)
	1484 (5)	1488(17)	1484.1(0.1)	442(1)	444 (7)

[a,b] See corresponding footnotes for Table III.

II[2]. Predictions based upon similar theory by Curvers *et al.*[4] (but without any error considerations) are rather closer to their experimental values than those given here.

Because both predicted elution temperatures[2] and predicted retention indices generally compare well with experiment, it may be supposed that comparison of *calculated* equivalent temperatures (both types) and *calculated* "comparison temperatures" (three kinds as given in Tables I and II) corresponds reasonably closely with comparison of *experimental* values. The difference in nature between the two types of equivalent temperature [retention time type $T_{eq(1)}$ (Tables I and II) and retention index type $T_{eq(2)}$ (Tables III–V)] has been emphasised in Part I[1]. Comparison of values for corresponding eluent and PTGC conditions certainly indicate significant differences in many cases. Furthermore, there are some significant differences between values of $T_{eq(2)}$ calculated by the two different methods; incidentally, the generally higher estimated standard deviations by method (b) arise from the involvement of *all* *n*-alkanes [in contrast with only two for method (a)] in the linear regression aspect of

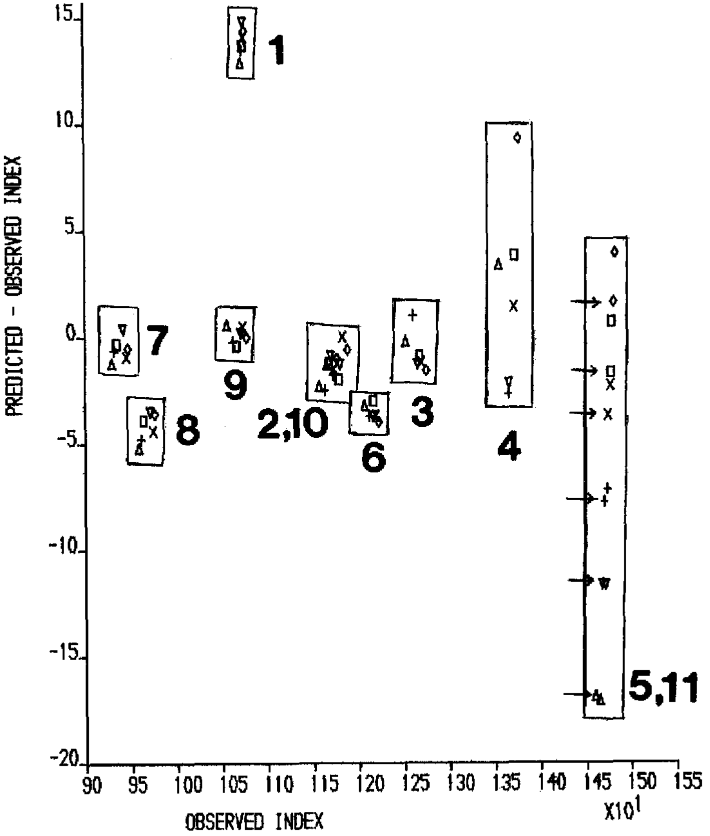


Fig. 1. Comparison of observed and predicted PTGC retention indices. Box numbering corresponds to compound numbering in Table III; for the box containing data for hexanophenone and 1-phenyloctane, the arrowed points are those for the former compound. The point symbols correspond to the pairs of initial temperatures/K and heating rates/K min^{-1} as follows: △ = 333.16, 2.00; ▽ = 393.16, 2.00; + = 333.16, 7.00; × = 393.16, 7.00; □ = 333.16, 15.00; ◇ = 393.16, 15.00.

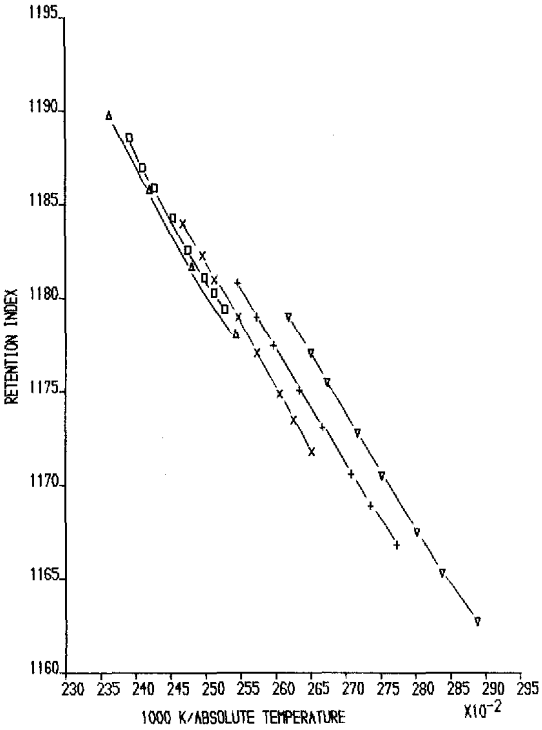


Fig. 2. Test of arithmetic mean of initial and experimental elution temperature as an approximator of $T_{eq,2}$ for propiophenone: △ = IGC retention index *vs* 1000 K/isothermal temperature; ▽ + × □ = experimental PTGC retention index *vs.* 1000 K/arithmetic mean temperature for initial temperatures of 333.16, 353.16, 373.16 and 393.16 K, respectively. For each temperature, points from the bottom of the line upwards are for heating rates of 1.00, 2.00, 3.00, 5.00, 7.00, 10.00, 12.00 and 15.00 K min^{-1}.

TABLE VI

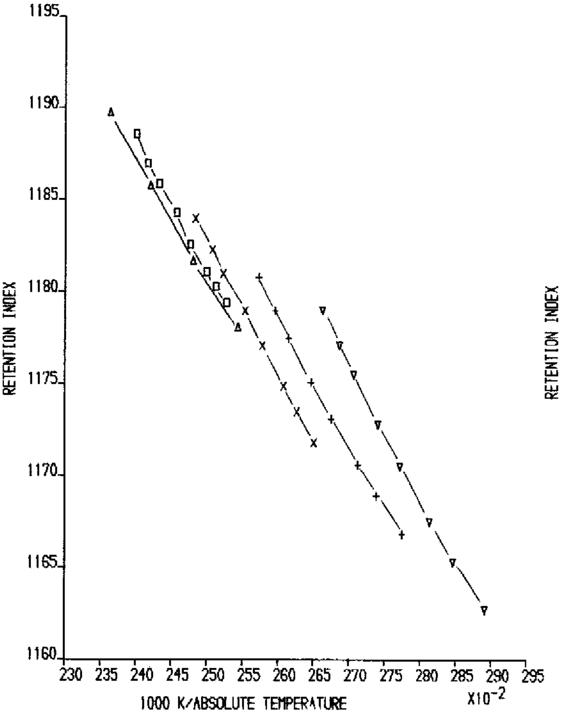
CALCULATED EQUIVALENT TEMPERATURES (RETENTION INDEX TYPE) FOR HYPOTHETICAL COMPOUND

$\ln(k_1) = -12.2$ (0.02), $k_2 = 5000$ (10) K, covariance −0.2. Column dead time/temperature dependence as eqn. 1; initial temperature = 333.16 K.

Heating rate/K min^{-1}	*Equivalent temperature/K (and "estimated standard deviation")*	
	(a)	*(b)*
1.00	1140 (1932)	422(126)
2.00	1939 (17 632)	417 (70)
3.00	−9762(4 089 722)	416 (66)
5.00	−154 (4045)	415(116)
7.00	146 (1052)	415 (72)
10.00	283 (321)	414(138)
12.00	326 (186)	414 (64)
15.00	364 (59)	414(117)

the method. There is certainly a possibility of ill-conditioning in the calculation of $T_{eq(2)}$ in situations where the IGC (Kováts) indices are only very slightly dependent on temperature. To illustrate this, a hypothetical example [for which[1] $\ln(k_1) = -12.2$ (0.02) and $k_2 = 5000$ (10) K; covariance = −0.2; ln (k_1) and k_2 are the intercept and slope, respectively, of the least squares linear plot of ln (isothermal capacity factor) against reciprocal absolute temperature] gave the absurd results shown in Table VI; at least in this example, there is more "stability" in $T_{eq(2)}$ values obtained by method (b).

In comparing both $T_{eq(1)}$ (all compounds) and $T_{eq(2)}$ (inapplicable for the *n*-alkanes) with the various comparison temperatures given in Tables I and II, it is apparent that *generally* (and there are exceptions) (i) neither equivalent temperature compares well with the Giddings significant temperature, (ii) $T_{eq(1)}$ compares better with one or other of the means of initial and elution temperatures than does $T_{eq(2)}$. The quality of various comparison temperatures as approximators of $T_{eq(2)}$ has been previously[5] approached in a different way, *viz.*, by plotting experimental IGC retention indices against reciprocal absolute temperature (this being nearly linear, and equivalent to a plot of PTGC index against experimental $T_{eq(2)}{}^{-1}$), and then examining the proximity of points [(experimental comparison temperature)$^{-1}$, experimental PTGC index] to the plot; the closer the points, the better the comparison temperature as an approximator of $T_{eq(2)}$. This approach is illustrated in Figs. 2–4 for propiophenone; experimental IGC indices at 393.16, 403.16, 413.16 and 423.16 K are 1178.1, 1181.7, 1185.8 and 1189.8, respectively. Generally, and this is particularly true at



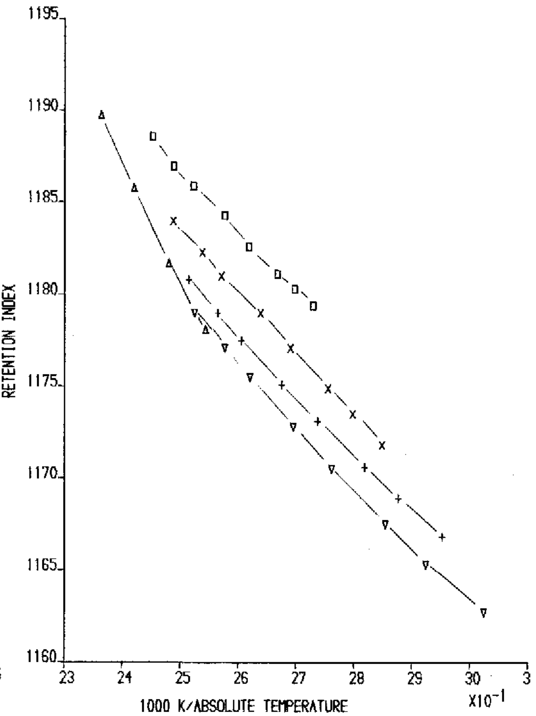


Fig. 3. Test of harmonic mean of initial and experimental elution temperature as an approximator of $T_{eq,2}$ for propiophenone: △ = IGC retention index *vs.* 1000 K/isothermal temperature; ▽ + × □ = experimental PTGC retention index *vs.* 1000 K/harmonic mean temperature for initial temperatures of 333.16, 353.16, 373.16 and 393.16 K, respectively. For each temperature, points from the bottom of the line upwards are for heating rates of 1.00, 2.00, 3.00, 5.00, 7.00, 10.00, 12.00 and 15.00 K min^{-1}.

Fig. 4. Test of Giddings significant temperature as an approximator of $T_{eq,2}$ for propiophenone: △ = IGC retention index *vs* 1000 K/isothermal temperature; ▽ + × □ = experimental PTGC retention index *vs.* 1000 K/Giddings significant temperature for initial temperatures of 333.16, 353.16, 373.16 and 393.16 K, respectively. For each temperature, points from the bottom of the line upwards are for heating rates of 1.00, 2.00, 3.00, 5.00, 7.00, 10.00, 12.00 and 15.00 K min^{-1}.

higher initial column initial temperatures, the arithmetic mean (and to a slightly lesser extent the harmonic mean) is a better $T_{eq(2)}$ approximator than is the Giddings significant temperature. The same tendency applies for other eluents.

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