A SECOND-ORDER REACTION ON A GAS CHROMATOGRAPHIC COLUMN

I. COMPUTATIONAL ANALYSIS BY THE PLATE THEORY

L. G. HARRISON AND Y. KOGA

Department of Chemistry, The University of British Columbia, Vancouver 8, B.C. (Canada)

AND

P. MADDEROM

Computing Centre, The University of British Columbia, Vancouver 8, B.C. (Canada)

SUMMARY

Plate theory is used to compute the behaviour of a system in which a reversible bimolecular reaction $A + C \rightleftharpoons 2B$ is occurring during the passage of a mixture of A, B and C through a gas chromatographic column. An apparent equilibrium constant calculated from the elution profile will usually be much less than the true equilibrium constant. Curves are presented showing in detail how the apparent equilibrium constant and centre band width in the elution profile vary with feed pulse volume and with flow rate.

INTRODUCTION

Reaction on a gas chromatographic column has drawn wide attention in theory and in practice. As reactors, chromatographic columns have an entirely different character from ordinary steady flow reactors. Sometimes the conversion becomes much higher than expected from the equilibrium constant, which is understood easily since reactants and products are separated as they flow through a chromatographic reactor. Dehydrogenation reactions are among the best examples of this, since the hydrogen liberated usually has less affinity for a column and flows faster than the reactant and the other product. Indeed patents[1-3] have been awarded for this type of reactor.

Various theoretical treatments[4-10] have been developed, for various types of reactions on chromatographic columns, treating the extent of conversion, the elution curve profile, the effect of the shape of the feed pulse, and so forth. These treatments, however, neglect the band-broadening caused by diffusion and other non-idealities in chromatographic behaviour.

KOCIRIK[11] applied rate theory[12] to take band broadening into account for the case of a first order reaction. If, however, a reaction with a rate law more complicated than first order is to be considered, application of rate theory results in too complicated

a mathematics to be solved analytically, and too many adjustable parameters (such as diffusion constant, mass transfer coefficient, and fractions of volumes of mobile and stationary phases, besides reaction rate constants) when a numerical solution is attempted.

We therefore wish to report the results of applying the plate theory[12-15] to reactions of the type A + C $\rightleftharpoons$ 2B on a chromatographic column. The plate theory has been criticised[16] because of the obscurity of its relationship to physical mechanisms. But it is very useful in a study in which the mechanisms of band broadening are not going to be analysed in detail, because it expresses broadening in terms of a single parameter, the number of theoretical plates. The theory also leads to economical computer programmes, which proved convenient in varying parameters to match the experimental results reported in Part II[17].

METHOD OF ANALYSIS

In taking the material balance at the i-th plate in a conventional manner, the rate of production of components A, B and C is included. If we assume that the reaction A + C $\rightleftharpoons$ 2B occurs in the stationary phase, and that the rates may be expressed as those of a bimolecular reversible process, the material balances become,

$$(V_G + K_A V_L)\,(\mathrm{d}A_i/\mathrm{d}t) = w(A_{i-1} - A_i) + k_0(B_i^2 - K_e A_i C_i)$$

$$(V_G + K_B V_L)\,(\mathrm{d}B_i/\mathrm{d}t) = w(B_{i-1} - B_i) - 2k_0(B_i^2 - K_e A_i C_i)$$

$$(V_G + K_C V_L)\,(\mathrm{d}C_i/\mathrm{d}t) = w(C_{i-1} - C_i) + k_0(B_i^2 - K_e A_i C_i) \qquad (1)$$

where:

A_i, B_i, C_i = concentrations of components in stationary phase of i-th plate

V_G, V_L = volumes of mobile (gaseous) and stationary (liquid) phase in a plate

K_A, K_B, K_C = partition coefficients of components between mobile and stationary phases

w = volume rate of flow of carrier gas

K_e = equilibrium constant for the reaction A + C $\rightleftharpoons$ 2B in the mobile phase

$k_0 = V_L k K_B^2$, where k is the second-order rate constant in the stationary phase

For the first plate (i = 1), A_0, B_0 and C_0 appear in eqns. 1. These designate concentrations in the feed pulse.

Experimentally, retention volumes V_{RA}, V_{RB} and V_{RC} for the three separate components can be found either by feeding each component separately or, if practicable, by choosing conditions so that k_0 is negligibly small. (The retention volumes are to be understood as those measured when the feed pulse V_0 is small compared to the retention volume.) Then the number of theoretical plates, n, and hence $V_G + K_A V_L$, etc., can be calculated by n = $16 V_{RA}^2/$(band width)$_A^2$ and $n(V_G + K_A V_L)$ = V_{RA} and similar equations with subscripts B and C replacing A.

The numerical solution of eqns. 1 was computed with an IBM 7044 computer under the following conditions:

$t \leq 0$: $A_i = B_i = C_i = 0$ for $0 \leq i \leq n$

$0 \leq t \leq t_0$: $A_0 = A_0^0\,\varphi(t)$; $B_0 = B_0^0\,\varphi(t)$; $C_0 = C_0^0\,\varphi(t)$

$t > t_0$: $A_0 = B_0 = C_0 = 0$

where $\varphi(t)$ is a step function, but with infinities at the steps avoided by rounding off in an arbitrary manner, for which purpose a cosine curve was used:

$$0 \le t \le zt_0: \qquad \varphi = 0.5[1 - \cos(\pi t/zt_0)]$$
$$zt_0 \le t \le (1 - z)t_0: \quad \varphi = 1$$
$$(1 - z)t_0 \le t \le t_0: \quad \varphi = 0.5[1 + \cos\{\pi(t - t_0 + zt_0)/zt_0\}]$$

The arbitrary width z was taken to be 0.05.

For a finite reaction rate, eqns. 1 were solved by the method of HAMMING[18]. For an infinite reaction rate, a treatment similar to MAGEE's for instantaneous reactions[8] was applied. Instead of eqns. 1, the following equations have to be solved:

$$(V_G + K_A V_L)\,(dA_i/dV) = (A_{i-1} - A_i) + \delta_i$$
$$(V_G + K_B V_L)\,(dB_i/dV) = (B_{i-1} - B_i) - 2\delta_i$$
$$(V_G + K_C V_L)\,(dC_i/dV) = (C_{i-1} - C_i) + \delta_i$$
$$B_i^2/A_i C_i = K_e \tag{2}$$

where $dV = wdt$, the volume of carrier gas passing through a plate in time dt, and δ_i is the amount of conversion required to establish the equilibrium instantaneously. Eqns. 2 were also solved numerically with the IBM 7044 computer.

In the numerical work, concentrations can be expressed in terms of an arbitrary concentration unit, provided that k_0 is related to that same unit. The feed pulse was assumed to contain an equilibrium mixture of the components, and the value (100) chosen for the equilibrium constant was close to experimentally attainable values for the reaction $I_2(g) + Br_2(g) \rightleftharpoons 2IBr(g)$.

Values chosen for parameters arose from preliminary work on the Br_2–IBr–I_2 system, but are mostly somewhat different from the values required in Part II. They are:

$$A_0{}^0 = C_0{}^0 = 1.0 \text{ conc. unit, and } K_e = 100, \text{ hence } B_0{}^0 = 10.0 \text{ conc. unit}$$
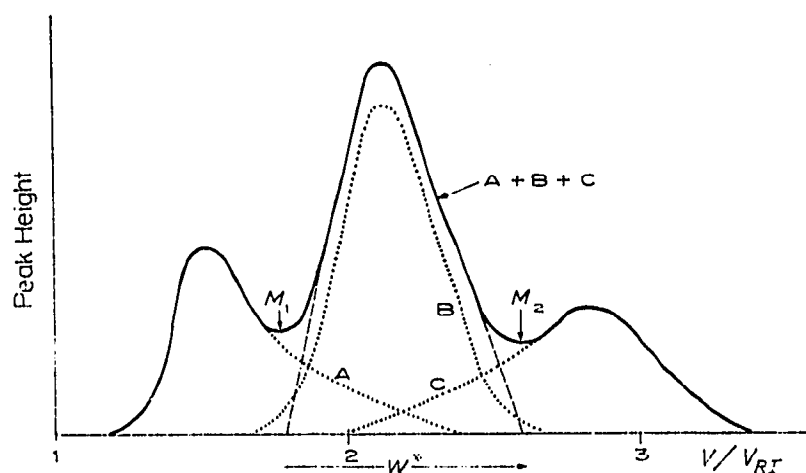$$V_{RA} = 54.0 \text{ ml}; \ V_{RB} = 74.8 \text{ ml}; \ V_{RC} = 108.0 \text{ ml}$$

Fig. 1. A typical computed elution profile (A + B + C), with dotted lines showing the contributions from the separate components. M_1 and M_2 are minima used in calculating $K_{eff}{}^*$. W^* is the centre band width from tangents at inflection points. $n = 200$; $K_e = 100$; $V_0 = 0.5$ ml $= 0.0136\ V_{RI}$; $k_0 = 200$ ml min^{-1} (conc. unit)$^{-1}$; $w = 76$ ml/min. From the profile, $K_{eff} = 2.94$ and $K_{eff}{}^* = 9.01$.
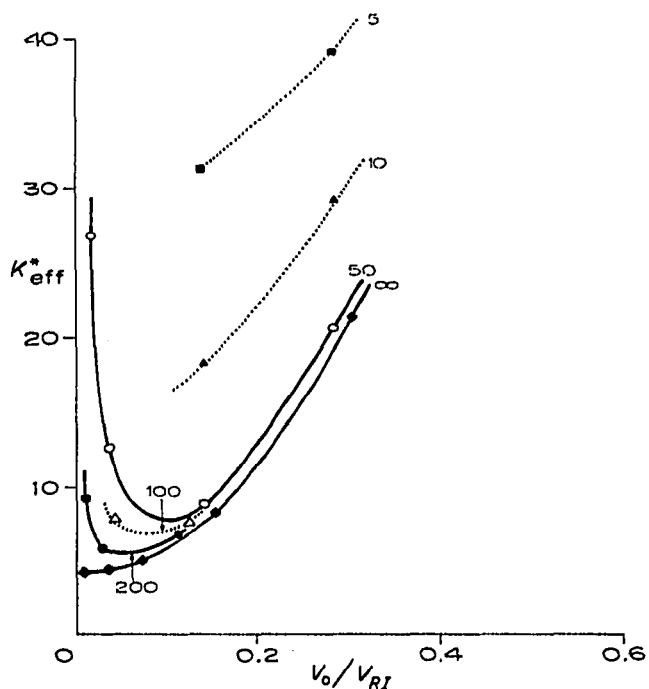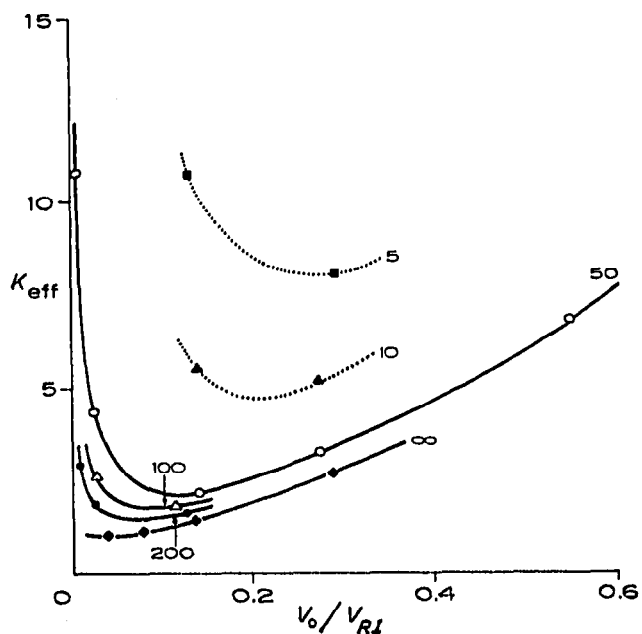
Fig. 2. Variation of apparent equilibrium constant K_{eff} with feed pulse volume V_0. Numbers on curves are values of reaction rate parameter k_0. n, w and K_e are the same as in Fig. 1.

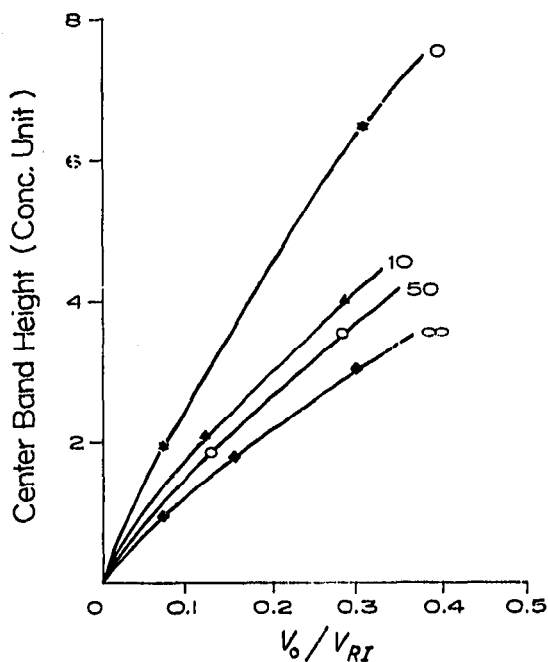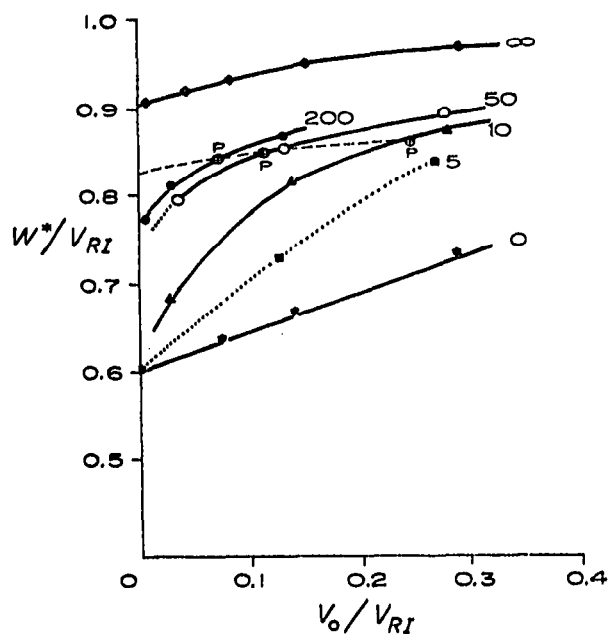Fig. 3. The same as Fig. 2, for K_{eff}^* instead of K_{eff}.

Fig. 4. Centre band width W^* against feed pulse volume V_0. Numbers on curves are values of k_0. Points marked P correspond to minima in Fig. 2. The dotted line is the locus of P (essentially constant W^*). n, w and K_e are the same as in the previous figures.

Fig. 5. Centre band height against feed pulse volume V_0 for various k_0 (numbers on curves). n, w and K_e are the same as in the previous figures.

$V_{RI} = nV_G = 36.8$ ml $=$ retention volume of a component which has no affinity with the stationary phase (zero partition coefficient); in practice, this was regarded as being the same as the retention volume of air, designated V_{RAIR}.

$n = 200$

$w = 30.0, 76.0, 120.0$ ml/min

$V_0 = wt_0 = 0.5$ to 20 ml

$k_0 = 5, 10, 50, 100, 200$ ml min^{-1} (conc. unit)$^{-1}$
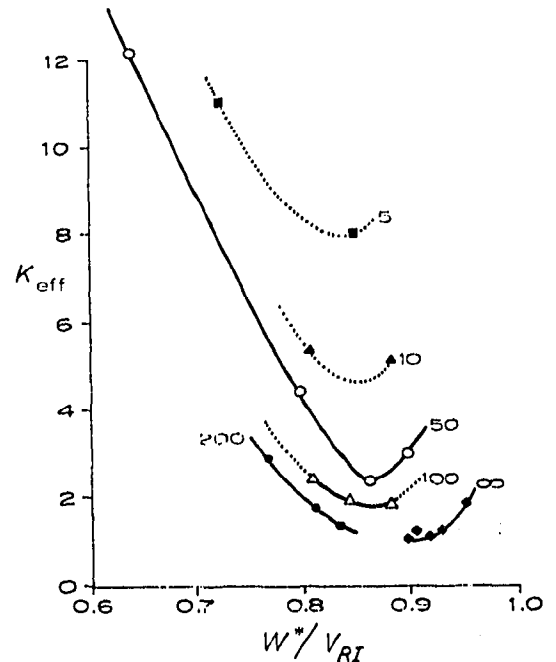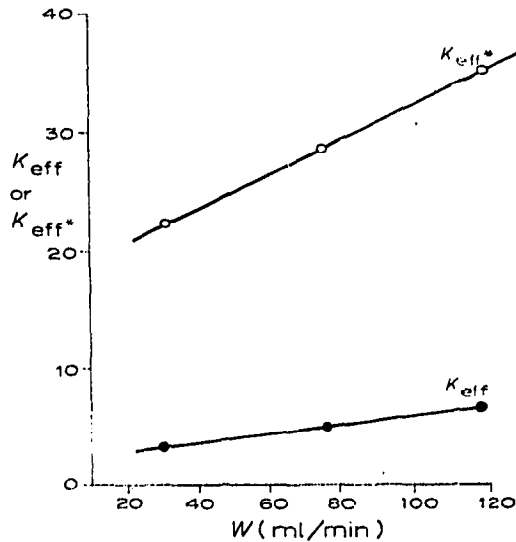

Fig. 6. Apparent equilibrium constants K_{eff} and $K_{eff}*$ against flow rate for a low reaction rate, $k_0 = 10$ ml min^{-1} (conc. unit)$^{-1} \cdot V_0/V_{RI} = 0.272$; n and K_e are the same as in the previous figures.

Fig. 7. K_{eff} against centre band width $W*$ for various k_0 (numbers on curves). n, W and K_e are the same as in Figs. 1-5.

A typical computed elution profile is shown in Fig. 1. To describe the behaviour of the system the following quantities were chosen:

$$K_{eff} = [\int_0^\infty B(t)dt]^2/[\int_0^\infty A(t)dt \int_0^\infty C(t)dt]$$

$$K_{eff}* = [\int_{M_1}^{M_2}(A + B + C)dt]^2/[\int_0^{M_1}(A + B + C)dt \int_{M_2}^\infty (A + B + C)dt]$$

where:

M_1 and M_2 are minima in the elution profile, as marked in Fig. 1;

$W*$ = band width parameter = distance in volume units between intersections of tangents at the inflection points of the centre band of the profile with the horizontal axis;

K_{eff} is an apparent equilibrium constant related to the actual total amounts of A, B and C in the eluted material; but it is not accessible to experimental measurement, because of band overlap in the elution profile;

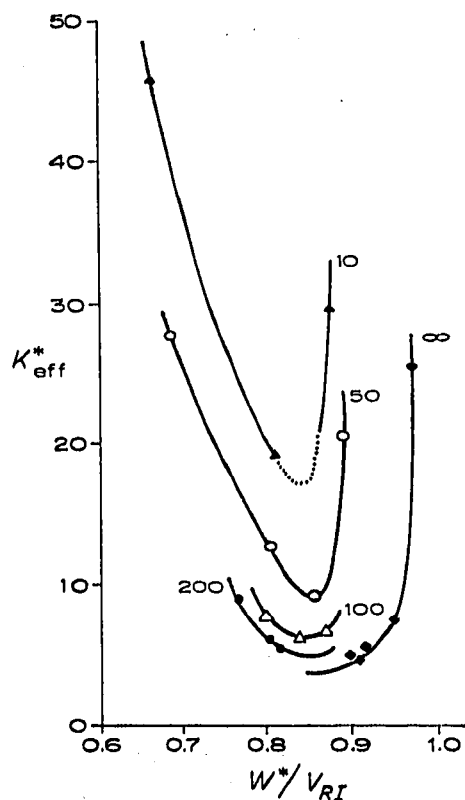$K_{eff}*$ is a parameter which can be calculated from an experimental elution

Fig. 8. The same as Fig. 7, for $K_{eff}*$ instead of K_{eff}.

profile; it should normally have a value similar to K_{eff}, but is not precisely related to total amounts of A, B and C.

Results of computations are displayed in Figs. 2–8.

DISCUSSION

Chromatographic separation must slow down the combination of A and C relative to the decomposition of B; thus K_{eff} and $K_{eff}*$ are always less than the true equilibrium constant K_e. The precise value of K_{eff} can be thought of as depending on two factors, which sometimes compete with each other so that, for example, K_{eff} passes through a minimum as V_0 is varied at constant k_0. These two factors are: (a) The reaction rate term, which increases both with the rate parameter k_0 and with the concentration term at any plate $(B_i^2 - K_e A_i C_i)$. A higher reaction rate term tends to decrease K_{eff}. (In Fig. 2, for any constant V_0, K_{eff} becomes smaller as k_0 increases.) (b) The degree of overlapping of the two peaks. Clearly, greater overlapping tends to bring K_{eff} closer to the true K_e.

When the feed pulse volume V_0 is increased, both the concentrations at any plate and the overlapping become larger. At low V_0 the concentration effect is dominant, and at high V_0 the overlapping effect. This occurs because, as discussed by VAN DEEMTER et al.[12], the concentration of any single component (e.g. A) increases linearly with V_0 up to $V_0 n^{\frac{1}{2}}/V_{RA} \sim 1$, and thereafter increases more slowly (compare Fig. 5, showing centre band height against V_0); whereas the band width increases slowly at the beginning, but linearly above $V_0 n^{\frac{1}{2}}/V_{RA} \sim 2.5$.

Hence each curve of K_{eff} against V_0 in Fig. 2 has a minimum, except that for $k_0 = \infty$. In that case, the reaction is completed at each plate no matter how small the concentrations are. The curve displays the overlapping effect by itself, and K_{eff} increases monotonically with V_0.

The band width parameter W^* (Fig. 4) depends chiefly on the component B, but is larger than the true band width of B because of overlapping (Fig. 1). At any constant V_0, W^* increases with reaction rate parameter k_0. This is because the increasingly rapid production of A and C from B causes the overlapping to become worse; in terms of band shape, the A and C bands (Fig. 1) become asymmetric, with "tails" pointing towards the centre band.

A curve of W^* against V_0 for constant k_0 (Fig. 4) seems to be divisible into two parts: an initial rapid increase, with strong curvature, followed by a slower, more nearly linear increase. This is best seen at $k_0 = 10$, 50 or 200. The transition between the two regions lies roughly at the point marked P on some of the curves in Fig. 4; this is the point at which K_{eff} has its minimum value (Fig. 2). Up to the point P, K_{eff} decreases as V_0 rises, which means that the peaks for A and C are increasing relative to B, so that their tails are contributing increasingly to W^*. Beyond the point P, this effect is reversed; the A and C peaks thereafter contribute successively less and less to the centre peak, and W^* increases less rapidly than in the case of symmetrical bands, $k_0 = 0$.

It is interesting that the points P, for a wide range of k_0 values, lie at roughly the same W^*; thus the importance of extent of overlapping in the dependence of K_{eff} on V_0 can be seen in a surprisingly simple way, in relation to band width.

The flow rate dependence of K_{eff} is shown in Fig. 6. Clearly, a higher flow rate gives less time for reaction to occur, and K_{eff} rises with the flow rate. This effect becomes smaller as reaction rate increases and ultimately, for instantaneous reaction ($k_0 = \infty$), K_{eff} does not depend on flow rate.

In the last two diagrams (Figs. 7 and 8) K_{eff} and K_{eff}^* are plotted against W^*. These diagrams are useful in practice because W^* is easily evaluated from the chromatogram, whereas the feed pulse volume V_0, used as independent variable in Figs. 2 and 3, is rather difficult to evaluate experimentally because, for example, the kinetics of evaporation of a liquid sample in the injector are not known.

ACKNOWLEDGEMENTS

REFERENCES

1 J. A. DINWIDDIE(to Esso Research and Engineering Co.), U.S. Pat., 3, 243, 472 (March 29, 1966).
2 J. A. DINWIDDIE AND W. A. MOYAN (to Esso Research and Engineering Co.), U.S. Pat., 2, 976, 132 (March 21, 1961).
3 E. M. MAGEE (to Esso Research and Engineering Co.), Can. Pat., 631, 882 (Nov. 28, 1961).
4 J. C. GIDDINGS, J. Chromatog., 3 (1960) 443.
5 S. Z. ROGINSKII, M. I. YANOVSKII AND G. A. GAZIEV, Kinetika i Kataliz, 3 (1962) 529.
6 D. W. BASSETT AND H. W. HABGOOD, J. Phys. Chem., 64 (1960) 769.

7 G. A. GAZIEV, V. YU. FILINOVSKII AND M. I. YANOVSKII, *Kinetika i Kataliz*, 4 (1963) 688.

8 E. M. MAGEE, *Ind. Eng. Chem., Fundamentals*, 2 (1963) 32.

9 H. SAITO, Y. MURAKAMI AND T. HATTORI, *Kagaku Kogaku*, 29 (1965) 585 or in the abridged English edition, *Chem. Engineering (Tokyo)*, 4 (1966) 42.

10 F. E. GORE, *Ind. Eng. Chem., Process Design Develop.*, 6 (1967) 10.

11 M. KOČIŘÍK, *J. Chromatog.*, 30 (1967) 459.

12 J. J. VAN DEEMTER, F. J. ZUIDERWEG AND A. KLINKENBERG, *Chem. Eng. Sci.*, 5 (1956) 271.

13 T. KAMBARA, *J. Chromatog.*, 19 (1965) 478.

14 T. KAMBARA AND K. OZEKI, *J. Chromatog.*, 21 (1966) 383.

15 A. J. P. MARTIN AND R. L. M. SYNGE, *Biochem. J.*, 35 (1941) 1358.

16 J. C. GIDDINGS, in J. C. GIDDINGS AND R. A. KELLER (Editors), *Chromatographic Science Series, Vol. 1, Dynamics of Chromatography, Part 1, Principles and Theory*, Marcel Dekker, New York, 1965, p. 20.

17 L. G. HARRISON AND Y. KOGA, *J. Chromatog.*, 52 (1970) 39.

18 R. HAMMING, *J. Assoc. Comput. Machin.*, 6 (1959) 37.