Journal of Chromatography, 248 (1982) 1–6
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 15,092

CORRECTION OF GAS CHROMATOGRAPHIC RETENTION VOLUMES FOR SMALL TEMPERATURE CHANGES

J. R. CONDER
Chemical Engineering Department, University College of Swansea, Singleton Park, Swansea SA2 8PP (Great Britain)

(Received April 25th, 1982)

SUMMARY

Two simple equations are proposed of sufficient accuracy for correcting retention volumes for small changes in column temperature. One equation (eqn. 1) is suitable for use when column temperature is sufficiently close to the boiling point; otherwise eqn. 2 is more accurate. The equations are derived and shown to be valid for most solutes over a wide range of gas–liquid chromatographic conditions.

INTRODUCTION

Since retention varies with temperature, retention volumes often have to be corrected for small changes in column temperature, *e.g.* when oven temperature drifts with change in ambient temperature. The need for a suitable correction equation arises in two applications of gas chromatography. In analytical work, identification and accurate quantitation of peaks depends on accurate determination of the retention volume: in particular, automatic data processing requires a simple means of correcting for variations in column temperature. Secondly, in applications to physicochemical measurement[1], retentions often need to be measured with great accuracy. The significance of the problem is seen in the fact that a temperature change of only 0.3°K is sufficient to change the retention by 1% or so, an amount which may be enough to vitiate measurement of a physicochemical property or cause wrong identification of a peak. Even with use of an internal standard, peaks can be misidentified because, as a second order effect, the relative retention may also change with temperature[2].

We will show that the correction can be made with the aid of the simple equation

$$\frac{\delta V_N}{V_N} = -9.7 \frac{\delta T_c}{T_c} \tag{1}$$

when column temperature is sufficiently close to the boiling point of the solute concerned, and otherwise with the equation

$$\frac{\delta V_N}{V_N} = -\frac{\delta T_c}{T_c}\left[\frac{17.1\ T_b}{T_c} - 7.4\right] \tag{2}$$

In these equations, V_N is the net retention volume, T_c and T_b are respectively the temperature of the column and the normal boiling point of the solute, in °K, and δV_N is the correction to be made to the retention volume for a change δT_c in column temperature. The negative sign arises because retention falls as temperature rises. Eqn. 2 reduces to eqn. 1 as $T_c \rightarrow T_b$. Eqn. 1 is independent of solute parameters.

We consider, first, the derivation of these equations, and then their accuracy and applicability.

DERIVATION OF EQUATIONS

Combining the Clausius–Clapeyron equation

$$\frac{1}{p^0}\frac{dp^0}{dT_c} = \frac{\lambda_c}{RT_c^2}$$

and Trouton's rule,

$$\tau = \lambda_b/T_b = 85\ \text{J mol}^{-1}\ {}^\circ\text{K}^{-1}$$

we obtain

$$\frac{\delta p^0}{p^0} = \frac{\tau}{R}\frac{\lambda_c T_b}{\lambda_b T_c}\frac{\delta T_c}{T_c} = 10.2\,\frac{\lambda_c T_b}{\lambda_b T_c}\frac{\delta T_c}{T_c} \tag{3}$$

where p^0 is the saturation vapour pressure of pure solute at column temperature T_c, λ its latent heat, τ is Trouton's constant and $R = 8.314$ J mol^{-1} °K^{-1}, the gas constant. Therefore, if the column temperature is close to the boiling point,

$$\frac{\delta p^0}{p^0} = 10.2\,\frac{\delta T_b}{T_b} \tag{4}$$

whence we have the useful rule of thumb that a temperature rise of 1°K raises the vapour pressure by *ca.* 3 % for a liquid boiling in the 310–380°K region, or 2.5 % for a liquid boiling in the range 380–450°K.

The net retention volume is given by

$$V_N = \frac{R\ T_c W_L}{\gamma\, p^0 M_L}$$

where W_L and M_L are the mass and molecular weight of liquid stationary phase in the column[3], and γ is the activity coefficient of solute at infinite dilution in the liquid at temperature T_c. Differentiating, we obtain

$$\frac{\delta V_N}{V_N} = \frac{\delta T_c}{T_c} - \frac{\delta p^0}{p^0} - \frac{\delta\gamma}{\gamma} \tag{5}$$

In many cases the third term, $\delta\gamma/\gamma$, is the smallest of the three on the right-hand side and a mean value of minus half the first term is assumed, as explained below. If, in addition, $T_c \approx T_b$, substitution of eqn. 4 in eqn. 5 yields eqn. 1, which is thereby proved.

If these assumptions are not satisfied, we obtain, instead of eqn. 1,

$$\frac{\delta V_N}{V_N} = -\frac{\delta T_c}{T_c}\left[\frac{\tau\,\lambda_c T_b}{R\,\lambda_b T_c} - 1 - \frac{T_c}{\gamma}\frac{d\gamma}{dT_c}\right]$$

$$= -\frac{\delta T_c}{T_c}\left[\frac{\tau}{R}\left\{1 + \frac{1}{\lambda_b}\frac{d\lambda}{dT}(T_c - T_b)\right\}\frac{T_b}{T_c} - 1 - \frac{T_c}{\gamma}\frac{d\gamma}{dT_c}\right] \tag{6}$$

The normal boiling point of a pure liquid is *ca.* two-thirds of its critical temperature[4]. Hence, from the universal normalised plot of latent heat of vaporisation against reduced temperature[5], we find

$$\frac{1}{\lambda_b}\cdot\frac{d\lambda}{dT}\bigg|_{T_b} = -\frac{1}{1.5\,T_b} \tag{7}$$

In eqn. 6, $d\lambda/dt$ is evaluated at a mean temperature between T_b and T_c. Accordingly we write

$$k = \left(\frac{d\lambda}{dT}\bigg|_{(T_b+T_c)/2} \bigg/ \frac{d\lambda}{dT}\bigg|_{T_b}\right) - 1 \tag{8}$$

noting that $k \ll 1$ since λ falls by only 0.15–0.3% for each 1°K rise in temperature around the normal boiling point. Combination of the last three equations and some manipulation then gives

$$\frac{\delta V_N}{V_N} = -\frac{\delta T_c}{T_c}\left[(1.67 + 0.67k)\frac{\tau\,T_b}{R\,T_c} - 0.67\frac{\tau}{R} - 0.67\frac{\tau k}{R} - 1 - \frac{T_c}{\gamma}\frac{d\gamma}{dT_c}\right] \tag{9}$$

This equation is simplified by assigning, as before, an average value of -0.5 to the final term within the square brackets and setting $k \approx 0$, giving

$$\frac{\delta V_N}{V_N} = -\frac{\delta T_c}{T_c}\left[\left(1.67\frac{\tau}{R}\right)\frac{T_b}{T_c} - \left(0.67\frac{\tau}{R} + 0.5\right)\right] \tag{10}$$

which yields eqn. 2 when $\tau = 85$ J mol^{-1} °K^{-1} and $R = 8.314$ J mol^{-1} °K^{-1}.

APPLICABILITY OF EQUATIONS

Because of the assumptions and approximations made in the derivation, the accuracy of eqns. 1 and 2 is affected by five considerations.

(1) Variation of activity coefficient with temperature

Inspection of published chromatographic data for a variety of solute–liquid phase systems shows that the last term within the square brackets in eqn. 9, (T_c/γ) $(\mathrm{d}\gamma/\mathrm{d}T_c)$, usually lies between 0 and -1, so contributing less than 10% to the square-bracketed summation in eqn. 9. Assigning the mean value -0.5 in deriving eqns. 1 and 2 means that the error in the equations from this source is usually less than 5%. However, charge transfer or other complexing interactions between solute and stationary phase (or occasionally pronounced steric effects) can give values of $(T_c/\gamma) \times (\mathrm{d}\gamma/\mathrm{d}T_c)$ as large as $+2$ or -5 or occasionally larger. Even larger variations in activity coefficient may be observed over narrow ranges of temperature in liquid crystalline transitions[6-8], in cases where a low-loaded liquid (usually a long straight-chain methylenic molecule) forms an oriented monolayer[9,10], or in other types of phase transition[11]. In these circumstances, both eqns. 1 and 2 break down.

In gas–solid chromatography, the analogue of the (T_c/γ) $(\mathrm{d}\gamma/\mathrm{d}T_c)$ term may be expected to be small for physically adsorbed solutes having heats of adsorption similar to their heats of liquefaction. However, in many cases the difference in the heats is too large[12] for this term to be neglected.

(2) Trouton's rule

Trouton's constant, τ, is 85 ± 6 J mol^{-1} °K^{-1} for most organic and inorganic liquids, solids and vapours, giving the constants shown in eqns. 1 and 2. The main exceptions are: liquids, such as water, alcohols and amines, which associate through hydrogen bonding in the liquid phase, giving high values of τ; carboxylic acids in which the hydrogen-bonding persists into the vapour phase, giving low values of τ; and some permanent gases and inorganic solids[13-15]. Examples of these solutes are given in Table I, together with corresponding revised values of the constants in eqns. 1 and 2.

TABLE I

REVISED CONSTANTS IN EQNS. 1 AND 2 FOR SOME SOLUTES WHICH DO NOT OBEY TROUTON'S RULE

Solute	*τ (J mol^{-1} °K^{-1})*	*Constant in eqn. 1*	*Constants in eqn. 2 from eqn. 10*	
		$\left(\frac{\tau}{R} - 0.5\right)$	$1.67\frac{\tau}{R}$	$0.67\frac{\tau}{R} + 0.5$
Most solutes (obeying Trouton's rule)	85 ± 6	9.7 ± 0.7	17.1 ± 1.2	7.4 ± 0.5
Water	109	12.6	21.9	9.3
Methanol	104	12.0	20.9	8.9
Ethanol	110	12.7	22.1	9.4
Methylamine	97	11.1	19.4	8.3
Dimethylamine	94	10.8	19.0	8.1
Formic acid	64	7.2	12.9	5.7
Acetic acid	62	7.0	12.5	5.5
Potassium chloride	100	11.5	20.1	8.6

(3) *Relation between boiling and critical temperatures*

In deriving eqns. 9 and 2 it is assumed that the ratio of the normal boiling point to the critical temperature is *ca.* two-thirds. Values of this ratio tabulated by Moelwyn-Hughes[4] range between extremes of 0.58, for certain small molecules containing less than five atoms, and 0.74 for long, unbranched hydrocarbons (*n*-decane). At these extremes, eqn. 2 is 5% in error, which is quite acceptable as a "correction to a correction".

(4) *Closeness of column temperature to boiling point*

When the boiling point of a solute is equal to column temperature, eqn. 2 reduces to eqn. 1. The effect of using a column temperature different from the boiling point may be examined by comparing eqns. 1, 2 and 9, which are successively more accurate in this order when $T_b \neq T_c$, and taking τ as 85 J mol^{-1} °K^{-1} and the final term in square brackets in eqn. 9 as -0.5. Values of k were obtained from eqn. 8 and the universal normalised plot of latent heats of evaporation against reduced temperature. The calculated errors due to difference between T_b and T_c are shown in Table II. The error in using eqn. 2 is *ca.* a quarter of that in eqn. 1. If a 10% error in δV_N is acceptable, eqn. 1 is useable up to values of $|T_b - T_c|$ of 12 and 25°K for solutes boiling at 230 and 470°K, respectively. With the same error and solutes eqn. 2 is useable up to *ca.* 45 and 100°K, respectively. The boiling points 230 and 470°K are quoted as representative of the more extreme values encountered in most gas–liquid chromatographic work, even though the technique is available for solutes boiling well outside this range.

TABLE II

ERROR IN $\delta V_N/V_N$ PREDICTED BY EQNS 1 AND 2 AS A FUNCTION OF DEVIATION OF T_b/T_c FROM UNITY

$\left\lvert\frac{T_c - T_b}{T_c}\right\rvert$	*Percentage error in*	
	Eqn. 1	*Eqn. 2*
0.05	9	2.5
0.1	*ca.* 20	5
0.2	>40	10

(5) *Size of δT_c*

The substitution of finite differences for differentials restricts the validity of eqns. 1 and 2 to small temperature corrections, δT_c. The error in both equations reaches *ca.* 2.7% when δT_c reaches 2°K and 5.5% at 4°K.

CONCLUSIONS

For making retention volume corrections to an accuracy of 10% in δV_N, eqn. 1 is useable at column temperatures within 12–25°K of the boiling point of the solute concerned. Eqn. 2, which is *ca.* four times as accurate, is useable up to temperatures differing by much more from the boiling point, *i.e.* by *ca.* 45–100°K for 10% accuracy. These ranges cover the great majority of column temperatures normally used: keeping the temperature in the general region of the boiling points of the solutes chromatographed not only ensures a satisfactory compromise between resolution and analysis time but also gives peaks whose symmetry is least sensitive to large samples. The simple form of these equations, particularly eqn. 1, which is solute-independent with few exceptions, makes them quick to apply and suitable for automatic data processing.

Since the equations are intended for obtaining small corrections, 10% accuracy in the correction term itself is usually sufficient. Both equations are accurate to this level or better for most combinations of organic or inorganic solutes with a liquid stationary phase, with the few exceptions listed under headings 1 and 2 above. The equations will cope with temperature changes δT_c up to at least 0.5°K for 0.15% accuracy in the corrected V_N, or 3°K for 1%.

REFERENCES

1 J. R. Conder and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, Chichester, 1979.
2 M. Riedmann, *Chromatographia*, 6 (1973) 129.
3 J. R. Conder and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, Chichester, 1979, Ch. 5.
4 E. A. Moelwyn-Hughes, *Physical Chemistry*, Pergamon Press, Oxford, 2nd ed., 1961, p. 603.
5 G. J. Su, *Ind. Eng. Chem.*, 38 (1946) 923; reported in J. M. Smith and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill, New York, 2nd ed., 1962, p. 134.
6 D. E. Martire, P. A. Blasco, P. F. Carone, L. C. Chow and H. Vicini, *J. Phys. Chem.*, 72 (1968) 3489.
7 L. C. Chow and D. E. Martire, *J. Phys. Chem.*, 75 (1971) 2005.
8 H. T. Peterson and D. E. Martire, *Mol. Cryst. Liq. Cryst.*, 25 (1974) 89.
9 J. Serpinet, *J. Chromatogr.*, 68 (1972) 9; *J. Chromatogr. Sci.*, 12 (1974) 833; *Chromatographia*, 8 (1975) 18.
10 J. Rayss and A. Waksmundzki, *J. Chromatogr.*, 217 (1981) 225.
11 Ref. 1, Ch. 7.
12 D. O. Hayward and B. M. W. Trapnell, *Chemisorption*, Butterworths, London, 2nd ed., 1964, Ch. VI.
13 J. S. Rowlinson, *Liquids and Liquid Mixtures*, Butterworths, London, 2nd ed., 1969, p. 26.
14 E. A. Moelwyn-Hughes, *Physical Chemistry*, Pergamon Press, Oxford, 2nd ed., 1961, p. 273.
15 G. M. Barrow, *Physical Chemistry*, McGraw-Hill, New York, 2nd ed., 1966, p. 532.