

# GAS-LIQUID CHROMATOGRAPHY

## A CONTRIBUTION TO THE THEORY OF SEPARATION IN OPEN HOLE TUBES

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### INTRODUCTION

The degree of separation obtained in a chromatographic column depends upon the overlap of the elution curves of the components emerging successively from the column. The separation performance will be introduced as a measure of the degree of separation between two components irrespective of their relative volatility. The proposed measure will fully describe the influence of the physical properties of the components, the column properties and the operating conditions upon the separation. It has become common practice to consider the number of theoretical plates ( $n$ ), or the length of a column equivalent to a theoretical plate (H.E.T.P.), as a measure of the separating capacity of gas chromatographic columns. The latter concept originates from the theory of distillation, where it has proved its practical value. It is, however, an empirical quantity and the theory, especially in packed columns, does not deal with the mechanisms that determine this quantity.

In chromatography, when comparing a coated capillary column and a packed column, both columns having an equal number of theoretical plates for a given component, it appears that with the latter the degree of separation is, as a rule, appreciably higher. This effect will be more pronounced at high vapour pressures of the components to be separated. From this it follows that the theoretical plate concept is only to a limited extent suitable to describe column resolution. It will be shown that the height equivalent to a transfer unit,  $H_{OG}$ , is a true measure of what a column can do in separating a given pair of components, independent of their relative volatility.

### PRACTICAL ASPECTS OF THE TRANSFER UNIT

The degree of separation,  $S$ , of two neighbouring components will be simply defined as:

$$S = \frac{t_2 - t_1}{w} \quad (1)$$

In this expression the retention times  $t_1$  and  $t_2$  are obtained by dividing the column length  $l$  by  $v_1$ , and  $v_2$ , the velocities of components 1 and 2 respectively;  $w$  is the mean width of the two components (in time units) at the baseline, between the tangents to

their elution curves. The number of theoretical plates,  $n$ , is related to  $t$  and  $w$  by:

$$w = \frac{4t}{\sqrt{n}} \quad (2)$$

If  $w$  is small as compared to  $t$ , for  $S$  may be written:

$$S = \left( \frac{v_1}{v_2} - 1 \right) \frac{\sqrt{n}}{4} \quad (3)$$

The elution velocity of a component is equal to the gas velocity  $v_0$  times its fractional occurrence in the gas phase. If  $y$  and  $x$  are the mole fractions of a component in the gas phase and in the stationary phase respectively, the number  $N_g$  of moles in the gas phase can be expressed by:

$$N_g = y \frac{V_g p \times 273}{T \times 22.4 \cdot 10^3} = y \frac{V_g p}{82 T} \quad (4)$$

and the number of moles  $N_s$  in the stationary phase by:

$$N_s = x \frac{V_s \rho_s}{M_s} \quad (5)$$

The relation between  $x$  and  $y$  at phase equilibrium reads (for ideal gases):

$$\frac{x}{y} = \frac{p}{\gamma P} \quad (6)$$

The fractional occurrence of a component in the gas phase is equal to:

$$\frac{N_g}{N_g + N_s}$$

which by applying eqms. (4), (5) and (6) leads to:

$$v = v_0 \left( 1 + \frac{82 V_s \rho_s T}{\gamma P V_g M_s} \right)^{-1} = \frac{v_0}{1 + k} \quad (7)$$

where  $k$ , the capacity ratio is:

$$k = \frac{82 V_s \rho_s T}{\gamma P V_g M_s} \quad (8)$$

The relative elution velocity  $v_1/v_2$  can now be written as:

$$\frac{v_1}{v_2} = \frac{1 + k_2}{1 + k_1} \quad (9)$$

The relative volatility of two components is defined as:

$$\alpha_{1,2} = \frac{\gamma_1 P_1}{\gamma_2 P_2} = \frac{k_2}{k_1} \quad (10)$$

Substituting eqns. (9) and (10) in eqn. (3):

$$S = \frac{k_1}{1 + k_1} (\alpha_{1,2} - 1) \frac{\sqrt{n}}{4} \quad (10)$$

(For closely neighbouring components,  $k_1 \cong k_2$ ,  $k_1$  in eqn. (11) may be replaced by  $k$ .)

From eqn. (11) it will be evident that the degree of separation, as defined by eqn. (1), is not determined only by  $\alpha_{1,2}$  and  $n$ , but also by the value of  $k$ . The factor  $k/(1+k)$  becomes of importance if 1 is not small as compared to  $k$ , that is for small values of  $k$  (say  $< 5$ ). From eqn. (8) it follows that  $k$  will be small if  $V_s/V_g$  is small (thin liquid layers) and  $P$ , the vapour pressure of the pure component is large (high temperatures).

*The number of transfer units  $N_{OG}$*

CHILTON AND COLBURN<sup>1</sup> defined the number of transfer units  $N_{OG}$  on overall gas base as:

$$N_{OG} = \int_{c_1}^{c_2} \frac{dc}{c^* - c} \quad (12)$$

and the height of a transfer unit as:

$$H_{OG} = \frac{l}{N_{OG}} \quad (13)$$

VAN DEEMTER, ZUIDERWEG AND KLINKENBERG<sup>2</sup> have shown the relation between  $N_{OG}$  and  $n$  to be:

$$N_{OG} = 2 \left( \frac{k}{1+k} \right)^2 n \quad (14)$$

or:

$$\sqrt{0.5 N_{OG}} = \frac{k}{1+k} \sqrt{n}$$

by substituting  $N_{OG}$  for  $n$  in eqn. (11):

$$S = (\alpha_{1,2} - 1) \frac{\sqrt{0.5 N_{OG}}}{4} \quad (15)$$

According to this equation the degree of separation of two components is governed only by their relative volatility and the number of transfer units. Whereas the number of theoretical plates is a measure of column performance for large values of  $k$  only, the number of transfer units is a true measure of the separation performance irrespective of the value of  $k$ .

The number of transfer units can be readily obtained from the chromatogram:

$$N_{OG} = 32 \left( \frac{t - t_0}{w} \right)^2 \quad (16)$$

\* The problem of the imperfection of the theoretical plate concept has among others also been recognized by HALASZ<sup>3</sup>, who introduced the concept of a modified theoretical plate containing the same parameters.

where  $t$  is the retention time of the component and  $t_0$  that of the carrier gas (non-retained component).

To illustrate eqn. (15) the separation data are given of the system methyl ethyl ketone-methyl isopropyl ketone in a capillary column coated with dinonyl phthalate (see Table I).

TABLE I

SEPARATION OF METHYL ETHYL KETONE-METHYL ISOPROPYL KETONE IN A COPPER CAPILLARY COLUMN  
Length of the capillary 15 m, inner diameter 0.25 mm. Coating: dinonyl phthalate, coating thickness 1.5  $\mu$ ; nitrogen velocity 16.7 cm/sec at 22.5°; inlet pressure 1.28 kg/cm<sup>2</sup>; outlet pressure 1.00 kg/cm<sup>2</sup>.

Separation data	Temperature (°C)				
	22.5	50	75	100	125
$P_{11}^1$	0.1117	0.385	0.860	1.87	3.79
$P_{22}^1$	0.034	0.166	0.550	1.51	3.54
$t_{11}$	20.9	9.5	6.8	5.4	4.95
$w_{11}$	0.90	0.35	0.21	0.15	0.125
$t_{22}$	35.5	13.5	8.7	6.25	5.47
$w_{22}$	1.50	0.45	0.27	0.175	0.135
$t_0$	3.00	3.26	3.47	3.64	3.84
$\bar{n}$	8,800	13,100	16,700	20,600	25,600
$N_{OG,1}$	12,680	10,140	8,040	4,580	2,520
$N_{OG,2}$	15,040	16,600	12,000	7,100	4,680
$\alpha_{1,2}$	1.82	1.64	1.57	1.48	1.46
$H_{11}$	5.95	1.90	0.96	0.48	0.29
$H_{22}$	10.8	3.14	1.50	0.72	0.43
$S$	12.2	10.0	7.9	5.2	4.0

The variation of the number of transfer units and of the number of theoretical plates with temperature and with degree of component separation are presented in Figs. 1 and 2 respectively.

#### THEORY OF THE TRANSFER UNIT

The mass transfer in a column is governed by: (a) rate of mass transfer in the gas phase, (b) rate of mass transfer in the stationary phase, and (c) longitudinal and radial diffusion in the gas phase.

##### Mass transfer in the gas phase

JAKOB<sup>4</sup> derived an exact equation describing the heat transfer in a round tube for constant wall temperature and laminar gas flow. By analogy between heat and mass transfer his equation can be rewritten as:

$$\frac{c_0 - \bar{c}_0}{c_0 - c_i} = 1 - 0.820 e^{-m_1 l} - 0.097 e^{-m_2 l} - 0.0135 e^{-m_3 l} \quad (17)$$

where:

$$m_0 = \frac{3.66 D_g}{r^2 v_0}; m_1 = \frac{22.1 D_g}{r^2 v_0} \text{ and } m_2 = \frac{53.0 D_g}{r^2 v_0}$$

The distribution of a component in a capillary tube can be approximated by a Gaussian curve. Consequently the integrated driving force over the length of the

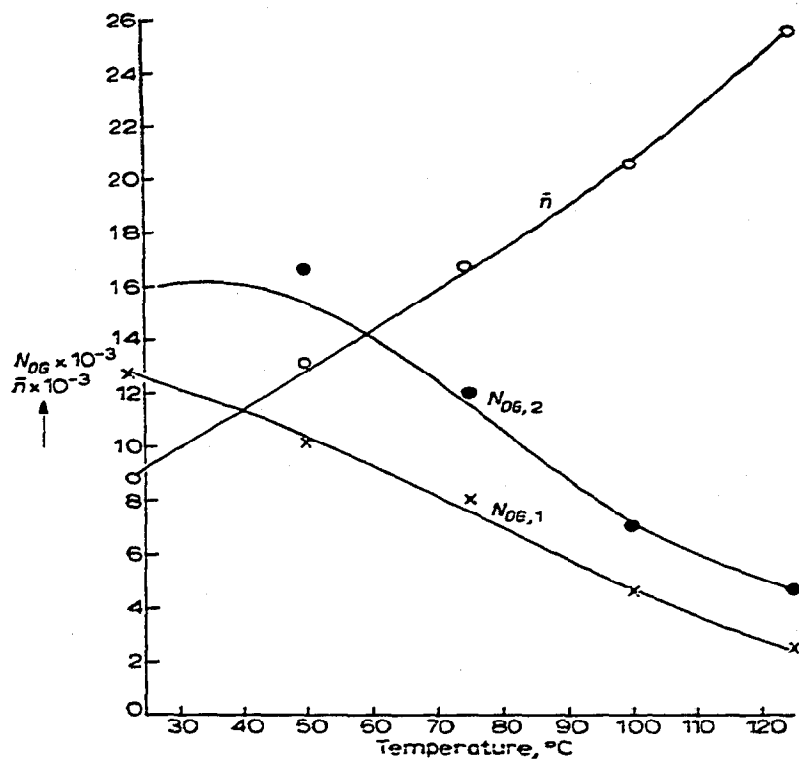


Fig. 1. Effect of temperature upon number of theoretical plates and number of transfer units

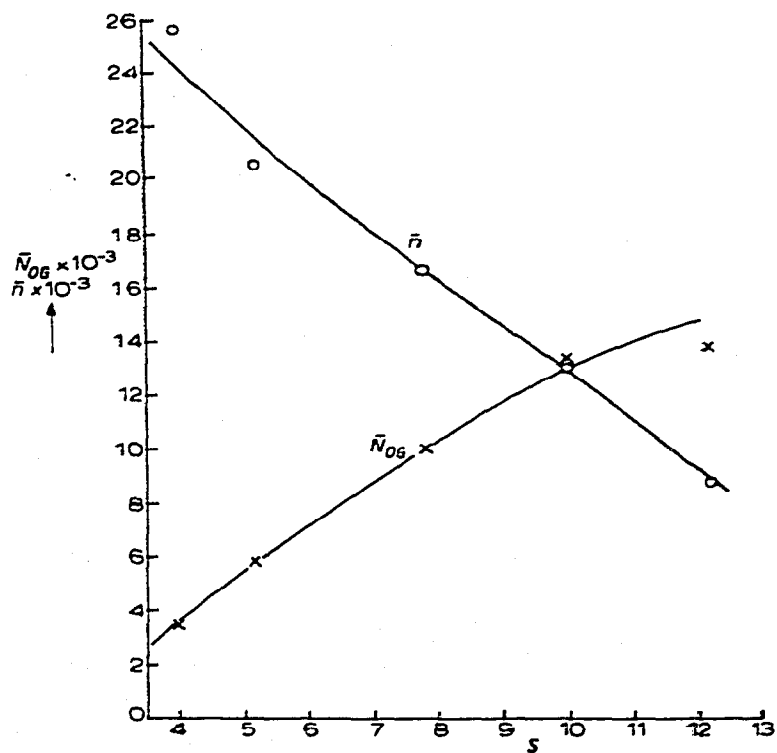


Fig. 2. Effect of number of theoretical plates and of number of transfer units on degree of component separation.

capillary is zero. In JAKOB's model a zero driving force is equivalent to  $\theta \rightarrow \infty$  ( $l \rightarrow \infty$ ). For large values of  $l$  eqn. (17) reduces to:

$$\frac{c_0 - c_\theta}{c_0 - c_i} = 1 - 0.820 e^{-\frac{3.66 D_g l}{r^2 \tau_0}} \quad (18)$$

The amount of mass  $N$ , transferred during a time  $\theta$  is given by:

$$N = V_g (c_\theta - c_0) \quad (19)$$

From eqns. (18) and (19) it follows that:

$$-N = V_g (c_0 - c_i) \left( 1 - 0.820 e^{-\frac{3.66 D_g l}{r^2 \tau_0}} \right) \quad (20)$$

Replacing  $l/v_0$  by  $\theta$  and differentiating eqn. (20) with respect to  $\theta$ :

$$\frac{dN}{d\theta} = -V_g (c_0 - c_i) 0.820 e^{-\frac{3.66 D_g l}{r^2 \tau_0}} \cdot \frac{3.66 D_g}{r^2} \quad (21)$$

The mass transfer coefficient  $K_g$ , in the gas phase is defined as:

$$\frac{dN}{d\theta} = -K_g (c_\theta - c_i) \quad (22)$$

and eqn. (21) may be modified to:

$$K_g = \frac{c_0 - c_i}{c_\theta - c_i} \frac{3.66 D_g}{r^2} 0.820 V_g e^{-\frac{3.66 D_g l}{r^2 \tau_0}} \quad (23)$$

From eqns. (23) and (18) it follows that:

$$K_g = \frac{3.66 D_g}{r^2} V_g \quad (24)$$

#### *Mass transfer coefficient in the stationary phase*

For a constant interfacial concentration NEWMAN<sup>5</sup> derived for the mass transfer in a slab:

$$\frac{c_\theta - c_i}{c_0 - c_i} = \frac{8}{\pi^2} \left( e^{-\frac{D_s \theta \pi^2}{4z^2}} + \frac{1}{9} e^{-\frac{9 D_s \theta \pi^2}{4z^2}} + \frac{1}{25} e^{-\frac{25 D_s \theta \pi^2}{4z^2}} + \dots \right) \quad (25)$$

For the same reasons as apply to the gas phase the relation reduces to:

$$\frac{c_\theta - c_i}{c_0 - c_i} = \frac{8}{\pi^2} e^{-\frac{D_s \theta \pi^2}{4z^2}} \quad (26)$$

The mass  $N$  transferred in time  $\theta$  is:

$$N = V_s (c_\theta - c_0) \quad (27)$$

Substitution and differentiation to  $\theta$  gives::

$$\frac{dN}{d\theta} = -V_{ss} (\alpha_0 - \alpha_i) \frac{8 D_s r^2}{\pi^2 4 z^2} e^{-\frac{D_s \theta r^2}{4 z^2}} \quad (28)$$

Again the coefficient of mass transfer  $K_s$  in the stationary phase is::

$$\frac{dN}{d\theta} = -K_s (\alpha_0 - \alpha_i) \quad (29)$$

which leads to:

$$K_s = V_{ss} \frac{\pi^2 D_s}{4 z^2} \quad (30)$$

#### OVERALL NUMBER OF TRANSFER UNITS IN THE GAS PHASE

According to the double film theory::

$$\frac{1}{K_{OG}} = \frac{1}{K_g} + \frac{K}{K_s} \quad (31)$$

where  $K_{OG}$  represents the overall coefficient of mass transfer on gas base and

$$K = \frac{\alpha_g}{\alpha_s} \text{ (equilibrium constant).}$$

From:

$$N_{OG} = \int_{\alpha_i}^{\alpha_0} \frac{d\alpha}{\alpha^* - \alpha} = \frac{K_{OG} \Delta}{G} \quad (32)$$

and:

$$H_{OG} = \frac{l}{N_{OG}} = \frac{lG}{K_{OG} \Delta} \quad (33)$$

for a capillary column it is derived::

$$H_{OG} = \frac{u_0 V_g}{K_{OG}} \quad (34)$$

After substituting eqns. (24), (30) and (31) into eqn. (34)::

$$H_{OG} = \frac{u_0 r^2}{3.66 D_g} + K \frac{4 z^2 u_0 V_g}{\pi^2 D_s V_{ss}} = \frac{u_0 r^2}{3.66 D_g} + \frac{\pi 4 z^2 u_0}{k \pi^2 D_s} \quad (35)$$

#### Radial and longitudinal diffusion

From a study by WESSENER<sup>6</sup> the effect of radial and longitudinal diffusion on the H.E.T.P. can be obtained:

$$\text{H.E.T.P.} = \frac{u_0 r^2}{24 D_g} + \frac{2 D_g}{u_0} \quad (36)$$

or in terms of transfer units:

$$H_{OG} = \frac{(1+k)^2}{k^2} \left( \frac{v_0 r^2}{48 D_g} + \frac{D_g}{v_0} \right) \quad (37)$$

The overall transport in the capillary column is obtained by adding the heights of the transfer units for the different transport phenomena:

$$H_{OG} = \frac{(1+k)^2}{k^2} \frac{D_g}{v_0} + \frac{1+2k+14k^2}{48 k^2} \frac{v_0 r^2}{D_g} + \frac{1}{k} \frac{4 v_0 z^2}{\pi^2 D_s} \quad (38)$$

The degree of separation of two components is then:

$$S = (\alpha_{1,2} - 1) \left[ \frac{(1+k)^2}{k^2} \frac{D_g}{v_0} + \frac{1+2k+14k^2}{48 k^2} \frac{v_0 r^2}{D_g} + \frac{1}{k} \frac{4 v_0 z^2}{\pi^2 D_s} \right]^{-1/2} \left( \frac{l}{32} \right)^{1/2} \quad (39)$$

#### CONCLUSION

The H.E.T.P. concept in gas-liquid chromatography might be misleading. The example represented in Fig. 2, clearly demonstrates that the operating conditions leading to an increase of the number of theoretical plates result in a decrease of the separation. The number of transfer units, however, is the exact measure of separation performance.

From eqn. (38) it can be deduced that for low values of  $k$  ( $k < 5$ ) the number of transfer units decreases sharply with a decrease of  $k$ . The effect upon  $k$ , by the coating thickness, capillary diameter, vapour pressure of component, temperature and properties of the stationary phase follows from eqn. (8).

The height of a transfer unit, for most practical purposes, will be controlled by the rate of mass transfer in the stationary phase. The relevant term in eqn. (38) reads in physical units:

$$0.005 \frac{\gamma P}{T} \frac{M_s}{\rho_s D_s} r v_0 z \quad (40)$$

This expression shows the significance of small capillary diameters, low molecular weight of the stationary phase, low gas velocity and thin coating layers. The first derivatives with respect to  $T$  of  $\gamma P/T$  and of  $r/D_s$  are positive and negative respectively and not of the same order of magnitude. Roughly at values of  $\gamma P$  between 0.5 and 1.0 the ratio  $\gamma P/T D_s$  will pass through a minimum.

In eqn. (38) the diffusion coefficient in the gas phase,  $D_g$ , is the only parameter that is pressure dependent. Low pressures result in high values of  $D_g$ . At very low pressures, the height of a transfer unit according to eqn. (38) will be controlled by the first term, representing the longitudinal diffusion.

#### LIST OF SYMBOLS

- $c_0$  = concentration after time zero (g/cm<sup>3</sup>)
- $c_\theta$  = concentration after time  $\theta$  (g/cm<sup>3</sup>)
- $c_i$  = concentration at interphase gas-stationary phase (g/cm<sup>3</sup>)
- $c^*$  = concentration in one phase in equilibrium with concentration in the other phase (g/cm<sup>3</sup>)



- $e$  = base of natural logarithms  
 $D_g$  = diffusion coefficient in the gas phase (cm<sup>2</sup>/sec)  
 $D_s$  = diffusion coefficient in the stationary phase (cm<sup>2</sup>/sec)  
 $G$  = gas rate (cm<sup>3</sup>/sec)  
 $H_{OG}$  = height of a transfer unit, based on gas-film resistance (cm)  
H.E.T.P. = height equivalent to a theoretical plate (cm)  
 $K_g$  = mass transfer coefficient in the gas phase (cm<sup>2</sup>/sec)  
 $K_s$  = mass transfer coefficient in the stationary phase (cm<sup>2</sup>/sec)  
 $K_{OG}$  = overall gas phase mass transfer coefficient (cm<sup>2</sup>/sec)  
 $K = c_g/c_s$ , equilibrium constant  
 $k$  = ratio of quantity of component in stationary phase and in gas phase  
 $l$  = length of column (cm)  
 $M_s$  = molecular weight of stationary phase (g/mole)  
 $N_{OG}$  = number of transfer units  
 $n$  = number of theoretical plates  
 $N$  = mass transferred (g/cm<sup>2</sup>)  
 $O$  = area of interphase gas phase-stationary phase  
 $p$  = pressure (atm)  
 $P$  = vapour pressure of component (atm)  
 $r$  = inner radius of capillary (cm)  
 $S = (t_1 - t_2)/w$  degree of separation  
 $T$  = temperature (°K)  
 $t$  = retention time of a component emerging from column (sec)  
 $t_0$  = retention time of air peak (sec)  
 $v$  = velocity of component in column (cm/sec)  
 $v_0$  = average velocity of gas stream in column (cm/sec)  
 $V_g$  = volume of gas phase/unit interphase (cm)  
 $V_s$  = volume of stationary phase/unit interphase (cm)  
 $w$  = basewidth of component (sec)  
 $x$  = mole fraction of component in stationary phase  
 $y$  = mole fraction of component in gas phase  
 $z$  = thickness of stationary phase (cm)  
 $\alpha_{1,2} = \gamma_1 P_1 / \gamma_2 P_2$  relative volatility  
 $\gamma$  = activity coefficient of component  
 $\rho_s$  = density of stationary phase (g/cm<sup>3</sup>).

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## SUMMARY

The height equivalent to a transfer unit ( $H_{OG}$ ) is, as opposed to the height equivalent to a theoretical plate (H.E.T.P.), an exact measure of the separation performance of gas-liquid chromatography columns.

A relation between physical properties of the stationary phase, physical properties of components to be separated, dimensions and operating conditions of capillary columns on the one hand and the  $H_{OC}$  on the other hand is derived. It is shown that a decrease of  $k$ , the capacity ratio of stationary phase to gas phase for a given component, results in an increase of the  $H_{OC}$  and a decrease in the H.E.T.P.

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