

## THERMODYNAMICS OF MIXTURES FROM GAS-LIQUID CHROMATOGRAPHY

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## INTRODUCTION

Gas-liquid chromatography finds increasing use for the determination of thermodynamic data. Following a suggestion by EVERETT AND STODDART<sup>1</sup> several workers have indicated that, from measurement of the variation of net retention volume of a solute with the pressure of the carrier gas, one may obtain the activity coefficient of the solute at infinite dilution ( $\gamma_1^\infty$ ) in the stationary liquid and the second virial coefficient ( $B_{12}$ ) characterising unlike pair interactions between solute vapour and carrier gas.

The treatment of DESTY *et al.*<sup>2</sup> leads to the equation:

$$\ln V_N = \ln k^\circ V^l + \beta p_0 J_2^3 \quad (1)$$

where  $V_N$  is the net retention volume, and  $k^\circ$  is the partition coefficient at zero pressure related to the activity coefficient ( $\gamma_1^\infty$ ) by:

$$\ln k^\circ = \ln \frac{n^l RT}{V^l \gamma_1^\infty p_1^\circ} - \frac{(B_{11} - v_1^\circ) p_1^\circ}{RT} \quad (2)$$

(where  $n^l$  is the number of moles and  $V^l$  the total volume of stationary liquid,  $p_1^\circ$  is the vapour pressure of the solute,  $v_1^\circ$  the molar of the solute and  $B_{11}$  the second virial coefficient of pure solute).

$\beta$  is related to the second virial coefficient ( $B_{12}$ ) by:

$$\beta = \frac{2B_{12} - v_1^\infty}{RT} \quad (3)$$

(where  $v_1^\infty$  is the partial molar volume of the solute at infinite dilution in the stationary liquid) and we have used the notation<sup>3</sup>:

$$J_m^n = \frac{n (p_i/p_o)^m - 1}{m (p_i/p_o)^n - 1} \quad (4)$$

where  $p_i$  and  $p_o$  are the column inlet and outlet pressures respectively.

EVERETT'S<sup>3</sup> treatment leads to the equation:

$$V_N = k^\circ V^l (1 + \beta p_0 J_3^4) \quad (5)$$

and CRUICKSHANK, WINDSOR AND YOUNG's<sup>4</sup> treatment leads to:

$$\ln V_N = \ln k^0 V^l + \beta p_0 J_3^4 \quad (6)$$

Each of these equations (1), (5) and (6) leads to the application of a different plotting procedure to experimental net retention volumes obtained over a range of pressure, if  $\gamma_1^\infty$  and  $B_{12}$  are to be determined. They cannot all be right. CRUICKSHANK, WINDSOR AND YOUNG<sup>4</sup> have investigated this problem rigorously and we present here a rather different approach which is both mathematically and conceptually simpler. The two approaches are complementary.

#### DESCRIPTION OF THE ELUTION PROCESS

We consider a column of total length  $L$  divided into equal segments of length  $dl$  each containing the same weight of stationary liquid. For an incompressible carrier gas, theories of chromatography give the following expression for the net retention volume per segment ( $v_N$ ) of a solute:

$$v_N = k \cdot v^l \cdot dl \quad (7)$$

Where  $v^l$  is the volume of stationary liquid per unit length of the column and  $k$ , the partition coefficient of the solute, is defined by:

$$k = C^l / C^g \quad (8)$$

( $C^l$  and  $C^g$  are the concentrations of solute in liquid and carrier gas respectively.)

Since:

$$v_N = t_N \cdot u \quad (9)$$

where  $t_N$  is the net retention volume per segment and  $u$  is the flow rate of the carrier gas, then:

$$t_N = \frac{k \cdot v^l \cdot dl}{u} \quad (10)$$

If the length of a segment is small the carrier gas pressure within that segment will be effectively constant and equation (10) will be valid for a compressible carrier gas. Since  $dl = L/N$  where  $N$  is the number of segments in the column, we may write:

$$t_N = \frac{L}{N} \cdot \frac{k v^l}{u} \quad (11)$$

Thus the total retention time for the column  $T_N$  is:

$$T_N = \frac{V^l}{N} \sum_{i=0}^N \frac{k}{u} \quad (12)$$

where  $V^l = L \cdot v^l$ , the total amount of stationary liquid on the column. To calculate  $T_N$  it is therefore necessary to know the values of  $k$  and  $u$  in each of the  $N$  segments of the column.

EVERETT<sup>3</sup> has shown that the partition coefficient,  $k$ , of a solute depends on the carrier gas pressure, and is given by:

$$k = k^0 \cdot e^{\beta p} \quad (13)$$

where  $k^0$  is the partition coefficient at zero pressure which is simply related to the activity coefficient of the solute at infinite dilution in the stationary liquid and  $\beta$  is simply related to the second virial coefficient ( $B_{12}$ ) characterising unlike pair interactions between the solute vapour and the carrier gas. In order to make use of equation (12) we need to know the variation of pressure along the length of the column and this can be obtained from Darcy's Law:

$$\frac{dp}{dl} = \frac{u \cdot n \cdot \alpha}{K} \quad (14)$$

where  $n$  is the viscosity of the carrier gas,  $\alpha$  is the cross-sectional area of the column and  $K$  is the permeability of the column packing. We shall consider the use of eqn. (14) to obtain the pressure ( $p$ ) at any point in the column in terms of the inlet pressure ( $p_i$ ) and the outlet pressure ( $p_o$ ) for an ideal and a non-ideal carrier gas.

(a) *Ideal carrier gas*

The pressure  $p$  is given by:

$$p = \left( p_i^2 - \frac{l}{L} (p_i^2 - p_o^2) \right)^{1/2} \quad (15)$$

where  $l$  is the distance from the column inlet. The variation of flow rate  $u$  with pressure for an ideal gas is:

$$u = \frac{p_o u_o}{p} \quad (16)$$

where  $u_o$  is the flow rate at column outlet. The pressure  $p$  in any segment can be calculated from eqn. (15) hence  $k$  and  $u$  in any segment can be calculated by use of eqns. (13) and (16). The total retention time may be obtained by summing over all the  $N$  segments according to eqn. (12). It is customary in GLC to convert retention volumes measured at outlet pressure to conditions of "mean column pressure" ( $\bar{p}$ ):

$$\bar{p} = p_o J_2^3 \quad (17)$$

Hence the net retention volume ( $V_N$ ) is given by:

$$V_N = T_N \cdot \bar{u} \quad (18)$$

where:

$$\bar{u} = \frac{p_o u_o}{\bar{p}}$$

For any chosen set of values of  $p_i$ ,  $p_o$ ,  $L$ ,  $k^\circ$ ,  $\beta$ ,  $u_o$  a single value of  $V_N$  may be calculated. This is conveniently carried out by means of a digital computer and the procedure is shown in Fig. 1.

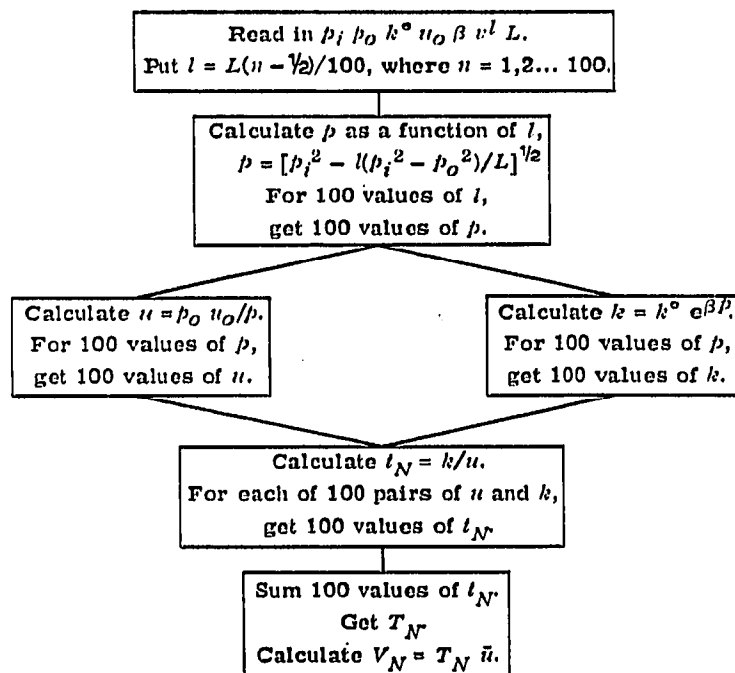


Fig. 1. Scheme of numerical calculation of net retention volume values.

### (b) Non-ideal carrier gas

In the case of a non-ideal carrier gas eqn. (16) is replaced by:

$$u = \frac{p_o u_o}{p} \left[ 1 - \frac{B(p_o - p)}{RT} \right] \quad (19)$$

where  $B$  is the second virial coefficient of the carrier gas, and eqn. (15) is replaced by:

$$p = \left[ p_i^2 - \frac{l}{L} (p_i^2 - p_o^2) - \frac{2B}{3RT} \left\{ \frac{p_i^3 - p^3}{p_i^2 - p_o^2} + \frac{p_i^3 - p_o^3}{p_i^2 - p_o^2} (p_i^2 - p^2) \right\} \right]^{1/2} \quad (20)$$

In calculating  $p$  by this equation it is sufficiently accurate to replace  $p$  in the third term on the r.h.s. of the equation by eqn. (15). The net retention volume  $V_N$  may then be calculated in an exactly analogous way to that shown in Fig. 1 by using the new eqns. (19) and (20) and assuming a value for  $B$ .

In this treatment we have ignored the small pressure-dependence of carrier gas viscosity but the results are unaffected by including a term for this effect. To assess the reliability of the summation procedure we can, in the case of an ideal gas, derive an expression for  $V_N$  that can be integrated analytically.

From eqn. (10) the total retention time  $T_N$  may be written:

$$T_N = \frac{V^l}{L} \int_0^L \frac{k}{u} \cdot dl \quad (21)$$

and substituting for  $h$  from eqn. (13) and for  $u$  from eqn. (16):

$$T_N = \frac{k^0 V^l}{p_0 u_0 L} \int_0^L p \cdot e^{\beta p} dl \quad (22)$$

Use of Darcy's law (eqn. 14) gives:

$$T_N = \frac{k^0 V^l K}{p_0 u_0 L n \alpha} \int_{p_i}^{p_0} \frac{p \cdot e^{\beta p}}{u} \cdot dp \quad (23)$$

and:

$$L = \int_0^L dl = \frac{K}{n \alpha} \int_{p_i}^{p_0} \frac{1}{u} \cdot dp \quad (24)$$

and substitution of eqn. (24) into eqn. (23) gives:

$$T_N = \frac{\frac{k^0 V^l}{p_0 u_0} \int_{p_i}^{p_0} p^2 \cdot e^{\beta p} \cdot dp}{\int_{p_i}^{p_0} p \cdot dp} \quad (25)$$

The integral  $\int p^2 \cdot e^{\beta p} \cdot dp$  is a standard integral<sup>5</sup> of which the solution is:

$$\int p^2 \cdot e^{\beta p} dp = \frac{e^{\beta p}}{\beta^3} (\beta^2 p^2 - 2\beta p + 2) \quad (26)$$

Therefore:

$$T_N = \frac{\frac{k^0 V^l}{p_0 u_0} \left[ \frac{e^{\beta p}}{\beta^3} (\beta^2 p^2 - 2\beta p + 2) \right]_{p_i}^{p_0}}{0.5 \left[ p^2 \right]_{p_i}^{p_0}} \quad (27)$$

we may finally express  $V_N$  as:

$$V_N = \frac{\frac{k^0 V^l J_3^2}{p_0} \left[ \frac{e^{\beta p}}{\beta^3} (\beta^2 p^2 - 2\beta p + 2) \right]_{p_i}^{p_0}}{0.5 \left[ p^2 \right]_{p_i}^{p_0}} \quad (28)$$

Table I gives a comparison between values of  $V_N$  obtained by analytical integration (eqn. 28) and by summation of eqn. (12). Results are given for various combinations of  $p_i$ ,  $p_0$  and  $\beta$  together with fixed values of  $k^0$ ,  $v^l$ ,  $u_0$  and  $L$ .

The results show that summation, with the number of segments ( $N$ ) equal to 100 or greater, gives results which agree to within 0.01% with those obtained by analytical integration.

TABLE I

VALUES OF  $V_N$  OBTAINED BY SUMMATION OF EQUATION (12)Analytical integration (equation 28) gives  $V_N = 50.0000$  in each case.

$\beta$ <i>atm</i> <sup>-1</sup>	$p_i$	$p_o$	Summation ( $N = \text{No. of segments}$ )		
			$N = 50$	$N = 100$	$N = 500$
-0.005	2	1	—	50.0001	—
-0.015	2	1	—	50.0005	50.0002
-0.015	3	1	—	—	49.9997
-0.015	4	1	50.0017	—	49.9999
-0.015	5	1	—	—	50.0002
-0.005	5	4	—	50.0000	—
-0.015	5	4	—	49.9999	—

## TESTING THE PLOTTING PROCEDURES

We can now test the various plotting procedures. The method is based on the ability of each plotting procedure to retrieve a specified value of  $\beta$ . To do this we first specify the value of  $\beta$  and then calculate values of  $V_N$  for a range of values of  $p_i$  and  $p_o$  (with fixed values of  $h^\circ$ ,  $v^l$ ,  $u_o$ ,  $L$ ,  $B$ ). These retention volumes are then treated as experimental data and subjected to the plotting procedures indicated by eqns. (1), (5) and (6) or by any other equation that might be proposed. In each case the data are "least-squares" fitted to a straight line as indicated by each equation. A comparison of assumed and retrieved values of  $\beta$  is given in Table II, the first six cases examined are of an ideal carrier gas, the other values are of a non-ideal carrier gas whose second virial coefficient is  $+20 \text{ cm}^3 \text{ mole}^{-1}$  and most carrier gases used in GLC do not have second virial coefficients greater than this in magnitude. It is seen that we have varied the conditions  $p_i$  and  $p_o$  considerably so as to test the equations over a wide range of possible experimental conditions. In all cases examined, except one, eqn. (6) retrieves  $\beta$  consistently most accurately. In this one case agreement for eqn. (5) is fortuitous, as the value of  $\beta$  retrieved is very sensitive to the value of  $B$ .

TABLE II

A COMPARISON OF ASSUMED AND RETRIEVED VALUES OF  $\beta$ 

$\beta$ assumed <i>atm</i> <sup>-1</sup>	$B$ <i>cm</i> <sup>3</sup> · <i>mole</i> <sup>-1</sup>	$p_i - p_o$ <i>atm.</i>	$p_o$ <i>atm.</i>	$\beta$ retrieved ( <i>atm</i> <sup>-1</sup> )		
				Equation (1)	Equation (5)	Equation (6)
-0.00500	—	1	1-15	-0.00498	-0.00480	-0.00500
-0.01500	—	1	1-15	-0.01495	-0.01336	-0.01500
-0.01500	—	0.5	1-15	-0.01499	-0.01338	-0.01500
-0.01500	—	1	10-50	-0.01500	-0.01033	-0.01500
-0.01500	—	1-7	1	-0.01713	-0.01430	-0.01495
-0.03000	—	1	1-15	-0.02990	-0.02403	-0.03000
-0.00500	+20	1	1-15	-0.00497	-0.00479	-0.00497
-0.01500	+20	1	1-15	-0.01494	-0.01335	-0.01499
-0.01500	+20	1-7	1	-0.01854	-0.01537	-0.01618
-0.03000	+20	1	1-15	-0.02989	-0.02403	-0.02999

assumed. Eqn. (1) is almost as successful as eqn. (5) though it fails where pressure drops ( $p_i - p_0$ ) are large. The values of  $\beta$  retrieved by the above procedure are the same (to four significant figures) as those obtained by CRUICKSHANK, WINDSOR AND YOUNG, who used a different equation. Although the procedure used by the latter authors is mathematically more elegant the method described here has the advantage that the summation procedure has a physical significance.

The values of  $k^{\circ}V^i$  retrieved by the equations may be examined in a similar way, the intercepts of the plots do not vary greatly, however, and retrieval of  $\beta$  is a much more sensitive test of the equations.

The above treatment shows that to derive reliable thermodynamic data from GLC, carrier gases which show small deviations from ideality should be used with columns across which the pressure drop is small; and that eqn. (6) should be used to analyse the retention volume data.

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#### SUMMARY

A theory for obtaining mixed second virial coefficients of a solute-carrier gas mixture and the activity coefficient of the solute at infinite dilution in the stationary liquid is given. The three approximate equations reported in the literature are compared with the exact relationship by numerical integration. The equation of CRUICKSHANK, WINDSOR AND YOUNG is shown to retrieve assumed values consistently most accurately.

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