515. *Diffusional Band-spreading in Gas-chromatographic Columns. Part II.*[1] *The Elution of Sorbed Vapours.*

By J. Bohemen and J. H. Purnell.

The elution of acetone and benzene vapour by hydrogen and nitrogen from columns differing in the particle size of the solid supports has been studied. The results are interpreted in terms of a rate equation with four constants and three variables. The evidence suggests that the labyrinth constant γ is probably unity and that the tortuosity constant λ is about 1·5. The need for a Golay-type term for the resistance to mass-transfer of gas in the rate equation for packed columns has been substantiated. A value of the proportionating constant has been deduced to modify the term, as theoretically deduced for uniform capillaries, for use with packed columns. The results indicate that the distribution of involatile solvent is of the droplet and not of the film type. The significance of the results in relation to high-speed chromatography is briefly discussed.

In Part I[1] of this work the chromatographic rate equation of van Deemter *et al.*[2] was modified so as to include a term for the mass-transfer of gas and corrections for the pressure-dependence of the various terms. It was shown that the theoretical plate height, H, and the linear inter-particle velocity (u_0) of the carrier gas at the column outlet-pressure (p_0) (recalculated to the value it would have at one atmosphere pressure, u') are related by the equation

$$H = A + B'/u' + C_g'u' + (C_l u'f)/p_0. \tag{1}$$

A and B' were defined earlier;[1] f is the pressure compressibility correction function of James and Martin.[3] An equation defining C_g' in terms of experimental quantities has been developed by Golay[4] for the particular case of uniform capillary columns. It is assumed here that Golay's theory is applicable to packed columns since, for theoretical purposes, these are usually regarded as bundles of non-uniform capillaries. For a packed column it is supposed that Golay's coefficient can be written

$$C_g' = \frac{\chi[1 + 6k' + 11(k')^2]d_p^2}{24(1 + k')^2 D_g'.}, \tag{2}$$

where $k' = KV_l/V_d$; K represents a partition coefficient, V_l the volume of solvent in a column, and V_d the total free gas space in the column (inter- + intra-particle). D_g' is the interdiffusion coefficient of the solute in the carrier gas at 1 atm. and at the column temperature while χ is a proportionating constant. In practice k' is the ratio of the true retention volumes of any solute and an inert gas. The expression for the liquid mass-transfer coefficient, C_l, deduced by van Deemter *et al.*,[2] is

$$C_l = \frac{2k'd_f^2}{3(1 + k')^2 D_l}, \tag{3}$$

where d_f is a representative solvent-film thickness and D_l is the interdiffusion coefficient of the solute in the stationary liquid in the conditions employed.

The application to experiment of the original van Deemter equation, which does not include the C_g' term, has been described by several investigators.[5-9] The results have

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[1] Part I, Bohemen and Purnell, *J.*, 1961, 360.
[2] van Deemter, Zuiderweg, and Klinkenberg, *Chem. Eng. Sci.*, 1956, **5**, 271.
[3] James and Martin, *Biochem. J.*, 1952, **50**, 679.
[4] Golay in " Gas Chromatography " (ed. D. H. Desty), 1958, Butterworths, London, p. 36.
[5] Scott, as in ref. 4, p. 189.
[6] Keulemans and Kwantes, " Vapour Phase Chromatography " (ed. D. H. Desty), 1957, Butterworths, London, p. 15.
[7] Bohemen and Purnell, as in ref. 4, p. 6.
[8] Purnell, *Ann. New York Acad. Sci.*, 1959, **72**, 592.
[9] Desty, Godfrey, and Harbourn, as in ref. 4, p. 200; de Wet and Pretorius, *Analyt. Chem.*, 1948, **30**, 325; Brennan and Kemball, *J. Inst. Petroleum*, 1958, **44**, 14.

usually shown qualitative agreement with the theory, but the quantitative data and evaluated coefficients of different workers are rarely concordant. The reasons are almost certainly failure to take account of extra-column processes, inappropriate methods of evaluating the coefficients, the use of gas velocities which are wrongly calculated, and the failure to introduce the Golay term. Elucidation of the true individual term contributions to the total value of H is important both from the theoretical standpoint and in attempts to obtain greater column efficiency [5,7,8] and speeds of analysis.[10] The work now described was carried out in order to obtain more reliable quantitative information about column performance and to determine whether or not the use of equation (1) would provide more consistent data with which to test the theory. The latter seemed likely since the equation has been shown [1] to be successful for the elution of unsorbed gases.

It was considered essential first to ensure that, so far as possible, extra-column processes, which are not accounted for in equation (1), contributed nothing to the results. Of these, the effects of sample size,[3,6,7,11,12] sample composition,[3,7,13] and anomalous katharometric response [14] have been studied in some detail and were not re-investigated. Other possible sources of band-broadening, however, such as excessive volume of sample feed and adsorption by solid supports, have received less attention and were thought to merit study.

EXPERIMENTAL

The apparatus and columns used were those described previously,[1] with inclusion of a needle valve and pressure gauge at the column outlet to allow column operation at elevated outlet-pressures. Nitrogen and hydrogen were used as carrier gases, and columns were controlled at 51° in all the experiments. The volume and band shape of the sample after injection, but immediately before entering the chromatographic column, were determined by passing the sample through one side of a twin-cell katharometer situated at the column head. An injection peak thus appeared on the chromatogram.

In the experiments relating to extra-column processes, 4-μl. liquid samples containing cyclohexane, acetone, benzene, and propan-2-ol in the ratio 0·3 : 0·7 : 1·0 : 4·6 were used, the propan-2-ol acting primarily as a diluent. These samples were injected into the carrier-gas stream through a rubber septum with an Agla micrometer syringe.[15] In the study of the column band-spreading processes, 1-μl. liquid samples of cyclohexane, acetone, and benzene in the ratio 0·3 : 0·7 : 1·0 were used. These were injected into the column by means of an O-ring rotary-valve system [1] used in conjuction with a modified Agla syringe.[16] The injection temperature for both injection methods was adjusted so that a further increase in temperature did not reduce the widths of the elution curves,[17] this temperature being about 130°.

RESULTS AND DISCUSSION

The Sample Feed Volume.—The theoretical limitation on the sample volume, such that it does not contribute to the shape and width of the elution curve, has been calculated by Glueckauf: [18] the injection band width, w_i, should be less than one-quarter of the emergent band width w_e. This result is equivalent to that suggested later by van Deemter *et al.*,[2] and shown by them to be approximately true in practice. Experiments were carried out in order to ascertain whether this applied in our conditions.

The feed volume was varied by altering the time of injection of the liquid samples. Since the feed width was measured directly, this method is more reliable than that in

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[10] Purnell and Quinn, 3rd Symp. Gas Chromatography Discussion Group, Edinburgh, June 1960, Preprints, p. 154; " Gas Chromatography " (ed. Scott), Butterworths, London, 1960, p. 184.

[11] Mellor, as in ref. 6, p. 63.

[12] Pollard and Hardy, as in ref. 6, p. 115.

[13] Littlewood, as in ref. 4, p. 23.

[14] Bohemen and Purnell, *Chem. and Ind.*, 1957, 815; *J. Appl. Chem.*, 1958, **8**, 433.

[15] Ray, *J. Appl. Chem.*, 1954, **4**, 21.

[16] Lichtenfels, Fleck, Burow, and Coggeshall, *Analyt. Chem.*, 1956, **28**, 1376.

[17] Pollard and Hardy, *Chem. and Ind.*, 1955, 1145.

[18] Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 34.

which the sampler volume is changed and the feed volume is assumed to be that of the sampler. Both the emergent band width w_e and the feed width w_i were measured directly from the recorder chart with a travelling microscope. Fig. 1 shows a plot of w_e against w_i for the four solutes used; also shown is the line representing the theoretical relation $w_e/w_i = 4$. It is evident that the agreement between theory and experiment is good. Owing to its short retention time, it was never possible to inject cyclohexane rapidly enough to achieve the condition $w_e/w_i > 4$. In fact, when the results contained in Fig. 1 were used to compute the maximum sample of cyclohexane which should be used in the column studies proper it was found that with the solvent and temperature used even the smallest sample which could be handled gave an excessive feed volume. In consequence, the results obtained for this solute are not discussed further. This result emphasises the fact that excessive feed volume is liable to be an important source of the inconsistencies in much published work.

Adsorption by the Support.—Although reduction of the ratio of stationary phase to solid upport may increase the column efficiency,[6,19] increased adsorption of the solute by the greater uncovered area of the support is likely to cause undesirable band-broadening and -distortion and altered retention yolumes.[20] Experiments were carried out to determine the conditions under which the solid support could, for the purposes of this work, be regarded as inert, a condition necessary if evaluation of k' is to be realistic. The specific retention volumes,[21] V_g, of acetone and benzene were determined for different ratios of stationary phase to solid support. These are listed in Table 1, the values quoted being the mean of at least ten measurements over a wide variety of flow rates. They indicate that

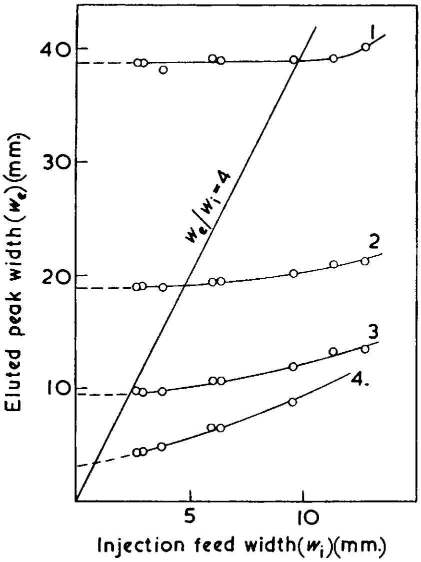

FIG. 1. *Plot of eluted band width against injection band width.*

1, *Propan-2-ol.* 2, *Benzene.* 3, *Acetone.* 4, *Cyclohexane.*

TABLE 1. *Variation of specific retention volume with the amount of stationary phase. Column temp.* 51°.

Polyethylene glycol 400 (g.) per 100 g. of Sil-O-Cel	2·0	5·0	10·2	20·1
Spec. retention vol. (V_g) (ml. of N_2): acetone	103·1	90	87	86
benzene	195	176	168	165

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[19] Ring, First I.S.A. Symposium, East Lansing, Michigan, August, 1957; Cheshire and Scott, *J. Inst. Petroleum*, 1958, **44**, 74.

[20] Adlard, as in ref. 6, p. 98.

[21] Ambrose, Keulemans, and Purnell, *Analyt. Chem.*, 1958, **30**, 1582.

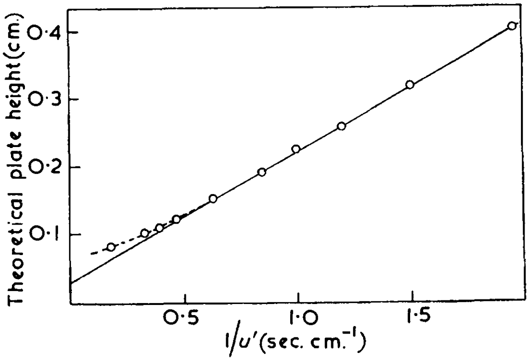
20% w/w columns of polyethylene glycol on Sil-O-Cel are suitable for use throughout the work subsequently carried out.

The Reproducibility of Column Construction.—Reproducibility was studied by making pairs of columns with supports of different particle sizes. The supports used for the 30—40 mesh columns were prepared from batches of firebrick screened on different occasions, while the 50—60 and 100—150 mesh supports were each screened in one operation. The efficiencies of these columns were determined many times at each of many different linear gas velocities. From plots of the mean H against the true average linear gas velocity $\bar{u} = u'f/p_0$, the values of H for the different columns at $\bar{u} = 10$ and 15 cm./sec. were evaluated for the comparison illustrated in Table 2.

TABLE 2. *Reproducibility of column construction.*

Mesh range (IMM)	d_p (mm.)	10^2H (cm.) Acetone $\bar{u}$ (cm./sec.) 10	15	Benzene $\bar{u}$ (cm./sec.) 10	15
20—30	0·32	14·1	17·2	16·2	20·2
30—40	0·33	14·4	18·9	15·8	20·3
30—40	0·21	10·3	13·0	11·6	14·6
50—60	0·16	6·6	6·9	6·6	7·5
50—60	0·17	6·8	7·5	6·6	7·6
100—150	0·10	4·7	5·2	4·8	5·3
100—150	0·10	4·6	4·9	4·5	4·9

FIG. 2. *Plot of H against* $1/u'$. *Slope* $= B'$, *intercept* $= A$. *Data for elution of benzene by nitrogen at 51° from column of* d_p 0·016 *cm. Broken line shows increasing importance of C terms at high* u'.



A series of measurements, under fixed conditions, with a given column showed that the reproducibility of H was about $\pm 2{\cdot}5\%$ with the direct injection system. The agreement between the pairs of 50—60 and 100—150 mesh column is thus satisfactory. However, the efficiency of the first 30—40 mesh column listed in Table 2 was much lower than of the other. Permeability measurements showed that the particle size, d_p, of the support in the former was considerably greater than expected, and corresponded reasonably closely to 20—30 mesh (data for a column containing 20—30 mesh Sil-O-Cel are listed for comparison). Thus, our procedure for constructing columns is reasonably reproducible but the findings add weight to the view[1] that d_p can only be evaluated properly for theoretical purposes from studies of column permeability to gas flow.

Coefficient Evaluation.—Up to this time, only a three-constant equation has been employed to represent packed-column data, while several methods of representing the carrier-gas velocity have been used. One common approach is to divide the column length by the air peak-retention time, a procedure which yields $\bar{u}$ for a capillary or glass-bead column but something closer to $\bar{u}/2$ for a column with porous packing.[1] Alternatively, a velocity, u_0, calculated by dividing the rate of gas flow at the column outlet by the free cross-sectional area can be used. For packed columns as well as capillaries the product u_0f gives the correct value of $\bar{u}$. Evidently, unambiguous determination of u_0, $\bar{u}$, or u' for packed columns requires measurement of free inter-particle cross-sectional area and, hence, of the column bulk-packing density.

Consideration of equation (1) reveals that, since it contains the three variables H, u' ($= u_0p_0$), and $\bar{u}$, there is no two-dimensional graphical method of representing the dependence of H upon velocity from which all coefficients can be simultaneously deduced. If a plot of H against $\bar{u}$ is employed, reasonable values of the C terms may be obtained, but derived values of A and B' will be very much in error. This is no small effect and values of B' which are several times too small can readily be derived for a column of any reasonable length. The methods of evaluating coefficients used in this work were as follows.

A large number of measurements of H, made at low velocities, were plotted as graphs of H against $1/u'$, as in Fig. 2. At very high values of $1/u'$ we can write equation (1) approximately as

$$H = A + B'/u', \tag{4}$$

and so, equally approximately, values of A and B' can be obtained from the intercept and slope of the plot, respectively. There now remains the much more difficult problem of evaluating, even approximately, C_g' and C_l. The method developed for this was based on the use of the following modification of equation (1):

$$H_1 - H_2 = (A_1 - A_2) + \left(\frac{B_1'}{u_1'} - \frac{B_2'}{u_2'}\right) + (C_{g_1}'u_1' - C_{g_2}'u_2') + (C_{l_1}\bar{u}_1 - C_{l_2}\bar{u}_2),$$

the subscripts relating to values obtained for a given solute eluted either in different carrier gases or in the same gas at different outlet pressures.

In principle, both A and C_l are independent of the pressure and identity of carrier gas and so

$$\Delta H = \left(\frac{B_1'}{u_1'} - \frac{B_2'}{u_2'}\right) + (C_{g_1}'u_1' - C_{g_2}'u_2') + C_l(\bar{u}_1 - \bar{u}_2).$$

Because of the difference in the relation of pressure drop to volume flow for different gases or attending overall pressure change for a given gas, it is convenient to eliminate C_l by measuring ΔH at $\bar{u}_1 = \bar{u}_2$ when, of course, $u_1' \neq u_2'$. Then

$$\Delta H = \left(\frac{B_1'}{u_1'} - \frac{B_2'}{u_2'}\right) + (C_{g_1}'u_1' - C_{g_2}'u_2'). \tag{5}$$

The most convenient way to employ this equation was, not to calculate ΔH at different values of u_1' and u_2', but to use plots of H against $\bar{u}$ and to locate the point of crossing of plots, that is, $\Delta H = 0$. That this situation must always arise can be seen from equation (5). If $B_1' > B_2'$, then $C_{g_2}' > C_{g_1}'$, hence, at low velocities the term in the first parentheses contributes predominantly to ΔH and is positive, while at high velocities the second such term predominates and is negative. Thus, at the cross-over point,

$$\frac{B_1'}{u_1'} - \frac{B_2'}{u_2'} = C_{g_2}'u_2' - C_{g_1}'u_1'. \tag{6}$$

Once approximate values of B_1' and B_2' had been obtained, as from Fig. 2, then, since $B_1'/B_2' = C_{g_2}'/C_{g_1}'$, the C_g' terms could be calculated with an accuracy comparable to that of the approximate B' terms. Experience has shown that this is normally better than 25%.

Some evidence was found which indicated that ΔA was not zero with hydrogen as carrier gas. Thus, it was necessary to generalise equation (6) to

$$\Delta A + \left(\frac{B_1'}{u_1'} - \frac{B_2'}{u_2'}\right) = C_{g_2}'u_2' - C_{g_1}'u_1' \tag{7}$$

and to use the approximate value of ΔA found concurrently with B_1' and B_2'.

Whether or not it was necessary to use a value of ΔA, A, B', and C_g' were known and evaluation of C_l for a given system was completed by use of equation (1). All these values were of course approximate, but they served as the basis for subsequent modifications in which the values of the coefficients were altered slightly in turn and the values of calculated and experimental H compared. This process was continued until the comparison showed an agreement, within the estimated error of measurement of H, over the whole velocity range studied. The procedure is tedious, about six complete operations being usually required, but it has been found to be the most reliable yet devised in the absence of a computor.

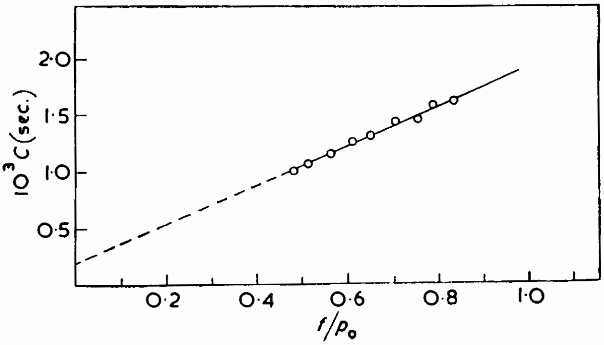


FIG. 3. *Plot, according to equation* (8), *of* C *against* f/p_0. *Data for elution of acetone by nitrogen at* 51° *from column of* d_p 0·010 *cm.*

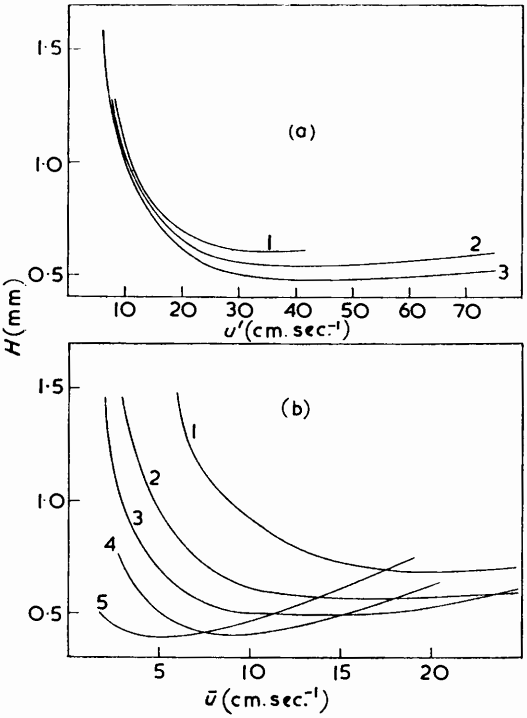


FIG. 4. *Plots of* H *against* (a) u' *and* (b) $\bar{u}$ *for the elution of benzene from column of* d_p 0·010 *cm. at* 51°.

1, Hydrogen, p_0 1 atm. 2, Hydrogen, p_0 2 atm. 3, Hydrogen, p_0 3 atm. 4, Nitrogen, p_0 1 atm. 5, Nitrogen, p_0 3 atm. *Each curve is drawn from at least* 40 *experimental measurements.*

A supplementary method of deriving values of C_g' and C_l is based on the following argument. We can write a total mass-transfer coefficient, C, defined by

$$C = fC_l/p_0 + C_g'. \tag{8}$$

A value of C at any value of H can be calculated for any individual high-velocity datum with considerable precision, even when the most approximate values of A and B' are used. From equation (8) we see that a plot of C against f/p_0, both of which vary with velocity, should be linear, of slope C_l and intercept C_g'. Fig. 3 shows such a plot, which is seen to fit the relation over a fairly wide range of values of f/p_0. However, there is some uncertainty in the value of C_g' obtained owing to the lengthy extrapolation. Even so, for the plot shown, the value of C_g' obtained was only about 40% lower than that given by the previous method. In order that a sufficiently wide range of f/p_0 values may be achieved, say, 1—0·5, it is necessary to use a column at least 5 ft. long if the support is of 100—150 mesh, or 30 ft. if it is of 30—40 mesh.

TABLE 3. *Rate equation coefficients for acetone and benzene eluted from* 20% w/w *polyethylene glycol* 400/Sil-O-Cel *columns at* 51°.

d_p cm.)	Carrier gas	A (cm.)		B' (cm.^{2} sec.$^{-1}$)		$10^3C_g'$ (sec.)		10^3C_l (sec.)	
		Acetone	Benzene	Acetone	Benzene	Acetone	Benzene	Acetone	Benzene
0·032	H_2	0·040	0·033	0·87	0·78	1·4	1·3	2·4	2·9
	N_2	0·051	0·058	0·210	0·165	5·8	6·2	2·4	2·9
0·016	H_2	0·026	0·011	0·92	0·84	0·3	0·3	1·1	1·6
	N_2	0·034	0·032	0·225	0·190	1·3	1·4	1·1	1,6
0·010	H_2	0·014	0·010	0·96	0·85	0·1	0·1	1·2	1·5
	N_2	0·011	0·009	0·254	0·224	0·4	0·4	1·2	1·5

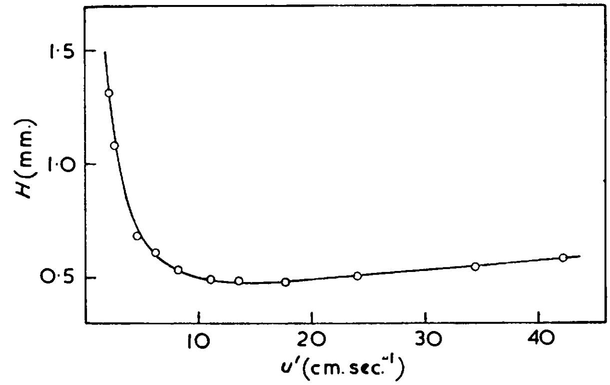


FIG. 5. *Plot of data for acetone eluted by nitrogen at* 51° *from column of* d_p 0·010 *cm.*

Full curve represents equation

$$H = 0{\cdot}011 + 0{\cdot}254/u' + 4 \times 10^{-4}u' + 1{\cdot}2 \times 10^{-3}\,u'f;$$

circles are experimental values.

Evaluated Data for Acetone and Benzene.—Coefficients were evaluated for acetone and benzene eluted from columns with supports of different sizes in experiments with hydrogen and nitrogen at outlet column pressures of 1—3 atm. at 51°; they are listed in Table 3. An example of the type of H–$\bar{u}$ plots obtained, with the corresponding H–u' plots, is shown in Fig. 4. The former (b) show the crossings predicted by equation (5), while the latter (a) substantiate the pressure corrections introduced into equation (1) since the curves tend to coincide at low velocity and move apart at high velocity. The results in Table 3 reproduce the experimental values of H to about ±1% over the velocity range 1—70 cm. sec.$^{-1}$, an example of the fit being shown in Fig. 5. Table 4 lists results deduced from those contained in Table 3 which are helpful in the further discussion. The values of λ quoted for nitrogen and hydrogen elution of both acetone and benzene are all very close to unity. On the other hand, those for hydrogen elution are not only most often lower than for nitrogen elution, but are also lower for benzene than for acetone. This peculiarity associated with hydrogen has been noted previously.[1,22] It seems a safe conclusion that, for the columns used here, λ is not greater than unity, the mean value being 0·86. A mean value of $\lambda = 0{\cdot}83$ was found[1] for the elution in nitrogen of both hydrogen and carbon dioxide from the same three columns. These results cannot be

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[22] Glueckauf, as in ref. 4, p. 33.

taken to imply that eddy diffusion as originally envisaged[2] operates in these systems, since the variations observed may, for example, reflect channelling effects. It is noticeable, for instance, that when $\lambda_{N_2}/\lambda_{H_2}$ is greater than unity for either benzene or acetone, $\gamma_{N_2}/\gamma_{H_2}$ is less than unity, and *vice versa*.

TABLE 4. *Rate equation terms evaluated from data in Table* 3. *Recorded values of* D_g' *used*: *acetone* (N_2) = 0·120; *benzene* (N_2) = 0·105; *acetone* (H_2) = 0·467; *benzene* (H_2) = 0·411 *cm.*^{2} *sec.*$^{-1}$.

d_p	λ		γ			χ		
(cm.)	N_2	H_2	N_2	H_2	B_{H_2}'/B_{N_2}'	N_2	H_2	$10^2 d_f^2/D_l$
Acetone					(theor. = 3·9)			
0·032	0·8	0·62	0·87	0·93	4·15	1·7	1·6	4·4
0·016	1·1	0·8	0·94	0·99	4·1	1·5	1·4	2·1
0·010	1·1	1·4	1·06	1·03	3·8	1·3	1·2	2·4
Benzene					(theor. = 3·9)			
0·032	0·9	0·52	0·79	0·95	4·7	1·5	1·3	9·4
0·016	1·0	0·34	0·91	1·02	4·4	1·3	1·1	5·5
0·010	0·9	1·0	1·07	1·03	3·8	1·3	1·0	5·5

An alternative explanation is that errors in the estimations of λ and γ are sufficient to cloud the issue. The ratios B_{H_2}'/B_{N_2}', while remarkably close to the theoretical value, when all is considered, show fairly large and random variations from system to system which are, in turn, reflected in γ and also in the variation of $\lambda_{N_2}/\lambda_{H_2}$. It is thus possible that λ merely represents the cumulative error involved in the elucidation of the other coefficients and that, in fact, $\lambda = 0$, as was postulated at one time by the authors.[7]

With one exception, all the values of γ quoted in Table 4 lie above 0·87. The probable error in the results is estimated at not less than $\pm 0{\cdot}06$. This estimate must be realistic since it is clear from the Table that values greater than unity, which are theoretically inadmissible, can be found. Since the mean of the results is 0·96, in the light of the immediately previous discussion it appears likely that, as in the elution of unsorbed gases, γ is unity.[1]

Considerable confidence in the essential correctness of equation (1) and the approach to the evaluation of the coefficients is derived from the quoted values of χ, which were calculated by comparison of the experimentally measured C_g' with equation (2). These range from 1·1 to 1·7, while for a given column no significant difference is observed between the values for hydrogen and nitrogen elution or between the data for acetone and benzene. Further, little change in χ is observed from d_p 0·032 to 0·016 cm. while C_l is halved. There appears to be a trend towards lower values of χ at low d_p but, again, computational errors are sufficient to make this too uncertain to merit discussion at this time. No great error is introduced if the mean value $\chi = 1{\cdot}5$ is taken as a general figure.

The data for the function d_f^2/D_l were calculated from C_l and k' values by using equation (3). These show that halving the particle size from 0·032 to 0·016 cm. almost exactly halves the function. Since D_l is presumably constant this implies that in this range of particle size $d_f \propto d_p^{\frac{1}{2}}$. On the other hand, on going from d_p 0·016 to 0·010 cm., d_f^2/D_l is virtually unchanged for both solutes. These variations might be attributed to error, were it not for the essential constancy of χ already noted and the accuracy with which C can be measured. The results, therefore, imply that solvent distribution is mainly of the droplet, and not of the film, type, the droplet size being determined by the identity, temperature, and pore structure of the solid support rather than by the particle size of the latter. Only with the coarsest support is the film thickness a function of particle size. If it is assumed that D_l for acetone is 10^{-7} cm.^{2} sec.$^{-1}$ the value of d_f for the two finer-mesh columns is $1{\cdot}6 \times 10^{-3}$ cm. This result is reasonable and corresponds well with general opinion. Since d_f is constant the results show that the ratio of D_l for benzene and acetone is 2·2 when $d_p = 0{\cdot}032$ cm., and 2·3 when $d_p = 0{\cdot}010$ cm. This remarkable constancy again supports the view that the derived values of d_f^2/D_l are realistic and that the function is important and occurs as written in the van Deemter equation.

The conclusions to be drawn from this and the earlier work [1] are that the rate equation for packed columns of porous support, such as were used in this work, can be written:

$$H = 1{\cdot}5d_p + \frac{2D_g'}{u'} + \frac{[1 + 6k' + 11(k')^2]d_p^2u'}{16(1 + k')^2D_g'} + \frac{2}{3}\frac{k'}{(1 + k')^2}\frac{d_f^2\bar{u}}{D_l}, \qquad (9)$$

the need to include the term $1{\cdot}5d_p$ being, perhaps, particular to the systems used here.

With the exception of the function d_f^2/D_l, every quantity in this equation can be measured by other than chromatographic methods. It seems, therefore, that further experiments designed to check the present findings, as expressed in equation (9), and to provide means of independent evaluation of d_f and D_l would be worth while. If the latter is achieved and equation (9) is further supported it should be possible to eliminate much of the effort now expended in column characterisation, in particular that carried out with analysis of maximum speed in view.

In connection with the latter, the finding that, with nitrogen as carrier gas, $C_g' \approx 2{\cdot}5C_l$ for the column of coarsest support, while $3C_g' \approx C_l$ for that with the finest support, is of considerable importance. It means that the conditions for fastest analysis are very different in the two cases,[10] and so the theory of high-speed analysis with packed columns must be extended to take this into account. Since, also, C_g' is so much greater in nitrogen than in hydrogen, it is evident that for fastest analysis the latter is the more desirable carrier. Finally, since it is clear that fastest analysis demands the smallest d_p, when, even in nitrogen, C_l is predominant, the key to higher speed lies in finding means of reducing resistance to mass transfer in solution.

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