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# CONTRIBUTION TO THE THEORY OF OPEN-TUBULAR (CAPILLARY) COLUMNS IN GAS–LIQUID CHROMATOGRAPHY*

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SUMMARY

The HETP and parallel diffusion and mass transfer processes in open-tubular (capillary) columns are discussed. The factors influencing the separation of peaks are incorporated into an extended Golay equation. The new equation has been tested in practice with both classical wall-coated capillaries and new types of open-tubular columns (support coated, porous layer, etc.). The parameters so derived lead to important correlations with optimal operating conditions ($\bar{u}_{opt}$, HETP$_{min}$, dynamic equilibrium).

INTRODUCTION

It is well known that in modern gas–liquid chromatography (GLC) the best separations are achieved with open-tubular (capillary) columns. The widespread use of capillary columns justifies the theoretical and practical discussion given here, despite the fact that many of the basic problems were solved over 15 years ago[1-7]. The treatment here is comparable to our previous investigations of the effectiveness of packed columns[8-10], based on the results of Costa Neto *et al.*[11]. For a long time the theory could not be tested with our practical results because the half-width (the peak width at half-height), which has a key role in theoretical investigations, could not be determined with sufficient precision when using capillary columns. Eventually we managed to determine the half-widths precisely, using a Hewlett-Packard 3388A reporting integrator.

THEORETICAL

For open-tubular columns, Golay[1] assumed that the velocity of the carrier gas is constant, even inside a gas packet (*i.e.*, the volume of the sample introduced into the column). Thus he was able to solve the general vectorial differential diffusion equation. The carrier gas changes its velocity in GLC in both the gas packet and in the column. Consequently, neglecting the change in velocity inside a gas packet

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* In memory of Professor László Erdey on the 10th anniversary of his death.

could result in errors. Some workers[12,13] have observed the change in the velocity of the carrier gas when an eluted gas packet had just left the column ("surge effect"). This effect has generally been interpreted in terms of a surplus of the eluted substance that has just left the stationary phase at the end of the column. Schay[14] demonstrated the incorrectness of this hypothesis. A gas packet has no longitudinal mobility in the stationary phase and so it can only go forward together with the carrier gas after it has left the stationary phase. This effect demonstrated by Schay[14] is real, not only at the end of the column but also at any cross-section of the column. Thus the "surge effect" provides conclusive proof of a change in the velocity of carrier gas inside a gas packet. On the other hand, the change in the velocity of the carrier gas equals the acceleration of the carrier gas. This requires modification of Golay's partial differential equation (ref. 1, eqn. 7) by $\partial(vf)/\partial x$, so the equation will be inhomogeneous:

$$D\left(\frac{\partial^2 f}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial f}{\partial r} + \frac{\partial^2 f}{\partial x^2}\right) = \frac{\partial f}{\partial t} + \frac{\partial(vf)}{\partial x} \tag{1}$$

where

$D$ = diffusion coefficient of sample in gas phase (cm$^2$/sec);
$f$ = gas packet density, normalized to unity (cm$^{-1}$);
$r$ = radial ordinate (cm);
$x$ = ordinate in direction of flow (cm);
$t$ = real time (sec);
$v$ = linear velocity of carrier gas (cm/sec).

The solution of this inhomogeneous partial differential equation is possible by iteration. Pethő[15] solved this equation by assuming that the velocity of longitudinal diffusion could be neglected.

Our iterative solution of the extended partial differential equation is as follows:

$$\text{HETP} = \frac{4\sqrt{D_G C'}}{3} + \frac{1}{\sqrt{3}}\left(\frac{2D_G}{\bar{u}} + C'\bar{u}\right) + \frac{1}{4\sqrt{D_G C'}}\left[\left(\frac{2D_G}{\bar{u}}\right)^2 + (C'\bar{u})^2\right] \tag{2}$$

where

HETP = $H$ = height equivalent to a theoretical plate (cm);
$D_G$ = diffusion coefficient of solute in gas phase at the column temperature with a pressure $p_{i,\text{opt}}$ of the carrier gas (cm$^2$/sec);
$p_{i,\text{opt}}$ = inlet pressure of the carrier gas (MPa/cm$^2$) at HETP$_{\text{min}}$;

$$C' = \frac{11V_N^2 + 6V_N V_G + V_G^2}{(V_N + V_G)^2}\cdot\frac{r^2}{24D_G} + \frac{8d_f^2}{\pi^2 D_L}\cdot\frac{V_N V_G}{(V_N + V_G)^2} \tag{3}$$

$V_N$ = net retention volume (ml of carrier gas);
$V_G$ = free gas volume of capillary column (cm$^3$);
$r$ = internal radius of capillary column (cm);
$d_f$ = stationary phase film thickness (cm);

$D_L$       = diffusion coefficient of solute in stationary phase at the column temperature with a pressure $p_{i,\text{opt}}$ of the carrier gas (cm²/sec);

$\bar{u}$       = average linear velocity of the carrier gas (cm/sec);

$\pi$       = 3.1416.

It must be mentioned that eqn. 3 differs from the usual form[1] and because of this it has some computing advantages. From

$$k' = V_N/V_G \tag{4}$$

and

$$k' + 1 = \frac{V_N + V_G}{V_G} \tag{5}$$

where $k'$ is the capacity ratio, eqn. 2 can be expressed in a simplified form:

$$H = A + \frac{B}{\bar{u}} + C\bar{u} + \frac{D}{\bar{u}^2} + E\bar{u}^2 \tag{6}$$

where

$$A = 4\sqrt{D_G C'}/3 \tag{7}$$

$A$ is a factor describing the overall effect on the peak broadening of the geometry of the capillary (internal and spiral diameter, etc.), the characteristics of the capillary (material, quality and method of preparation, distribution of the liquid film and/or porous layer, etc.) and their interactions with the investigated substance at the column temperature with a pressure $p_{i,\text{opt}}$ of the carrier gas. $A$ (cm) is independent of the carrier gas flow-rate.

$$B = 2D_G/\sqrt{3} \tag{8}$$

where $B$ (cm²/sec) is a factor describing the longitudinal molecular diffusion.

$$C = C'/\sqrt{3} \tag{9}$$

where $C$ (sec) is a factor characterizing the mass transfer of the solute.

$$D = D_G^2/\sqrt{D_G C'} \tag{10}$$

where $D$ (cm³/sec²) is a factor describing the effect of the acceleration of the solute molecules on the diffusion. The dimensions represent the carrier gas flow acceleration.

$$E = C'^2/4\sqrt{D_G C'} \tag{11}$$

where $E$ (sec$^2$/cm) is a factor describing the effect of the acceleration of the solute molecules on the mass transfer. The dimensions represent the reciprocal of the carrier gas linear acceleration.

The acceleration of the solute molecules required the introduction of $D$ and $E$. The published equations did not take account of acceleration of the solute molecules, although it is obvious that the sorbed solute molecules lost their velocities in the stationary phase. A solute packet has no longitudinal mobility in the stationary phase. After their desorption, the solute molecules will be accelerated to the flow-rate of the carrier gas and will then be moved to their sorption together with carrier gas, then their velocities will be zero again, they will be desorbed again, accelerated again, and so on. Thus, accelerations of solute molecules are also important parts of the chromatographic process involving elution, e.g., GLC. Of course, accelerations of solute molecules have effects both on diffusion and mass transfer processes. These effects were considered by the introduction of $D$ and $E$ terms, independently of the type of the columns used [coated, open-tubular (capillary) columns (wall-coated open-tubular, WCOT; support-coated open-tubular, SCOT; porous-layer open-tubular, PLOT; etc.)].

For the investigation of the half-width we started from Glueckauf's equation[6]:

$$n = 5.545 \left(\frac{t_R}{d}\right)^2 \tag{12}$$

where

$n$ = number of theoretical plates;
$t_R$ = retention time of the substance (sec);
$d$ = peak width at half-height (half-width) (sec).

Let us express the retention time $(t_R)$ from the following equation:

$$V_N = \bar{u}qt_R - V_G \tag{13}$$

where

$V_N$ = net retention volume (ml of carrier gas);
$\bar{u}$ = average linear carrier gas velocity (cm/sec);
$q$ = cross-section of capillary column (cm$^2$);
$V_G$ = free gas volume of capillary column (cm$^3$);

which gives

$$t_R = \frac{V_N + V_G}{\bar{u}q} \tag{14}$$

Then, by combining eqns. 15, 12 and 14:

$$H = L/n \tag{15}$$

where

$$L = \text{column length (cm)};$$

$$H = \frac{L q^2 \bar{u}^2 d^2}{5.545 (V_N + V_G)^2} \tag{16}$$

and by defining the following parameter:

$$F = \frac{L q^2}{5.545 (V_N + V_G)^2} \tag{17}$$

we have

$$H = F \bar{u}^2 d^2 \tag{18}$$

Then, by combining eqns. 2 and 18:

$$F \bar{u}^2 d^2 = \frac{4\sqrt{D_G C'}}{3} + \frac{1}{\sqrt{3}} \left( \frac{2 D_G}{\bar{u}} + C' \bar{u} \right) + \frac{1}{4\sqrt{D_G C'}} \left[ \left( \frac{2 D_G}{\bar{u}} \right)^2 + (C' \bar{u})^2 \right] \tag{19}$$

Let us express the half-width ($d$) from eqn. 19:

$$d = \frac{1}{\sqrt{F}} \left( \frac{2 D_G}{\bar{u}^2} + \frac{2}{\bar{u}} \sqrt{\frac{D_G C'}{3}} + C' \right) \cdot \frac{1}{2 \sqrt[4]{D_G C'}} \tag{20}$$

$$V_G = r^2 \pi L \tag{21}$$

by combining eqns. 5, 17 and 21, we obtain

$$F = \frac{1}{5.545 (k' + 1)^2 L} \tag{22}$$

and therefore

$$d = \frac{(k' + 1) \sqrt{5.545 L}}{2 \sqrt[4]{D_G C'}} \left( \frac{2 D_G}{\bar{u}^2} + \frac{2}{\bar{u}} \sqrt{\frac{D_G C'}{3}} + C' \right) \tag{23}$$

Eqn. 23 can be expressed in a simplified form:

$$d = \frac{a}{\bar{u}^2} + \frac{b}{\bar{u}} + c \tag{24}$$

where

$d$ = peak width at half-height (sec);
$\bar{u}$ = average linear carrier gas velocity (cm/sec)

$$a = \frac{(k' + 1)\sqrt{5.545L}}{\sqrt[4]{D_G C'}} \cdot D_G \qquad (cm^2/sec) \tag{25}$$

$$b = \frac{(k' + 1)\sqrt{5.545L}}{\sqrt{3}} \cdot \sqrt[4]{D_G C'} \qquad (cm) \tag{26}$$

$$c = \frac{(k' + 1)\sqrt{5.545L}}{2\sqrt[4]{D_G C'}} \cdot C' \qquad (sec) \tag{27}$$

It must be noted that eqn. 23 is not suitable for the description of the half-width if any kind of carrier gas programming[16] is used.

On the basis of a previous paper[9], the calculation of $\bar{u}_{opt}$ belonging to $HETP_{min}$ was investigated. It can be obtained with the help of the following equation:

$$\sqrt{3} \cdot 64C'^4 \, \bar{u}_{opt}^4 + 32C'^3 \, \bar{u}_{opt}^3 \, H_{min} - 4H_{min}^3 \, C' \, \bar{u}_{opt} - \sqrt{3} \cdot H_{min}^4 = 0 \tag{28}$$

where

$\bar{u}_{opt}$ = average linear carrier gas velocity at $HETP_{min}$ (cm/sec);
$HETP_{min}$ = the minimum HETP of values (cm):

$$HETP_{min} = 4\sqrt{D_G C'} \tag{29}$$

The earlier establishment is valid for the extended equation also, *i.e.*, the resultant effects of the diffusion and mass transfer processes are in dynamic equilibrium both with each other and the effects of the parameters of the column under the gas chromatographic condition of $HETP_{min}$:

$$\frac{4\sqrt{D_G C'}}{3} = \frac{2D_G}{\bar{u}_{opt}\sqrt{3}} + \frac{D_G^2}{\bar{u}_{opt}^2\sqrt{D_G C'}} = \frac{C'\bar{u}_{opt}}{\sqrt{3}} + \frac{(C'\bar{u}_{opt})^2}{4\sqrt{D_G C'}} \tag{30}$$

Eqn. 30 can be simplified to

$$A = \frac{B}{\bar{u}_{opt}} + \frac{D}{\bar{u}_{opt}^2} = C\bar{u}_{opt} + E\bar{u}_{opt}^2 \tag{31}$$

We should mention that the equality in eqn. 31 does not apply in practice owing to experimental errors. Finally, the separation of a pair of components 1 and 2 has been investigated with respect to the average linear carrier gas velocity, using the $R_s$ value:

$$R_s = 1.177 \cdot \frac{V_N(2) - V_N(1)}{[d(1) + d(2)]\bar{u}q} \tag{32}$$

where
$R_s$   = peak resolution;
$V_N$   = net retention volume (ml of carrier gas);
$d$   = peak width at half-height (sec);
$\bar{u}$   = average linear carrier gas velocity (cm/sec);
$q$   = cross-sectional area of capillary column (cm$^2$).

The use of eqn. 24 then allows eqn. 32 to be expressed as

$$R_s = 1.177 \cdot \frac{[V_N\,(2) - V_N\,(1)]\,\bar{u}}{\{[c\,(1) + c\,(2)]\,\bar{u}^2 + [b\,(1) + b\,(2)]\,\bar{u} + a\,(1) + a\,(2)\}\,q} \qquad (33)$$

EXPERIMENTAL

Before starting the experiments, the gas chromatographic system was cali-
brated with $n$-alkanes. The system was accepted as suitable if the standard deviation of
$b$ calculated from the $n$-alkanes was less than 0.004, where

$$b = \log t'_R\,(z + 1) - \log t'_R\,(z) \qquad (34)$$

$$t'_R = t_R - t_M \qquad (35)$$

$t'_R$ = adjusted retention time (sec);

$t_R$ = retention time (sec);

$t_M$ = dead time (sec)

$z$ and $z + 1$ = carbon numbers of consecutive $n$-alkanes.

If these values showed a higher standard deviation, the reason was investigated and
the experiment was re-started only after repeated checks and controls had been made.

As an illustration of the calculations we present the data obtained with the use
of a WCOT column (30.48 m × 0.25 mm I.D.) coated with squalane stationary
phase. The gas chromatographic conditions used for the experiment are summarized
in Table I.

Inserting values in eqn. 3 we obtain

$$C' = \frac{11 \cdot 2.11^2 + 6 \cdot 2.11 \cdot 1.5 + 1.5^2}{(2.11 + 1.5)^2} \cdot \frac{0.0125^2}{24 \cdot 0.0792} +$$

$$+ \frac{8\,(5.2 \cdot 10^{-5})^2}{3.14^2 \cdot 2.98 \cdot 10^{-6}} \cdot \frac{2.11 \cdot 1.5}{(2.11 + 1.5)^2} = 6.23 \cdot 10^{-4} \text{ sec} \qquad (36)$$

**TABLE I**

GAS CHROMATOGRAPHIC CONDITIONS FOR EXPERIMENTS WITH $n$-HEPTANE AT 75.0°C
ON SQUALANE STATIONARY PHASE

| Parameter | Conditions |
|---|---|
| Gas chromatograph | Modified Carlo Erba Fractovap 2300 |
| Detector | Flame ionization |
| Sensitivity | Varying between $1 \times 100$ and $8 \times 100$ |
| Introduction | 0.1 $\mu$l of mixture with a Hamilton syringe |
| Splitting ratio | Varying between 1:100 and 1:200 |
| Column | 30.48 m × 0.25 mm I.D., stainless-steel spiral, wall-coated with squalane stationary phase |
| Amount of squalane | $0.01 \pm 0.001$ g |
| Thickness of squalane film | $5.2 \cdot 10^{-5}$ cm |
| Ratio of phases | 120 |
| Column temperature | $75.0 \pm 0.1$°C |
| Detector temperature | $200 \pm 1$°C |
| Evaporator temperature | $200 \pm 1$°C |
| Carrier gas | Nitrogen |
| Carrier gas inlet pressure | Varying according to flow-rate |
| Carrier gas flow-rate | Varying according to HETP curve |
| Auxiliary gases | Hydrogen and air, inlet pressures and flow-rates optimized at average linear carrier gas velocity of 15.0 cm/sec |
| Recorder | Hitachi, 1.0 mV full-scale, 1.0 sec |
| Chart speed | 1.27 cm/min |
| Integrator | Minigrator |

So:

$$C = \frac{C'}{\sqrt{3}} = 3.60 \cdot 10^{-4} \text{ sec} \tag{37}$$

From eqn. 7:

$$A = \frac{4\sqrt{0.0792 \cdot 6.23 \cdot 10^{-4}}}{3} = 9.38 \cdot 10^{-3} \text{ cm} \tag{38}$$

With the help of eqn. 8 we obtain

$$B = \frac{2 \cdot 0.0792}{\sqrt{3}} = 9.15 \cdot 10^{-2} \text{ cm}^2/\text{sec} \tag{39}$$

From eqns. 10 and 11:

$$D = \frac{0.0792^2}{\sqrt{0.0792 \cdot 6.23 \cdot 10^{-4}}} = 0.893 \text{ cm}^3/\text{sec}^2 \tag{40}$$

and

$$E = \frac{(6.23 \cdot 10^{-4})^2}{4\sqrt{0.0792 \cdot 6.23 \cdot 10^{-4}}} = 1.383 \cdot 10^{-5} \text{ sec}^2/\text{cm} \tag{41}$$

The following equation was given by using the above constants, which provided the data in Table II:

$$H_{N_2}^{SQ(75^\circ C)} (n\text{-}C_7) = 9.38 \cdot 10^{-3} + \frac{9.15 \cdot 10^{-2}}{\bar{u}} + 3.60 \cdot 10^{-4} \bar{u} + \frac{8.93 \cdot 10^{-1}}{\bar{u}^2} +$$
$$+ 1.383 \cdot 10^{-5} \bar{u}^2 \tag{42}$$

where SQ = squalane stationary phase, $N_2$ = nitrogen carrier gas and $n$-$C_7$ = $n$-heptane.

The values of the different terms in eqn. 42 and their influence on HETP as a function of the average linear carrier gas velocity can be seen with the help of the data in Table II. It is important from both the theoretical and practical points of view.

TABLE II

VARIATION OF HETP WITH AVERAGE LINEAR CARRIER GAS VELOCITY AT 75.0°C ON SQUALANE STATIONARY PHASE USING $n$-HEPTANE WITH NITROGEN AS CARRIER GAS

The value of A was $9.38 \cdot 10^{-3}$ cm.

| $\bar{u}$ (cm/sec) | $B/\bar{u}$ (cm) | $C'\bar{u}$ (cm) | $D/\bar{u}^2$ (cm) | $E\bar{u}^2$ (cm) | HETP (cm) |
|---|---|---|---|---|---|
| 1 | 0.092 | <0.001 | 0.893 | <0.001 | 0.995 |
| 2 | 0.046 | 0.001 | 0.223 | <0.001 | 0.279 |
| 5 | 0.018 | 0.002 | 0.036 | <0.001 | 0.066 |
| 10 | 0.009 | 0.004 | 0.009 | 0.001 | 0.032 |
| 15 | 0.006 | 0.005 | 0.004 | 0.003 | 0.028 |
| 20 | 0.005 | 0.007 | 0.002 | 0.006 | 0.029 |
| 30 | 0.003 | 0.011 | 0.001 | 0.012 | 0.037 |
| 40 | 0.002 | 0.014 | 0.001 | 0.022 | 0.049 |
| 50 | 0.002 | 0.018 | <0.001 | 0.035 | 0.064 |
| 60 | 0.002 | 0.022 | <0.001 | 0.050 | 0.083 |
| 70 | 0.001 | 0.025 | <0.001 | 0.068 | 0.104 |
| 80 | 0.001 | 0.029 | <0.001 | 0.089 | 0.128 |
| 90 | 0.001 | 0.032 | <0.001 | 0.112 | 0.155 |
| 100 | 0.001 | 0.036 | <0.001 | 0.138 | 0.185 |

The approximate equation describing the peak shape can also be obtained in a simple manner from eqns. 25–27:

$$a = \frac{(1.41 + 1) \sqrt{5.545 \cdot 3048}}{\sqrt[4]{0.0792 \cdot 6.23 \cdot 10^{-4}}} \cdot 0.0792 = 296.12 \text{ cm}^2/\text{sec} \tag{43}$$

$$b = \frac{(1.41 + 1)\sqrt{5.545 \cdot 3048}}{\sqrt{3}} \cdot \sqrt[4]{0.0792 \cdot 6.23 \cdot 10^{-4}} = 15.17 \text{ cm} \qquad (44)$$

$$c = \frac{(1.41 + 1)\sqrt{5.545 \cdot 3048}}{2\sqrt[4]{0.0792 \cdot 6.23 \cdot 10^{-4}}} \cdot 6.23 \cdot 10^{-4} = 1.17 \text{ sec} \qquad (45)$$

The following equation was obtained by using the above constants:

$$d\,(n\text{-}C_7) = \frac{296.12}{\bar{u}^2} + \frac{15.17}{\bar{u}} + 1.17 \qquad (46)$$

Gas chromatographic parameters are given in Table I.

The resultant effects of the diffusion and mass transfer processes can be calculated by use of eqn. 30:

$$D_r = \frac{9.15 \cdot 10^{-2}}{16} + \frac{8.93 \cdot 10^{-1}}{16^2} = 9.2 \cdot 10^{-3} \text{ cm} \qquad (47)$$

and

$$E_r = 3.6 \cdot 10^{-4} \cdot 16 + 1.38 \cdot 10^{-5} \cdot 16^2 = 9.3 \cdot 10^{-3} \text{ cm} \qquad (48)$$

where

$D_r$ = resultant effect of the diffusion processes (cm);
$E_r$ = resultant effect of the mass transfer processes (cm).

The resultant effect of the column parameters is the $A$ value. The results are summarized in Table III, from which it can be seen that the resultant values are nearly identical.

TABLE III

RESULTANT VALUES OF THE DYNAMIC EQUILIBRIUM FOR $n$-HEPTANE UNDER EXPERIMENTAL CONDITIONS OF TABLE I

$\bar{u}_{opt}$ = 16.0 cm/sec.

| $A$ (cm) | Diffusion processes: $D_r$ (cm) | Mass transfer processes: $E_r$ (cm) | HETP (cm) |
|---|---|---|---|
| $9.38 \cdot 10^{-3}$ | $9.18 \cdot 10^{-3}$ | $9.30 \cdot 10^{-3}$ | $2.78 \cdot 10^{-2}$ |

As an extreme example of the calculations, we show in Table IV the data obtained with the use of a fused silica WCOT column (25.0 m × 0.20 mm I.D.) coated with OV-101 stationary phase. The gas chromatographic conditions used for the experiments are summarized in Table V.

TABLE IV

COMPARISON OF MEASURED AND CALCULATED HETP DATA AT 40.0°C ON OV-101 STATIONARY PHASE USING n-HEPTANE

Gas chromatographic parameters are given in Table V. Carrier gas: nitrogen.

| $\bar{u}$ (cm/sec) | HETP (cm) | | |
|---|---|---|---|
| | Measured | Calculated | Difference |
| 30.2 | 0.075 | 0.060 | +0.015 |
| 43.0 | 0.123 | 0.095 | +0.028 |
| 49.6 | 0.158 | 0.118 | +0.040 |
| 60.4 | 0.174 | 0.160 | +0.014 |
| 65.1 | 0.179 | 0.181 | −0.002 |
| 73.1 | 0.217 | 0.219 | −0.002 |

TABLE V

GAS CHROMATOGRAPHIC CONDITIONS USED FOR THE EXPERIMENTS WITH n-HEPTANE AT 40.0°C ON OV-101 STATIONARY PHASE

| Parameter | Conditions |
|---|---|
| Gas chromatograph | Hewlett-Packard 5880A with Hewlett-Packard 3388A reporting integrator |
| Detector | Flame ionization |
| Introduction | 0.1 μl of mixture with a Hamilton syringe |
| Column | 25 m × 0.20 mm I.D. fused silica WCOT with OV-101 stationary phase |
| Thickness of OV-101 film | $1.75 \cdot 10^{-5}$ cm |
| Column temperature | 40.0°C |
| Detector temperature | 225°C |
| Injector temperature | 225°C |
| Carrier gas | Nitrogen |
| Carrier gas inlet pressure | Varying between 0.12 and 0.51 MPa/cm² |
| Carrier gas flow-rate | Varying between 5 and 100 cm/sec |
| Auxiliary gases | Hydrogen, flow-rate 25 ml/min; air, flow-rate 380 ml/min |
| Chart speed | 1.0 cm/min |

The calculated HETP values in Table IV give the following equation:

$$\text{HETP}_{N_2, n\text{-}C_7}^{OV\text{-}101(40°C)} = 1.1 \cdot 10^{-2} + \frac{0.079}{\bar{u}} + 5.83 \cdot 10^{-4} \bar{u} + \frac{5.7 \cdot 10^{-1}}{\bar{u}^2} + \\ + 3.09 \cdot 10^{-5} \bar{u}^2 \quad (49)$$

The effects of the $D$ and $E$ terms are summarized in Table VI.

We should mention that the square of the peak width bears a direct relationship with $D$ term, as shown with the help of eqns. 6 and 18:

$$d^2 = \frac{1}{F}\left(\frac{A}{\bar{u}^2} + \frac{B}{\bar{u}^3} + \frac{C}{\bar{u}} + \frac{D}{\bar{u}^4} + E\right) \quad (50)$$

TABLE VI

EFFECTS OF $D$ AND $E$ TERMS ON AVERAGE LINEAR CARRIER GAS VELOCITY UNDER
GAS CHROMATOGRAPHIC CONDITIONS IN TABLE V FOR $n$-HEPTANE AT 40°C ON OV-101

| $\bar{u}$ (cm/sec) | $D/\bar{u}^2$ (cm) | $D/\bar{u}^2$ in H (%) | $D/F\bar{u}^4$ in $d^2$ (%) | $E\bar{u}^2$ (cm) | $E\bar{u}^2$ in H (%) | $E/F$ in $d^2$ (%) | HETP (cm) |
|---|---|---|---|---|---|---|---|
| 1 | 0.572 | 86.275 | 55.617 | <0.001 | 0.005 | 0.003 | 0.663 |
| 2 | 0.143 | 73.333 | 42.871 | <0.001 | 0.064 | 0.037 | 0.195 |
| 5 | 0.023 | 43.396 | 23.522 | 0.001 | 1.887 | 0.793 | 0.053 |
| 10 | 0.006 | 17.647 | 9.789 | 0.003 | 8.824 | 5.280 | 0.034 |
| 20 | 0.001 | 2.500 | 2.435 | 0.012 | 30.000 | 21.013 | 0.040 |
| 30 | 0.001 | 1.667 | 0.845 | 0.028 | 46.667 | 36.907 | 0.060 |
| 40 | <0.001 | 0.416 | 0.362 | 0.049 | 56.977 | 50.043 | 0.086 |
| 50 | <0.001 | 0.192 | 0.180 | 0.077 | 64.706 | 60.522 | 0.119 |
| 60 | <0.001 | 0.100 | 0.099 | 0.111 | 69.811 | 68.908 | 0.159 |
| 70 | <0.001 | 0.057 | 0.058 | 0.151 | 74.020 | 75.709 | 0.204 |
| 80 | <0.001 | 0.035 | 0.037 | 0.197 | 76.953 | 81.307 | 0.256 |
| 90 | <0.001 | 0.022 | 0.024 | 0.250 | 79.618 | 85.984 | 0.314 |
| 100 | <0.001 | 0.015 | 0.017 | 0.309 | 81.530 | 89.941 | 0.379 |

where
$d$ = peak width at half-height (sec);
$\bar{u}$ = average linear carrier gas velocity (cm/sec);
$A$, $B$, $C$, $D$ and $E$ = constants of eqn. 6.

The value of $F$ in eqn. 50 was $9.2 \cdot 10^{-6}$ cm$^{-1}$. We can see from eqn. 50 that the $E$ term is independent of $\bar{u}$. Considering that an increase in $\bar{u}$ causes a large decrease in $d^2$, it is evident that the percentage of $E/F$ will be an important value (Table VI).

We obtained some interesting results in calculations based on the development of the additive elements of the retention time as a function of the average linear carrier gas velocity. The additive retention time elements studied were as follows:

(1) The residence time in the stationary phase ($\tau_1$) during a change of the phases (gas and stationary) (sec):

$$\tau_1 = \frac{j(t_R - t_M)}{n} \tag{51}$$

where
$j$ = compressibility factor according to James and Martin[17]:

$$j = 1.5 \left[ \frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \right] \tag{52}$$

$p_i$ = inlet pressure of the carrier gas (MPa/cm$^2$);
$p_0$ = outlet pressure of the carrier gas (MPa/cm$^2$);
$t_R$ = retention time (sec);
$t_M$ = dead time (sec);
$n$ = number of theoretical plates.

(2) The residence time in the gas phase ($\tau_2$) during a change of the phases (sec):

$$\tau_2 = \frac{j\,t_M}{n} \tag{53}$$

(3) The time of a change of the phases ($\tau_3$) (sec):

$$\tau_3 = \tau_1 + \tau_2 \tag{54}$$

The time of a change of the phases is equal to the time period between two entrances into the stationary phase. A change of the phases occurs on a theoretical plate. The results are summarized in Table VII.

TABLE VII

DEVELOPMENT OF THE ADDITIVE ELEMENTS OF RETENTION TIME OF $n$-HEPTANE AS A FUNCTION OF THE AVERAGE LINEAR CARRIER GAS VELOCITY UNDER GAS CHROMA-TOGRAPHIC CONDITIONS IN TABLE V

| $\bar{u}$ (cm/sec) | n | HETP (cm) | Residence time (sec) | | Time of a change (sec) |
|---|---|---|---|---|---|
| | | | In gas phase | In stationary phase | |
| 1 | 3772 | 0.663 | 0.632 | 1.138 | 1.770 |
| 2 | 12827 | 0.195 | 0.092 | 0.166 | 0.258 |
| 5 | 46800 | 0.053 | 0.010 | 0.018 | 0.028 |
| 10 | 74493 | 0.034 | 0.003 | 0.005 | 0.008 |
| 20 | 61899 | 0.040 | 0.002 | 0.003 | 0.005 |
| 30 | 41999 | 0.060 | 0.002 | 0.003 | 0.005 |
| 40 | 29067 | 0.086 | 0.002 | 0.003 | 0.005 |
| 50 | 20995 | 0.119 | 0.002 | 0.003 | 0.005 |
| 60 | 15772 | 0.159 | 0.002 | 0.003 | 0.005 |
| 70 | 12242 | 0.204 | 0.002 | 0.003 | 0.005 |
| 80 | 9760 | 0.256 | 0.002 | 0.003 | 0.005 |
| 90 | 7954 | 0.314 | 0.002 | 0.003 | 0.005 |
| 100 | 6602 | 0.379 | 0.002 | 0.003 | 0.005 |

It can be seen from Table VII that the retention time elements studied are independent of the flow-rate of the carrier gas above 20 cm/sec. It is evident that for desorption from the stationary phase of the molecules of the proporsion of sample introduced, a defined kinetic energy originating from collisions of the carrier gas molecules is needed under given gas chromatographic conditions. The time needed for transmitting the energy is the minimal time that occurs at 20 cm/sec and remains constant.

The time spent in the gas phase during a change of the phases is constant above the $\bar{u}_{opt}$ value because the surplus energy due to an increase in the carrier gas flow-rate is used to accelerate the desorbed molecules examined to a higher carrier gas velocity and to travel the required column length for higher HETP values.

In many instances calculated peak widths were compared with experimental results; two examples are given in Tables VIII and IX.

**TABLE VIII**

**COMPARISON OF THE MEASURED AND CALCULATED PEAK WIDTHS AT 40.0°C ON OV-101 FOR n-HEPTANE WITH PARAMETERS AS IN TABLE V**

| $\bar{u}$ (cm/sec) | d (measured) (sec) | d (calculated) (sec) | Difference (sec) |
|---|---|---|---|
| 30.2 | 3.00 | 2.76 | +0.24 |
| 43.0 | 2.70 | 2.43 | +0.27 |
| 49.6 | 2.64 | 2.33 | +0.31 |
| 60.4 | 2.28 | 2.23 | +0.05 |
| 65.1 | 2.22 | 2.19 | +0.03 |
| 73.1 | 2.10 | 2.15 | −0.05 |

**TABLE IX**

**COMPARISON OF MEASURED AND CALCULATED PEAK WIDTHS AT 75°C ON SQUALANE FOR n-HEPTANE**

Gas chromatographic parameters in Table I.

| $\bar{u}$ (cm/sec) | d (measured) (sec) | d (calculated) (sec) | Difference (sec) |
|---|---|---|---|
| 1 | 312.30 | 312.46 | −0.16 |
| 2 | 82.74 | 82.79 | −0.05 |
| 5 | 16.04 | 16.05 | −0.01 |
| 10 | 5.64 | 5.65 | −0.01 |
| 15 | 3.49 | 3.50 | −0.01 |
| 20 | 2.66 | 2.67 | −0.01 |
| 30 | 2.00 | 2.00 | 0 |
| 50 | 1.59 | 1.59 | 0 |

This is based on the separation of two examined components; thus we followed the way in which the separation of 2,2,4-trimethylpentane and n-heptane depended on the average linear carrier gas velocity. From eqn. 33 the result at 75.0°C on squalane stationary phase with nitrogen as the carrier gas is

$$R_s = \frac{240,37 \; \bar{u}}{2.94 \; \bar{u}^2 + 34.82 \; \bar{u} + 618.35} \tag{55}$$

The data obtained with the help of eqn. 55 are given in Table X, which show that the $R_s$ values have a maximum, as is well known.

The results obtained with the above equations are compared with literature data in Tables XI–XV. Unfortunately the results are generally given graphically in the literature for clarity[18–21]. We determined the values of $HETP_{min}$ and $\bar{u}_{opt}$ from the published figures[18–21] using a magnifying glass and two rectangular rulers before starting the calculations. For example, from Landault and Guiochon's paper[19] $HETP_{min} = 0.060$ cm and $\bar{u}_{opt} = 30.0$ cm/sec. From eqns. 29 and 30 we obtain

$$\frac{30C'}{\sqrt{3}} + \frac{900C'^2}{0.060} = 0.020 \tag{56}$$

TABLE X

SEPARATION OF 2,2,4-TRIMETHYLPENTANE AND *n*-HEPTANE AS A FUNCTION OF AVERAGE LINEAR CARRIER GAS VELOCITY AT 75°C ON SQUALANE STATIONARY PHASE

Gas chromatographic parameters in Table I.

| $\bar{u}$ (cm/sec) | $R_s$ | $\bar{u}$ (cm/sec) | $R_s$ |
|---|---|---|---|
| 1 | 0.37 | 30 | 1.67 |
| 2 | 0.69 | 40 | 1.43 |
| 3 | 0.96 | 50 | 1.24 |
| 4 | 1.19 | 60 | 1.09 |
| 5 | 1.39 | 70 | 0.96 |
| 10 | 1.91 | 80 | 0.87 |
| 15 | 2.00 | 90 | 0.78 |
| 20 | 1.93 | 100 | 0.72 |

TABLE XI

COMPARISON OF MEASURED (ETTRE[18]) AND CALCULATED HETP DATA FOR *n*-HEPTANE AT 75°C ON SQUALANE (PLOT COLUMN)

| $\bar{u}$ (cm/sec) | HETP (cm) | | |
|---|---|---|---|
| | Measured | Calculated | Difference |
| 6 | 0.142 | 0.167 | −0.025 |
| 12 | 0.094 | 0.092 | +0.002 |
| 19 | 0.090 | 0.088 | +0.002 |
| 27 | 0.105 | 0.103 | +0.002 |
| 43 | 0.162 | 0.159 | +0.003 |

TABLE XII

COMPARISON OF MEASURED (DESTY AND GOLDUP[2]) AND CALCULATED HETP DATA FOR *n*-HEPTANE AT 25°C ON SQUALANE (WCOT COLUMN)

| $\bar{u}$ (cm/sec) | HETP (cm) | | |
|---|---|---|---|
| | Measured | Calculated | Difference |
| 5.4 | 0.040 | 0.047 | −0.007 |
| 7.9 | 0.036 | 0.038 | −0.002 |
| 15.0 | 0.042 | 0.041 | +0.001 |
| 20.0 | 0.054 | 0.051 | +0.003 |
| 30.0 | 0.081 | 0.080 | +0.001 |
| 40.0 | 0.116 | 0.119 | −0.003 |

Rearranging and simplifying eqn. 56:

$$C'^2 + 1.15 \cdot 10^{-3} \, C' - 1.3 \cdot 10^{-6} = 0 \tag{57}$$

## TABLE XIII

COMPARISON OF MEASURED (LANDAULT AND GUIOCHON[19]) AND CALCULATED HETP DATA FOR n-HEPTANE AT 50°C ON SQUALANE (SCOT COLUMN)

| $\bar{u}$ (cm/sec) | HETP (cm) | | |
|---|---|---|---|
| | Measured | Calculated | Difference |
| 10 | 0.098 | 0.131 | −0.033 |
| 20 | 0.072 | 0.067 | +0.005 |
| 30 | 0.060 | 0.059 | +0.001 |
| 40 | 0.063 | 0.063 | 0 |
| 50 | 0.065 | 0.071 | −0.006 |
| 60 | 0.068 | 0.082 | −0.014 |
| 70 | 0.071 | 0.095 | −0.024 |
| 80 | 0.076 | 0.110 | −0.034 |
| 90 | 0.078 | 0.128 | −0.050 |
| 100 | 0.079 | 0.147 | −0.068 |

## TABLE XIV

COMPARISON OF MEASURED (CRONIN[20]) AND CALCULATED HETP DATA FOR 2-HEP-TANONE AT 120°C ON PEG-20M STATIONARY PHASE (PLOT COLUMN)

| $\bar{u}$ (cm/sec) | HETP (cm) | | |
|---|---|---|---|
| | Measured | Calculated | Difference |
| 3.6 | 0.120 | 0.119 | +0.001 |
| 6 | 0.136 | 0.142 | −0.006 |
| 8 | 0.156 | 0.181 | −0.025 |
| 10 | 0.196 | 0.232 | −0.036 |
| 12 | 0.239 | 0.293 | −0.054 |
| 14 | 0.275 | 0.364 | −0.089 |

## TABLE XV

COMPARISON OF MEASURED (FRITZ et al.[21]) AND CALCULATED HETP DATA FOR n-OCTANE AT 50°C ON SQUALANE (SANDWICHED COLUMN)

| $\bar{u}$ (cm/sec) | HETP (cm) | | |
|---|---|---|---|
| | Measured | Calculated | Difference |
| 2.7 | 0.138 | 0.137 | +0.001 |
| 3.7 | 0.160 | 0.150 | +0.010 |
| 4.7 | 0.183 | 0.170 | +0.013 |
| 5.7 | 0.217 | 0.201 | +0.016 |
| 6.7 | 0.254 | 0.239 | +0.015 |
| 7.7 | 0.296 | 0.282 | +0.014 |

Hence

$$C' = 7.14 \cdot 10^{-4} \text{ sec} \tag{58}$$

From eqn. 29:

$$D_G C' = 2.25 \cdot 10^{-4} \text{ cm}^2 \tag{59}$$

and so

$$D_G = 0.315 \text{ cm}^2/\text{sec} \tag{60}$$

Therefore

$$B = \frac{2D_G}{\sqrt{3}} = 0.364 \text{ cm}^2/\text{sec} \tag{61}$$

$$C = \frac{C'}{\sqrt{3}} = 4.12 \cdot 10^{-4} \text{ sec} \tag{62}$$

$$D = \frac{D_G^2}{\sqrt{D_G C'}} = 6.63 \text{ cm}^3/\text{sec}^2 \tag{63}$$

$$E = \frac{C'^2}{4\sqrt{D_G C'}} = 8.49 \cdot 10^{-6} \text{ sec}^2/\text{cm} \tag{64}$$

The constants in eqn. 6 were determined from the data for the diffusion processes of the dynamic equilibrium also. The results were as follows: $B = 0.371$ cm$^2$/sec, $C = 4.05 \cdot 10^{-4}$ sec, $D = 6.87$ cm$^3$/sec$^2$ and $E = 8.19 \cdot 10^{-6}$ sec$^2$/cm. The deviations of the calculated values are unimportant. The constants were calculated with Texas Instruments TI-57 and Hewlett-Packard HP-97 programmable calculators.

It should be mentioned that the data in Table XIII were calculated from the data for the diffusion processes of the dynamic equilibrium.

CONCLUSIONS

On the basis of a large number of experiments[8–10,16] the following conclusions can be drawn:

(1) It seems that an earlier statement by Giddings[22] about the theory of GLC is correct, as follows: "Logically, it would seem, there ought to be only one theory, or at least one true theory of chromatography". This theory is the plate theory. The

rate theory is only a dynamic form of the Glueckauf's equation[6]. Several "theories" have been developed to account for the shape of elution curves from the column; these will not be discussed here.

(2) The extended equation, eqn. 2, gives an adequate description of the diffusion and mass transfer processes. The mass transfer processes only start to play a role at values greater than $2\bar{u}_{opt}$, whereas the diffusion processes have no influence in this region. In most instances this demarcation coincides with the $2\bar{u}_{opt}$ value.

(3) Our experience showed that $HETP_{min}$ plays a more important role in GLC than we thought earlier.

(4) At the $\bar{u}_{opt}$ value the resultant values of the diffusion and mass transfer processes are almost identical. They are equal to $A$, and this value is one third of $HETP_{min}$. The gas chromatographic processes have a dynamic equilibrium at the $\bar{u}_{opt}$ value.

(5) Eqn. 23 gives a correct description of the peak width. Hence the measured and calculated values are virtually identical.

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