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On the Multiplicity of Resolution Equations in the Chromatographic Literature

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Abstract

It is shown that, in spite of the multiplicity of resolution equations in the literature, there are only three basic relations: the Purnell, Knox, and Said equations of resolution.

The Giddings equation for peak capacity in its differential form may also be extended to include resolution, leading to an alternative definition for it in which the width log mean average is used instead of the width arithmetic average. This definition is based on the continuity of peak width variation along the column and leads to numerical answers practically identical with those based on the original definition.

This new definition of resolution, which is not an approximation of the original one but stands on its own merits, gives strength to an already deduced and simple peak capacity equation, which was thought to be approximate, as being exact. This eliminates the necessity of lengthy algebraic derivations leading to complicated equations which give no more than the results obtained by the simple peak capacity equation.

Alternate resolution equations which are simple and exact were derived and a chart for the separation efficiency $\eta_{1:1}$ as a function of the number of theoretical plates N and the separation factor α' was prepared. The resolution R_s can be read on an extra scale in the plot. This chart may be used as a substitute for the controversial Glueckauf chart.

The average plate number N used in the resolution equation was studied when $N_1 \neq N_2$. The study leads to the conclusion that due to the large uncertainties in both the experimental and theoretical determination of N, any suggestion for N_{av} other than the simple arithmetic average cannot be justified.

Some erroneous equations and conclusions in the literature concerning resolution and peak capacity are pointed out.

INTRODUCTION

There are many resolution equations in the literature. They may look different because they are written in different forms using different notations, but all of them belong to three basic equations. References *1–7* represent only a partial list of these equations.

We will be concerned only with the development of a resolution equation for two overlapping Gaussian peaks. The base width of each peak w varies with its retention volume $\bar{V}$ and the number of theoretical plates N according to

$$N = \left(\frac{\bar{V}}{\sigma}\right)^2 = 16\left(\frac{\bar{V}}{w}\right)^2 \tag{1}$$

σ is the standard deviation of the peak.

Equation (1) follows from different theories of chromatography such as the plate theory developed by Martin and Synge (*8*) and amplified by this author (*9*), and the random walk theory developed by Giddings (*10*).

Another fundamental equation is the internationally accepted definition for resolution:

$$R_s = \frac{\bar{V}_2 - \bar{V}_1}{\frac{1}{2}(w_2 + w_1)} = \frac{\bar{V}_2 - \bar{V}_1}{w_a} \tag{2}$$

in which w_a is the peak width arithmetic average.

We will assume that N is the same for Components 1 and 2. Whether it is equal to N_2, N_1, or any of their averages goes under this assumption, which may be expressed mathematically as

$$N_1 = N_2 = N \tag{3}$$

The question concerning which N to use will be discussed separately in a later section.

THE THREE BASIC RESOLUTION EQUATIONS

In spite of the multiplicity of resolution equations in the literature, authors agree on the three well-known or basic resolution equations (*11*); the Purnell (*1*), the Knox (*2*), and the Said (*3*) equations. For example, the equation in Ref. *4* is a Said equation while that in Ref. *5* is a Purnell equation.

In order to make this study as complete and useful as possible, a brief mention of the steps involved in the development of these equations is presented here. Beside the three fundamental Eqs. (*1*), (*2*), and (*3*), the following well-known relations are also required for the derivation of the three basic resolution equations:

$$\bar{V}_2 = V_0(1 + k_2) \tag{4}$$

$$\bar{V}_1 = V_0(1 + k_1) \tag{5}$$

where V_0 is the void (air) peak retention volume and k_1 and k_2 are the respective capacity factors for Components 1 and 2.

From Eq. (1) one gets

$$\bar{V}_2/\bar{V}_1 = w_2/w_1 \tag{6}$$

The distribution ratio K is related to the capacity factor k by the formula

$$k = K\frac{V_s}{V_m}$$

where V_s and V_m are the stationary and mobile phase volumes, respectively.

The Purnell Equation

This is the first resolution equation in terms of α, N, and k, and the one usually referred to in the literature as "the well-known resolution equation." Quantity α is the capacity factor ratio

$$\alpha = k_2/k_1 = K_2/K_1$$

In the Purnell derivation, the following approximation in Eq. (2) was made:

$$\frac{w_1 + w_2}{2} = w_2 \tag{7}$$

In this case Eq. (2) becomes

$$R_s = \frac{\bar{V}_2 - \bar{V}_1}{w_2} \tag{2'}$$

Substituting from Eqs. (1), (4), (5), and (6) into Eq. (2'), one gets

$$R_{s,P} = \frac{\sqrt{N}}{4}\frac{\alpha - 1}{\left(\alpha + \dfrac{1}{k_1}\right)} = \frac{\sqrt{N}}{4}\frac{\alpha - 1}{\alpha}\left(\frac{k_2}{1 + k_2}\right) \tag{8}$$

Introducing other parameters such as Δk for $k_2 - k_1$, n for w_1/w_2 or

KV_s/V_m for k, the Purnell equation may be written in several other forms (Appendix I).

The Knox Equation

Here, the following approximation in Eq. (2) was made:

$$\frac{w_1 + w_2}{2} = w_1 \tag{9}$$

So that Eq. (2) becomes

$$R_s = \frac{V_2 - V_1}{w_1} \tag{2''}$$

and similarly, by substituting from Eqs. (1), (4), (5), and (6) into Eq. (2″) gives

$$R_{s,K} = \frac{\sqrt{N}}{4}\,\frac{\alpha - 1}{1 + \dfrac{1}{k_1}} = \frac{\sqrt{N}}{4}(\alpha - 1)\frac{k_1}{1 + k_1} \tag{10}$$

In spite of the simplicity of the Knox equation, it is not as widely quoted as the Purnell equation.

The Said Equation

In this case no approximation is made in Eq. (2). By substituting from Eqs. (1), (4), (5), and (6) into Eq. (2), one gets

$$R_s' = \frac{\sqrt{N}}{2}\,\frac{\alpha - 1}{\alpha + 1 + \dfrac{2}{k_1}} = \frac{\sqrt{N}}{2}\,\frac{\alpha - 1}{\alpha + 1}\,\frac{k}{1 + k} \tag{11}$$

where

$$k = (k_1 + k_2)/2 \tag{12}$$

With little algebraic manipulation, the Said equation (Eq. 11) may also be written in several other forms (Appendix II).

SEPARATION EFFICIENCY

The efficiency of a separation is often related to the purity of the fractions obtained. The resolution concept as given by Eq. (2) does not express the fractional impurity directly.

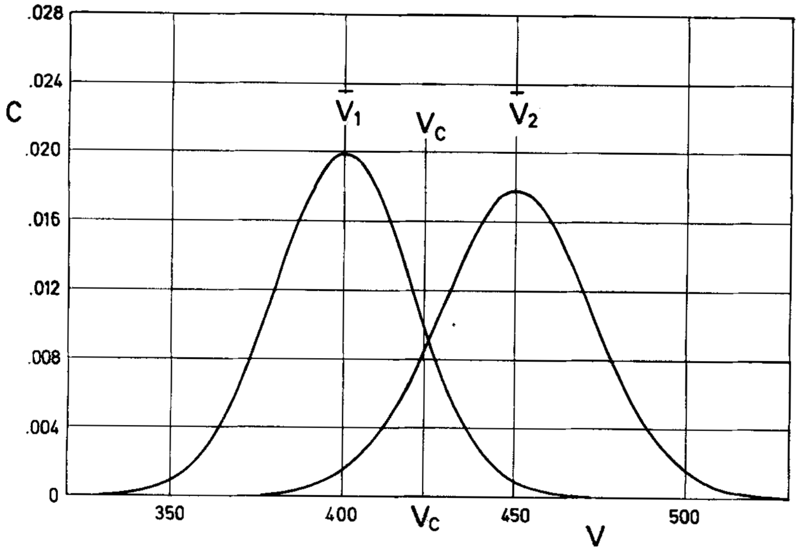

FIG. 1. Two overlapping Gaussian and equal chromatographic peaks with the cut at equal fractional impurity.

A relation exists between R_s and the separation efficiency $\eta_{1:1}$ for two equal and overlapping Gaussian chromatographic peaks. Here, $\eta_{1:1}$, as defined by Glueckauf (*12*), is the fractional impurity when a cut is made such that the fractional impurity is the same on both sides of the cut. This author showed (*13*) that the same value obtained for $\eta_{1:1}$ may be used without modification and with little error for two unequal and overlapping Gaussian peaks. By "two chromatographic peaks" it is meant that Eq. (6) is also satisfied as in Fig. 1 where $\overline{V_c V_c}$ represents the cut for equal impurity ratios on both sides. It should be noted that it does not pass by the point of intersection for two equal and overlapping Gaussian chromatographic peaks. It is displaced a little toward the fast moving peak.

For equal impurities the arguments of the two normal distributions must be equal so that

$$t_1 = t_2 = t \tag{13}$$

or

$$\frac{\bar{V}_2 - V_c}{\sigma_2} = \frac{V_c - \bar{V}_1}{\sigma_1} = t \tag{14}$$

This leads to

$$t = \frac{\bar{V}_2 - \bar{V}_1}{\sigma_1 + \sigma_2} = \frac{\bar{V}_2 - \bar{V}_1}{\frac{w_1 + w_2}{4}} = 2R_s \tag{15}$$

and therefore

$$\eta_{1:1} = A(t) = A(2R_s) \tag{16}$$

or

$$R_s = \frac{1}{2}A^{-1}(\eta_{1:1}) \tag{17}$$

$A(t)$ is the area under the normal curve of error (error integral) as given by the relation

$$A(t) = \frac{1}{\sqrt{2\pi}}\int_t^\infty e^{-t^2/2}\,dt = Q \tag{18}$$

and

$$A^{-1}(Q) = t \tag{19}$$

is the inverse error integral inasmuch as the log function is the inverse of the exponential function. Both the error and inverse error integral are tabulated in the literature (*14*).

Equation (16) shows that $\eta_{1:1}$ vs R_s is a straight line plot on probability graph paper as in Fig. 2. By substituting from Eq. (11) into Eq. (16), one gets the separation efficiency equation in terms of N, α, and k, so that

$$\eta_{1:1} = A\left[\sqrt{N}\frac{\alpha - 1}{\alpha + 1}\frac{k}{k + 1}\right] \tag{20}$$

POSITION OF THE CUT $\overline{V_c V_c}$ FOR EQUAL IMPURITY RATIO

Equation (1) shows that

$$\frac{\bar{V}_2}{\bar{V}_1} = \frac{\sigma_2}{\sigma_1} \tag{21}$$

Substituting into Eq. (14) gives

$$\frac{V_c - \bar{V}_1}{\bar{V}_1} = \frac{\bar{V}_2 - V_c}{\bar{V}_2}$$

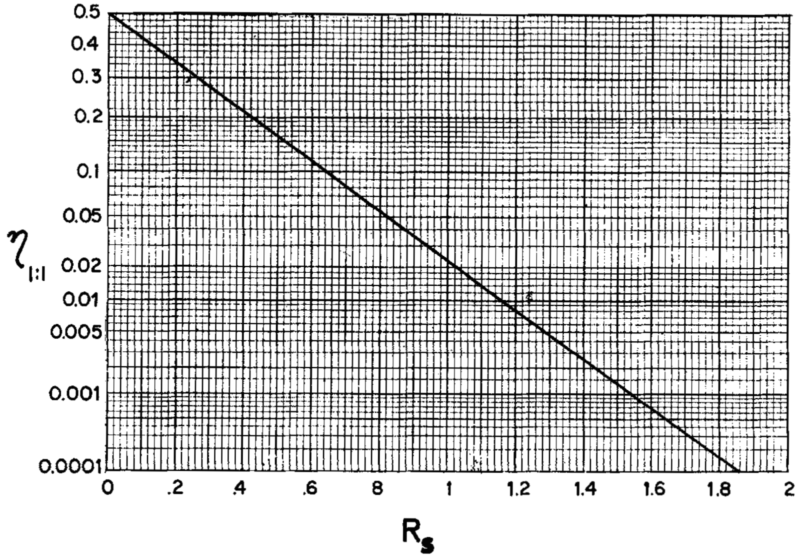

FIG. 2. Plot of Eq. (16) on probability graph paper.

which leads to

$$V_c = \frac{2\overline{V}_1\overline{V}_2}{\overline{V}_1 + \overline{V}_2} \tag{22}$$

Equation (22) shows that for an equal impurity ratio between two equal chromatographic and Gaussian peaks, the cut must be made at the harmonic average of $\overline{V}_2$ and $\overline{V}_1$, and not at their geometric average as deduced by Glueckauf (*12*).

PEAK CAPACITY

Most of the credit in developing the theroretical treatment of peak capacity goes to Giddings. Very little has been added to what he achieved in his brief but excellent note (*15*) on the subject.

In this study a slight modification in the definition of peak capacity *n* will be made. Here, we define *n* as the number of totally separated peaks between any two points 1 and 2 on the elution curve. By "totally separated" it is meant that tangents to peaks meet at the base line, in which case $R_s = 1$.

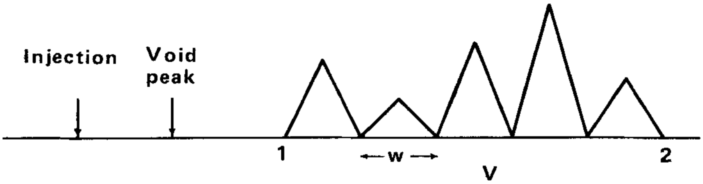

Fig 3a

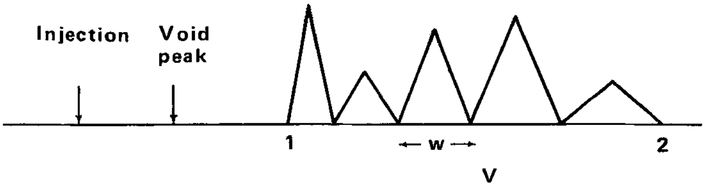

Fig 3b

FIG. 3. Schematic representation of totally separated peaks between points 1 and 2.

The total peak capacity n_t is the peak capacity between the void peak and the maximum of the last peak. Quantity n'_t is equal to $n_t + 1$ so that n'_t is the total number of peaks between and including both the void peak and the last peak. We also introduce the concept that n is not necessarily an integer.

The mathematics needed for the peak capacity treatment is quite simple. One needs no more than Eq. (1) and the Giddings peak capacity fundamental relation in its differential form (*16*). The latter may be easily deduced with reference to Fig. 3 as follows.

In Fig. 3(a), the peak width w does not change with V, contrary to the requirement of Eq. (1). In this case the peak capacity n between points 1 and 2 is given by

$$n = \Delta V/w \tag{23}$$

where $\Delta V = V_2 - V_1$.

According to Eq. (1), w should, however, change continuously as shown in Fig. 3(b) and, therefore, a differential equation must be set up and integrated. Equation (23) in its differential form becomes

$$dn = dV/w \tag{24}$$

which is the Giddings formula. Integrating between points V_1 and V_2, one gets

$$n = \int_{V_1}^{V_2} dV/w \tag{25}$$

When w is constant, one gets Eq. (23). For the actual case where $w = f(V)$ according to Eq. (1), one gets

$$n = \int_{V_1}^{V_2} \frac{\sqrt{N}\,dV}{4V} = \frac{\sqrt{N}}{4} \ln \frac{V_2}{V_1} \tag{26}$$

Equation (26) may be called the Giddings-Grushka equation. It was Grushka (*17*) who first integrated the Giddings differential equation (Eq. 24).

Similarly,

$$n_t = \frac{\sqrt{N}}{4} \ln \frac{V_f}{V_0} \tag{27}$$

and

$$n_t' = \frac{\sqrt{N}}{4} \ln \frac{V_f}{V_0} + 1 \tag{28}$$

where V_f is the final peak retention volume. Quantities n, n_t, or n_t' are quite easy to calculate from the above equations, or may be read from Fig. 4 where n is plotted vs V_2/V_1 on a semilog graph with $\sqrt{N}$ as the parameter. The plot is a family of straight lines meeting at the origin.

Alternative and probably more convenient plots are given in Figs. 5A and 5B which plot N vs n on log-log graph paper with α' as the parameter, giving a family of parallel lines. Quantity $\alpha' = V_2/V_1 = \bar{V}_2/\bar{V}_1 = (1 + k_2)/(1 + k_1)$, and may be called the separation factor. Of course, a plot of n vs N with α' as the parameter can also be plotted easily.

The peak capacity n as given by Eq. (26) may be defined as the number of continuously widening (or narrowing) peaks between points 1 and 2 on the chromatogram.

RELATION BETWEEN RESOLUTION AND PEAK CAPACITY

R_s is defined mathematically according to Eq. (2). With reference to the same equation, it may also be defined in words as being the number of average (arithmetic) peak widths between two neighboring peak maxima.

If the Giddings formula (Eq. 24) is integrated between limits $\bar{V}_1$ and $\bar{V}_2$,

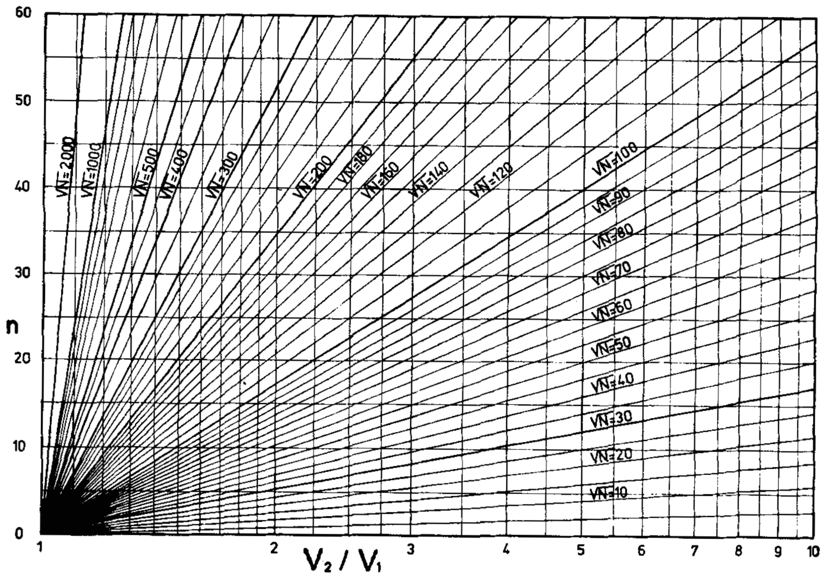

FIG. 4. Plot of Eq. (26) on semilog graph paper.

one gets

$$\bar{n} = \int_{\bar{V}_1}^{\bar{V}_2} \frac{dV}{w} = \frac{\sqrt{N}}{4} \ln \frac{\bar{V}_2}{\bar{V}_1} \qquad (29)$$

In this case, and in line with the definitions given above for peak capacity, $\bar{n}$ would be the number of continuously varying peak widths between the two neighboring peak maxima.

Comparison of this definition with the definition deduced from Eq. (2) for R_s shows that they are identical except for the continuity and discontinuity of the peak width. This shows that Eq. (29) can be used as the basis for an alternative definition for resolution which may be given the symbol $\bar{R}_s$:

$$\bar{R}_s = \frac{\sqrt{N}}{4} \ln \frac{\bar{V}_2}{\bar{V}_1} \qquad (30)$$

In terms of N, k, and α', one gets

$$\bar{R}_s = \frac{\sqrt{N}}{4} \ln \frac{1 + k_2}{1 + k_1} = \frac{\sqrt{N}}{4} \ln \alpha' \qquad (30')$$

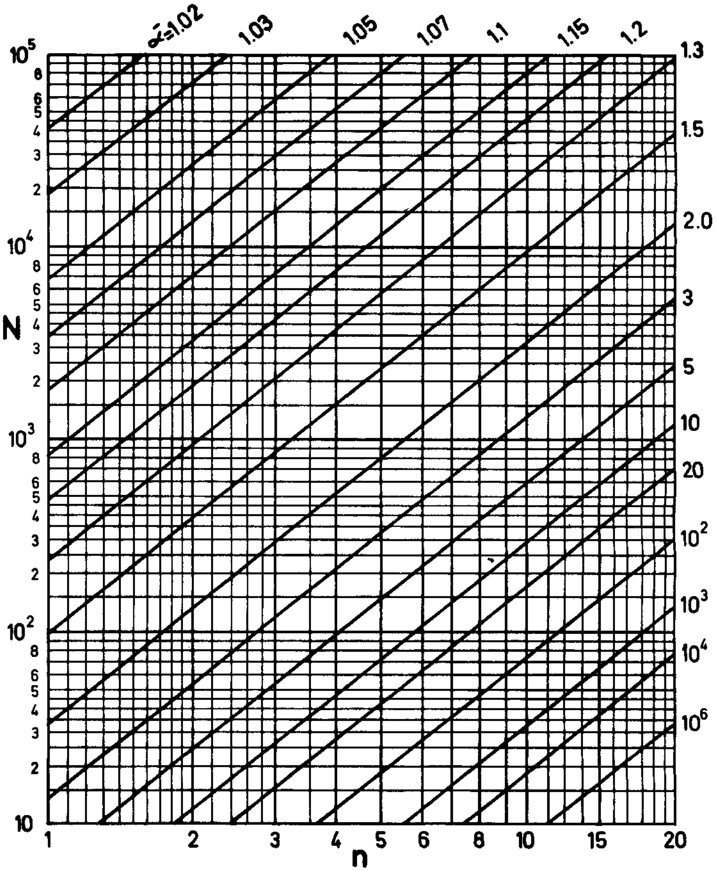

FIG. 5A. Plot of Eq. (26) on log-log graph paper.

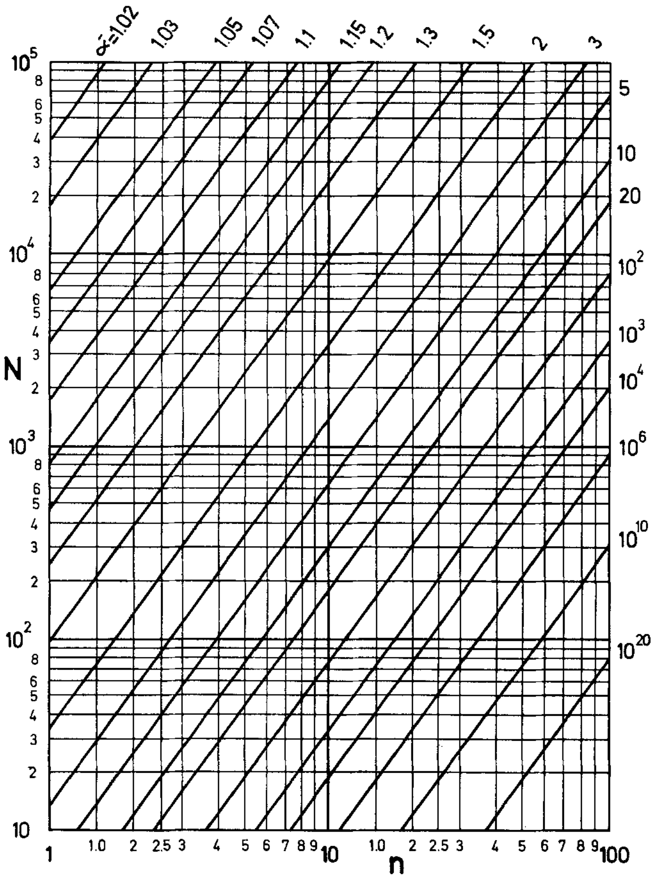

FIG. 5B. Plot of Eq. (26) on log-log graph paper.

Substituting for R_s from Eq. (30′) into Eq. (16) gives

$$\eta_{1:1} = A\left[\frac{\sqrt{N}}{2}\ln\frac{1+k_2}{1+k_1}\right] = A\left(\frac{\sqrt{N}}{2}\ln\alpha'\right) \tag{31}$$

Equation (31) is a simple relation between the separation efficiency $\eta_{1:1}$ and the parameters N, k_1, and k_2.

Equation (30) can be rearranged as

$$\bar{R}_s = \frac{\frac{\sqrt{N}}{4}(w_2 - w_1)}{\frac{w_2 - w_1}{\ln\frac{\bar{V}_2}{\bar{V}_1}}} \tag{32}$$

A substitution from Eqs. (1) and (6) into Eq. (32) leads to

$$\bar{R}_s = \frac{\bar{V}_2 - \bar{V}_1}{\frac{w_2 - w_1}{\ln\frac{w_2}{w_1}}} = \frac{\bar{V}_2 - \bar{V}_1}{w_l} \tag{33}$$

where w_l is the width log mean average.

We now have two fundamental relations for resolution. They are the last form of Eq. (2):

$$R_s = \frac{\bar{V}_2 - \bar{V}_1}{w_a} \tag{2}$$

and the new expression

$$\bar{R}_s = \frac{\bar{V}_2 - \bar{V}_1}{w_l} \tag{33}$$

Table 1 lists the values of w_a/w_l for different values of w_2/w_1 of chromatographic interest. Listed also are the corresponding percent deviations of Eq. (33) from Eq. (2) and the percent deviations of Eq. (2′) (Purnell approximation) from Eq. (2) for comparison.

If both Eqs. (2′) and (33) are considered two different approximations of Eq. (2), then the error in Eq. (33) is negligibly small compared to that in Eq. (2′), as can be seen from Table 1. When w_2/w_1 (which is equal to α') is equal to 1.1, the error in Eq. (33) is less than 0.1 % while the error in the Purnell approximation is 60 times greater.

Equation (33), therefore, cannot be considered an approximation of

TABLE 1

$\frac{w_2}{w_1}$	$\frac{w_a}{w_i}$	% Deviation of Eq. (33) from Eq. (2)	% Deviation of Eq. (2′) from Eq. (2)	Deviation ratio
1.00	1.0000	0.00	0.00	
1.01	1.0000	0.00	0.50	600
1.02	1.0000	0.00	0.98	300
1.05	1.0002	0.02	2.38	120
1.10	1.0008	0.08	4.55	60
1.20	1.0028	0.28	8.33	30

Eq. (2). It is rather an alternative definition of resolution leading to essentially the same answers. It may be used in place of Eq. (2) for the purpose of convenient and easy derivations, as in the case of peak capacity calculations.

This leads us also to the important conclusion that the above treatment of the peak capacity using the Giddings equation is an exact treatment based on an alternative definition, $\bar{R}_s$, of resolution no less elegant than the customary definition (Eq. 2) and leads to the same numerical values. One also concludes that the algebraic treatments, encountered in Refs. *18* and *19* become less important if not completely replaced by the Giddings-Grushka derivation (Appendix III).

Inasmuch as the Said equation of resolution is considered an exact equation (*4*, *20–23*), Eq. (30) is also an exact resolution equation leading to essentially the same answers.

We note that R_s and $\eta_{1:1}$ can be easily calculated from Eqs. (30) and (31), respectively, or they may be obtained from Fig. 6A which is identical to Fig. 4 except for the range on the ordinates. In other words, Fig. 6A is an expansion of a small area around the origin in Fig. 4. The usefulness of Fig. 6A was extended by adding an auxiliary scale to the right on which $\eta_{1:1}$ may be read directly. The scale was prepared using Eq. (17) and tables of the inverse error integral (*14*). There is no difference between Figs. 6A and 6B except that in the latter, the R_s and $\eta_{1:1}$ scales have been switched so that the $\eta_{1:1}$ scale becomes the main scale to the left and the R_s scale is the auxiliary scale to the right. Figure 7A is a plot of N vs R_s for Eq. (30) on a log-log graph with α' as the parameter, giving a family of parallel lines as in Fig. 5. An auxiliary upper scale on which $\eta_{1:1}$ may be read directly was also prepared to increase the usefulness of the chart. Figure 7B is the same chart as Fig. 7A except that $\eta_{1:1}$ becomes the main lower scale and R_s is the auxiliary upper scale in Fig. 7B.

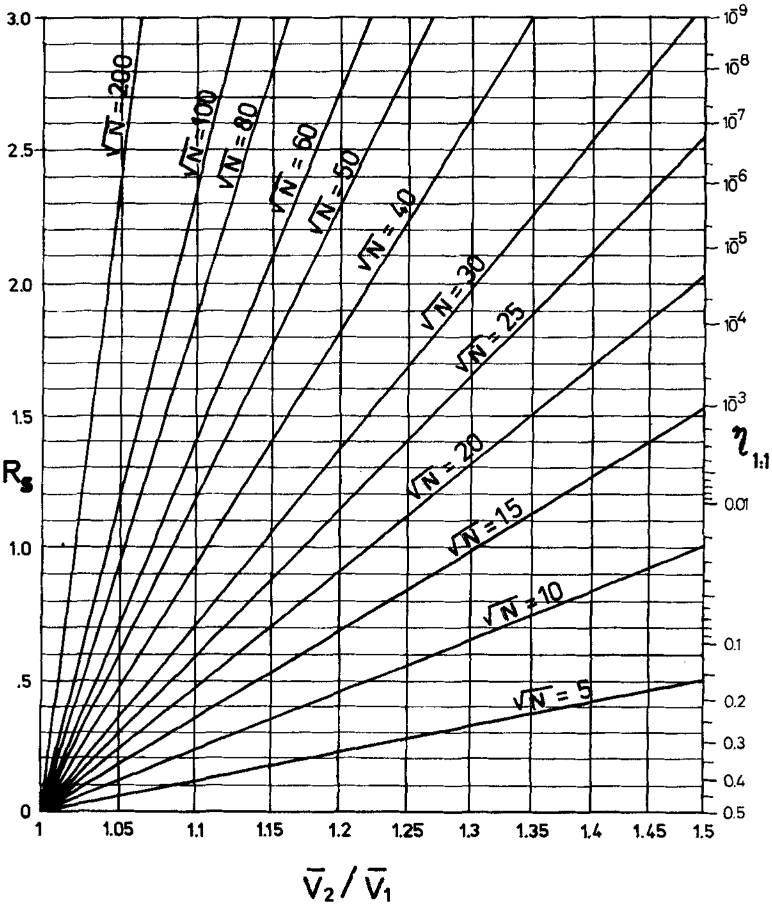

FIG. 6A. Plot of Eq. (30) on semilog graph paper with an auxilary scale for $\eta_{1:1}$.

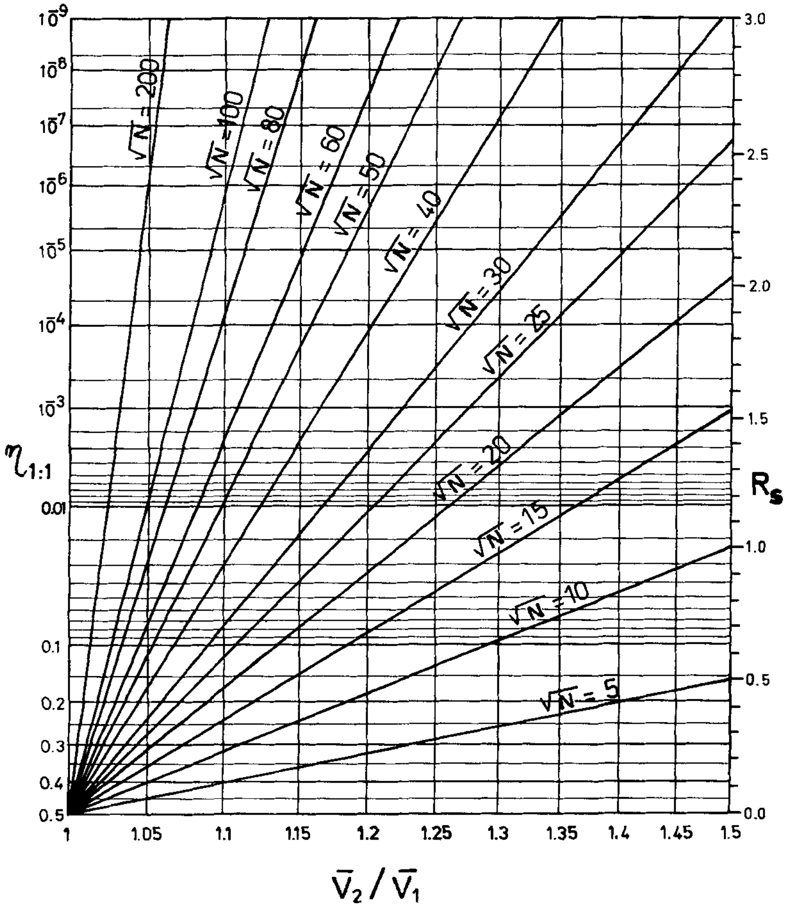

FIG. 6B. Plot of Eq. (31) on semilog graph paper with an auxiliary scale for R_s.

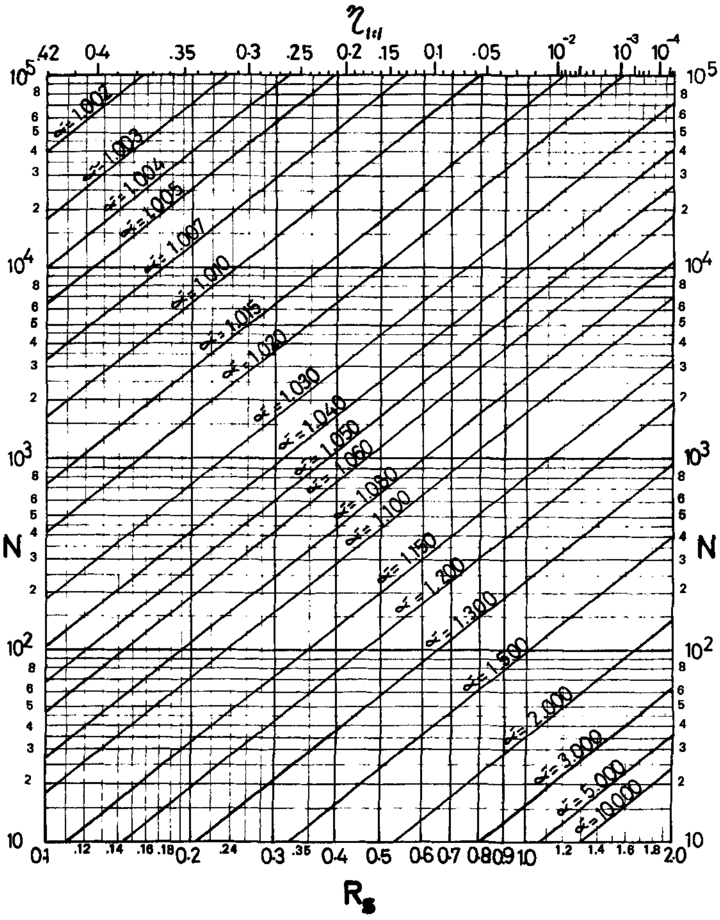

FIG. 7A. Plot of Eq. (30) on log-log graph paper with an auxiliary scale for $\eta_{1:1}$.

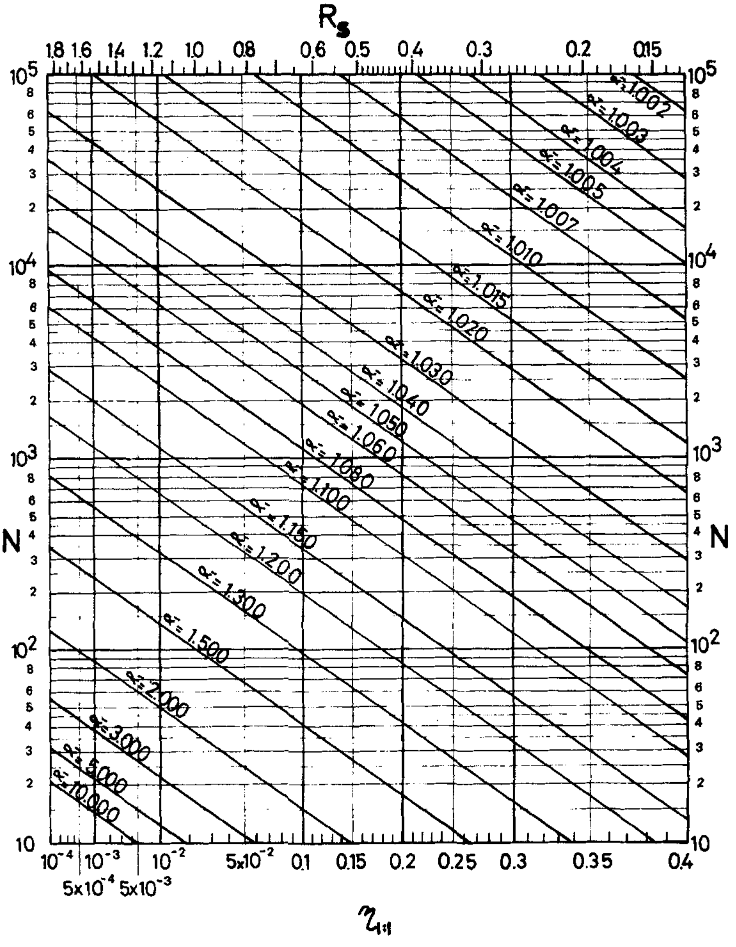

FIG. 7B. Plot of Eq. (31) on log-log graph paper with an auxiliary scale for *R*.

THE GLUECKAUF CHART

The Glueckauf chart is a plot of the number of theoretical plates N vs the separation efficiency η with the separation factor α' as the parameter. It suffers, however, from several drawbacks.

The original chart contains a relation between $\eta_{1:1}$ for two equal peaks and η for two unequal ones, which was shown to be incorrect by this author (*13*), who showed, however, that the two quantities are close to one another, thus correcting and at the same time simplifying its use. Since then, new charts have been published taking into account this correction (*25*, *26*). Other authors (for example, in Refs. *27–29*), apparently unaware of this correction or the reference to it in the literature (*24–26*, *30*, *31*), continue to publish the original uncorrected chart.

Although not explicitly stated, the parameter used in the Glueckauf chart is the separation factor α' which includes the void volume. If the exchange coefficient ratio α is used instead, then the value of N obtained is the number of theoretical plates when the void volume is neglected.

The chart was based on a complicated and also approximate equation, and steps toward the chart's construction are not indicated. Also, the η scale extends from 10^{-1} to 10^{-14}, which does not reflect the approximate nature of the equations upon which the chart was constructed.

Aside from these drawbacks and except for large α' values which are less important than small values, the chart gives results not much different from those obtained using the exact relation (Eq. 31). This is somewhat contrary to the findings of Tang and Harris (*32*) who recommend against the continued use of the Glueckauf chart. They based their conclusion upon significant deviations from the Purnell equation. This equation itself is an inexact one subject to the approximation given by Eq. (7) and therefore cannot be a satisfactory reference.

Figure 7B, while free of all the drawbacks of the Glueckauf chart, retains its good features and contains an extra scale for R_s. It is, therefore, an ideal substitute for it. The Glueckauf chart may have some merit and may be worth saving after correction and modification, but certainly not the Glueckauf treatment of the plate theory. Besides being approximate, it is also very complicated and has long since been replaced by better treatments (*9*, *33*). Some Glueckauf equations based on his treatment and appearing in textbooks are not well defined, lead to wrong answers, and are very difficult to trace in the original paper. An example of such equations is given in Ref. *34* and discussed in Appendix IV. This author recommends against the utilization of these equations which should be deleted from textbooks in future editions.

THE AVERAGE PLATE NUMBER

Throughout the above treatment the assumption was made that $N_1 = N_2 = N$. N is the best average plate number N_{av} from which the subscript "*av*" was dropped for convenience. In this section and because, here, we are looking for this best average, the same subscript will be retained.

Since the two exact resolution equations, Eqs. (11) and (30), are equivalent, we choose the one easier to handle. In this case it is Eq. (11) so that

$$R_s = \frac{\sqrt{N_{av}}(\alpha - 1)}{2\left(1 + \alpha + \dfrac{2}{k_1}\right)} \tag{34}$$

For $N_1 \neq N_2$, Eq. (1) leads to

$$\bar{V}_1 = \frac{\sqrt{N_1}}{4} w_1 \tag{35}$$

and

$$\bar{V}_2 = \frac{\sqrt{N_2}}{4} w_2 \tag{36}$$

Substituting from Eqs. (35), (36), (4), and (5) into Eq. (2) leads to the exact resolution equation when $N_1 \neq N_2$:

$$R_s = \frac{\sqrt{N_2}(\alpha - 1)}{2\left[\left(\alpha + \sqrt{\dfrac{N_2}{N_1}}\right) + \dfrac{1}{k_1}\left(1 + \sqrt{\dfrac{N_2}{N_1}}\right)\right]} \tag{37}$$

From Eqs. (34) and (37) one gets the exact relation for N_{av} when $N_1 \neq N_2$:

$$\sqrt{N_{av}} = \frac{\sqrt{N_2}\left(\alpha + 1 + \dfrac{2}{k_1}\right)}{\alpha + \sqrt{\dfrac{N_2}{N_1}} + \dfrac{1}{k_1}\left(1 + \sqrt{\dfrac{N_2}{N_1}}\right)} \tag{38}$$

Plate numbers N_1 and N_2 are two large numbers, and their ratio usually does not differ much from unity. In this case different averages differ only slightly from the arithmetic average N_a.

At present the uncertainties in the values of N_1 and N_2 determined experimentally are much greater than the differences between their different averages, and until these uncertainties fall below a certain level, the determination of R_s and N_{av} using the relatively difficult Eqs. (37) and (38) will be unjustified. At least for the present, using $N_{av} = N_a$ as suggested by Giddings (*6*) is sufficient.

For any two values such as N_1 and N_2 there are four primary or first averages. They are the arithmetic (N_a), the log mean (N_l), the geometric (N_g), and the harmonic (N_h) averages. They are defined by

$$N_a = \frac{1}{2}(N_1 + N_2) \tag{39}$$

$$N_l = \frac{N_2 - N_1}{\ln (N_2/N_1)} \tag{40}$$

$$N_g = \sqrt{N_2 N_1} \tag{41}$$

$$N_h = \frac{2N_1 N_2}{N_1 + N_2} \tag{42}$$

Other averages can be deduced by combining any two of the first averages; these are called second averages. There are several of these but only two of them are given here as examples.

$$N_{ah} = 2N_a - N_h = \frac{N_1{}^2 + N_2{}^2}{N_1 + N_2} \tag{43}$$

and

$$\frac{1}{N_{gh}} = \frac{1}{2}\left[\frac{1}{N_g} + \frac{1}{N_h}\right]$$

$$N_{gh} = \frac{4N_1 N_2}{N_1 + N_2 + 2\sqrt{N_1 N_2}} = \left(\frac{2\sqrt{N_1 N_2}}{\sqrt{N_1} + \sqrt{N_2}}\right)^2 = (\sqrt{N})_h{}^2 \tag{44}$$

Introducing two symbols γ_{av} and β, where

$$\gamma_{av} = N_{av}/N_a \qquad \text{and} \qquad \beta = N_2/N_1$$

and substituting in Eq. (38) gives

$$\sqrt{\gamma_{av}} = \frac{\sqrt{\dfrac{2\beta}{\beta + 1}}\left(\alpha + 1 + \dfrac{2}{k_1}\right)}{\alpha + \sqrt{\beta} + \dfrac{1}{k_1}(1 + \sqrt{\beta})} \tag{45}$$

Table 2 lists the values of γ_{av} for the above first and second averages for two values of β, namely, $\beta = 1.1$ and 1.2. The averages are arranged in descending order according to their magnitudes.

TABLE 2

γ Values for Different Averages

First	Second	$\beta = 1.1$	$\beta = 1.2$
	$\gamma_{ah} = \dfrac{2(1+\beta^2)}{(1+\beta)^2}$	1.0023	1.0083
$\gamma_a = 1$		1	1
$\gamma_l = \dfrac{2(\beta - 1)}{(1+\beta)\ln\beta}$		0.9992	0.9972
$\gamma_g = \dfrac{2\sqrt{\beta}}{1+\beta}$		0.9989	0.9959
	$\gamma_{gh} = \dfrac{8\beta}{(1+\beta)(1+\sqrt{\beta})^2}$	0.9983	0.9938
$\gamma_h = \dfrac{4\beta}{(1+\beta)^2}$		0.9977	0.9917

N_{av}/N_a or γ_{av} is a function of β, k_1, and α, as can be seen from Eq. (45). In Figs. 8A and 8B, γ_{av} is plotted for different values of k_1 and for β values equal to 1.1 and 1/1.1 (Fig. 8A) and β values equal to 1.2 and 1/1.2 (Fig. 8B).

The figure shows that at $\alpha = 0$, γ_{av} is very close to γ_{gh} but for practical values of α and k_1, γ_{av} could be any of the above first and second averages.

Vink (*19*) deduced an equation for N_{av} which reads

$$N_{av} = \left(\frac{2\sqrt{N_1N_2}}{\sqrt{N_1} + \sqrt{N_2}}\right)^2 \tag{46}$$

which is equivalent to N_{gh} as shown above. The Vink average is a function of N_1 and N_2 only and not of k_1 or α, contrary to Figs. 8A and 8B. The fact that the author was able to pinpoint a secondary average from a crowded spectrum of first and second averages is due to an unjustified approximation made in the course of the derivation. The Vink average is, therefore, not correct.

Table 2 also shows that, even if the Vink average were correct, γ_{gh} is too close to 1 to justify using a difficult N_{gh} average instead of the simple N_a average.

Karger (*4*) uses the approximation

$$N_{av} = N_2 \tag{47}$$

N_2 should probably be given more weight than N_1 in any resolution equa-

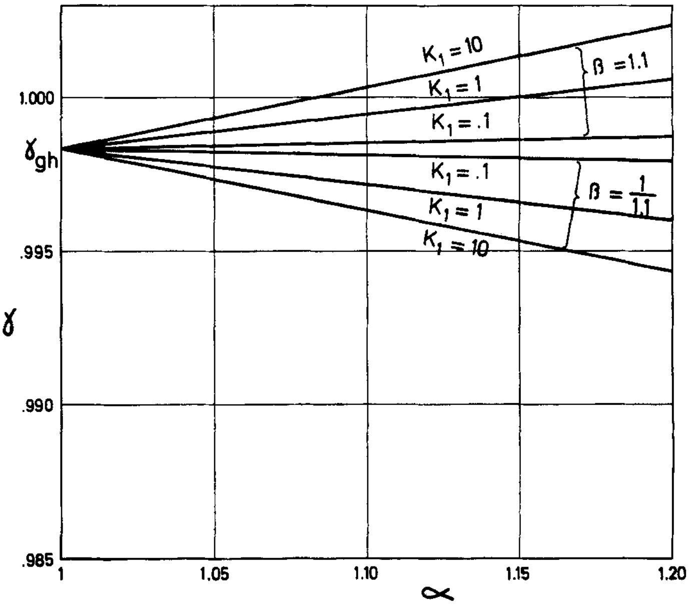

FIG. 8A. Plot of Eq. (45) for $\beta = 1.1$.

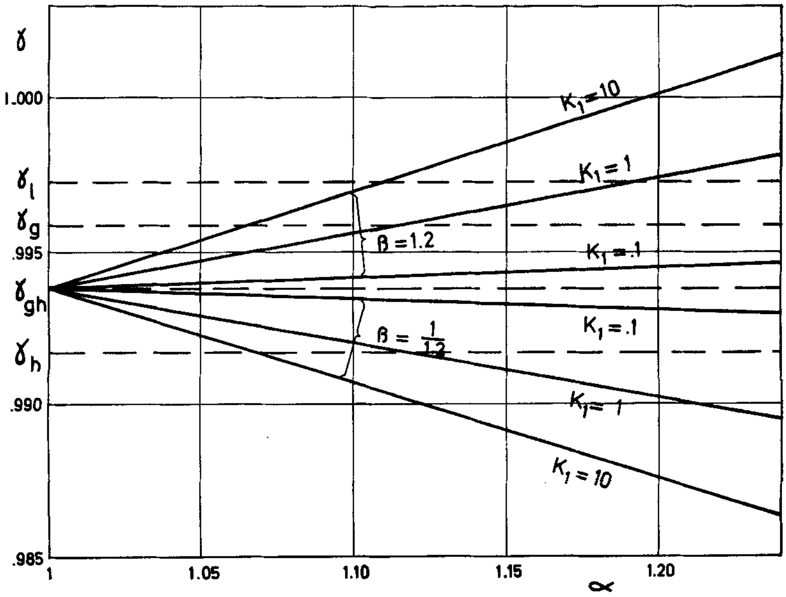

FIG. 8B. Plot of Eq. (45) for $\beta = 1.2$.

tion, but, in view of the above discussion, it would be difficult to prove that this approximation is better than the Giddings' approximation $N_{av} = N_a$, and for the present one has to settle for the arithmetic average as being the best average.

APPENDIX I: EQUATIONS EQUIVALENT TO THE PURNELL EQUATION IN THE LITERATURE

The Purnell equation is the first resolution equation and the one most widely used. It is usually referred to in the literature as "the well-known resolution equation."

By an equivalent equation, it is meant that it leads to numerical answers identical with those given by the Purnell equation. Such equations can be reduced to the Purnell equation by rearrangement and substituting the symbols, called "current symbols," given in this paper. Only one example is given here.

The Snyder Equation

As written in Ref. *5*, the Synder equation reads

$$R_s = \frac{1}{4}\left(1 - \frac{K_1}{K_2}\right)\sqrt{N}\frac{K_2}{K_2 + V^0/w}$$

Substituting current symbols, we find

$$R_s = \frac{1}{4}\left(1 - \frac{K_1}{K_2}\right)\sqrt{N}\frac{K_2}{K_2 + V_m/V_s}$$

but $K_2V_s/V_m = k_2$, and $K_1/K_2 = 1/\alpha$, so that

$$R_s = \frac{\sqrt{N}}{4}\frac{\alpha - 1}{\alpha}\frac{k_2}{k_2 + 1}$$

which is the Purnell equation.

APPENDIX II: EQUATIONS EQUIVALENT TO THE SAID EQUATION IN THE LITERATURE

Three equations are given. It is shown that on substituting current symbols and rearranging, one gets the Said equation of resolution.

The Karger Equation

As written in Ref. *4*, the Karger equation reads

$$R_s = \frac{\sqrt{N}}{2(1+n)} \frac{\alpha - 1}{\alpha} \frac{k_2}{1+k_2} \tag{a}$$

$$N = N_2, \qquad n = w_1/w_2$$

Term N will not be discussed here: it is a separate issue discussed in a separate section.

On substituting current symbols we get

$$R_s = \frac{\sqrt{N}}{2\left(1 + \dfrac{w_1}{w_2}\right)} \frac{\alpha - 1}{\alpha} \frac{k_2}{1+k_2} \tag{b}$$

but

$$\frac{w_1}{w_2} = \frac{V_1}{V_2} = \frac{1+k_1}{1+k_2} \tag{c}$$

also

$$\alpha = k_2/k_1 \tag{d}$$

Substituting for w_1/w_2 in (b) from (c), rearranging and then substituting for k_2/k_1 from (d), we get

$$R_s = \frac{\sqrt{N}(\alpha - 1)}{2\left(1 + \alpha + \dfrac{2}{k_1}\right)}$$

which is the Said equation. One can easily show that the following is also an exact equation:

$$R_s = \frac{\sqrt{N}}{2(1 + w_2/w_1)}(\alpha - 1)\frac{k_1}{1+k_1} \tag{e}$$

When $w_1 = w_2$, Eq. (a) reduces to the Purnell equation as pointed out by Karger, and Eq. (e) reduces to the Knox equation.

It is worthwhile pointing out the misleading results one may run into when dealing with approximate resolution equations. Here we have two exact equations with the same approximation, namely $w_1 = w_2$, but we get two different approximate relations leading to different answers.

The Giddings Equation

As written in Ref. *6*, the Giddings equation reads

$$R_s = \frac{\sqrt{N}}{4}\,\frac{\alpha\Delta K}{1+\alpha K}$$

$$\alpha = V_s/V_m, \qquad \Delta K = K_{\mathrm{II}} - K_{\mathrm{I}}$$

$$K = \frac{K_{\mathrm{II}} + K_{\mathrm{I}}}{2}, \qquad N = \frac{N_2 + N_1}{2}$$

By substituting current symbols, one gets

$$R_s = \frac{\sqrt{N}}{4}\,\frac{\frac{V_s}{V_m}(K_2 - K_1)}{1 + \frac{V_s}{V_m}\left(\frac{K_2 + K_1}{2}\right)}$$

but

$$\frac{V_s}{V_m}K_2 = k_2 \qquad \text{and} \qquad \frac{V_s}{V_m}K_1 = k_1$$

therefore

$$R_s = \frac{\sqrt{N}}{4}\,\frac{k_2 - k_1}{1 + \frac{k_2 + k_1}{2}}$$

also

$$k_2/k_1 = \alpha$$

so that

$$R_s = \frac{\sqrt{N}}{2}\,\frac{\alpha - 1}{1 + \alpha + \frac{2}{k_1}}$$

which is the Said equation.

The Conder-Purnell Equation

As written in Ref. *34*, the Conder-Purnell equation reads

$$N_{req} = \left(\frac{2Z}{a}\right)^2$$

where

$$a = 2\left(\frac{\alpha - 1}{\alpha + 1}\right)\left(\frac{k}{1 + k}\right)$$

$$\alpha = V_{N_2}/V_{N_1}, \qquad k = V_N/V_M{}^0$$

$$V_N = \frac{1}{2}[V_{N_1} + V_{N_2}]$$

According to Eq. (11) on page 357 of Ref. *35*, Z in the elution mode is the argument t of the normal distribution. On substituting current symbols, we get

$$N = \left(\frac{2t}{a}\right)^2 \qquad \text{(A)}$$

where

$$a = 2\left(\frac{\alpha - 1}{\alpha + 1}\right)\left(\frac{k}{1 + k}\right) \qquad \text{(B)}$$

also, from Eq. (15),

$$t = 2R_s$$

substituting from Eq. (15) into (A) gives

$$N = \left(\frac{4R_s}{a}\right)^2$$

or

$$R_s = \frac{\sqrt{N}}{4}a \qquad \text{(C)}$$

Equations (C) and (B) give

$$R_s = \frac{\sqrt{N}}{2}\left(\frac{\alpha - 1}{\alpha + 1}\right)\left(\frac{k}{1 + k}\right)$$

which is the Said equation.

In the previous year (1969), Conder and Purnell utilized the Purnell equation in a paper (*36*) on the same subject. In the years that followed 1970, Conder used the Said equation consistently in his publications (*37*). This indicates a switch to the Said equation by Conder and Purnell since 1970.

APPENDIX III: TO SHOW THAT THE GLUECKAUF EQUATION AS REPRODUCED IN REF. 34 IS NOT CORRECT

As presented by Tranchant (*34*, p. 17), the Glueckauf equation reads

$$n = 2\left(\frac{\alpha + 1}{\alpha - 1}\right)^2 \log_e \frac{2}{1 - \tau} \tag{I}$$

$$\alpha = t_{r_2}/t_{r_1}$$

τ = fractional purity = $1 - \eta$, where η is the fractional impurity. With current symbols, one gets

$$N = 2\left(\frac{\alpha' + 1}{\alpha' - 1}\right)^2 \log_e \frac{2}{\eta} \tag{II}$$

where

$$\alpha' = \frac{1 + k_2}{1 + k_1}$$

If Equation (II) is correct for any η, it is correct also for $\eta_{1:1}$ so that

$$N = 2\left(\frac{\alpha' + 1}{\alpha' - 1}\right)^2 \log_e \frac{2}{\eta_{1:1}} \tag{III}$$

The exact relation between $\eta_{1:1}$, N, and α' is given by Eq. (31):

$$\eta_{1:1} = A\left(\frac{\sqrt{N}}{2} \ln \alpha'\right)$$

which is plotted in Fig. 7B.

Values of N obtained from Eqs. (III) and (31) are tabulated in Table 3. The error in using Eq. (II) is also tabulated. It shows that this equation

TABLE 3

	N Values					
	$\alpha' = 1.1$			$\alpha' = 1.2$		
$\eta_{1:1}$	Eq. (31) exact	Eq. (III) Glueckauf	% Error	Eq. (31) exact	Eq. (III) Glueckauf	% Error
.1	720	2640	267	15	54	260
.01	2420	4670	93	49	95	94
.001	4200	6700	59	86	137	59
.0001	6150	8730	42	125	178	42

is not correct. The error does not change if α in Eq. (I) was meant to be the distribution coefficient ratio k_2/k_1, in which case the dead volume is neglected.

APPENDIX IV: COMPARISON BETWEEN *n* VALUES FOR DIFFERENT MODELS

The comparison here is between three *n* values obtained from three equations derived on the basis of three different models. The constant in the first two equations is adjusted only for the purpose of meaningful comparison. The equations are

$$n_1 = 0.5 + \frac{\sqrt{N}}{4} \ln \alpha' \qquad \text{(continuous model)} \qquad \text{(I')}$$

$$n_2 = 0.5 - \frac{\ln \alpha'}{\ln b} \qquad \text{(Giddings discontinuous model)} \qquad \text{(II')}$$

$$\frac{K}{K+1} = \frac{4}{\sqrt{N}}\left[\frac{1 - b^{n_3}}{1 - b} - 0.5\right] \qquad \text{(Scott's discontinuous model)} \quad \text{(III')}$$

where n_1, n_2, and n_3 are total peak capacities including the final peak. Also

$$b = \frac{N - 2\sqrt{N}}{N + 2\sqrt{N}}$$

$$\alpha' = k + 1 \qquad \text{(because } k \text{ for void peak} = 0\text{)}$$

and therefore

$$\frac{k}{k+1} = \frac{\alpha' - 1}{\alpha'}$$

An explicit relation for n_3 in Eq. (III') is possible, leading to

$$n_3 = \frac{\ln\left[1 - (1 - b)\left(\frac{\sqrt{N}}{4}\frac{\alpha' - 1}{\alpha'} + 0.5\right)\right]}{\ln b}$$

Values of n_1, n_2, and n_3 were calculated for $\alpha' = 2$ and 10, and for N values equal to 100, 400, 900, 1600, and 2500. The results are tabulated in Table 4.

It is clear from Table 4 that the differences in *n* values are too small to justify a lengthy algebraic treatment leading to a relatively complicated formula.

TABLE 4

	n Values					
	$\alpha' = 2$			$\alpha' = 10$		
N	n_1	n_2	n_3	n_1	n_2	n_3
100	2.23	2.21	2.16	6.26	6.18	6.13
400	3.97	3.95	3.93	12.01	11.98	11.95
900	5.70	5.69	5.67	17.77	17.74	17.72
1600	7.43	7.43	7.41	23.53	23.51	23.49
2500	9.16	9.16	9.15	29.28	29.27	29.25

At this point one may make a minor correction with regard to a statement in both Refs. *18* and *38*. It is stated that Giddings assumes that $(N - 2\sqrt{N})/(N + 2\sqrt{N})$ approaches unity and thus the peak capacities quoted by him are somewhat less than n_3 values. Actually, the approximation made by Giddings is

$$\frac{N + 2\sqrt{N}}{N - 2\sqrt{N}} \cong 1 + \frac{4}{\sqrt{N}}$$

which converts Eq. (II′) to Eq. (I′), and correspondingly n_2 values become equal to n_1 values, which are somewhat more and not less than n_3 values, as evidenced by the values listed in Table 4.

SYMBOLS

$A(t)$	$(1/\sqrt{2\pi})\int_t^\infty e^{-t^2/2}\,dt = Q$ area under the normal curve of error or error integral
$A^{-1}(Q)$	$= t$, inverse error integral or error integral argument
K	distribution coefficient
K_1, K_2	distribution coefficients for Components 1 and 2
k	$= KV_s/V_m$ = capacity ratio, in Eq. (11), $k = (k_1 + k_2)/2$
k_1, k_2	capacity ratios for Components 1 and 2
n	peak capacity between any two points 1 and 2 on a chromatogram
n_t	total peak capacity
n_t'	$= n_t + 1$ total peak capacity including final and void peaks
$\bar{n}$	peak capacity based on $\bar{R}$
N	number of theoretical plates or plate number

N_1, N_2	number of theoretical plates for Components 1 and 2
N_{av}	average plate number
N_a	$= (N_1 + N_2)/2$, arithmetic average plate number
N_g	$= \sqrt{N_1 N_2}$, geometric average plate number
N_h	$= 2N_1N_2/(N_1 + N_2)$, harmonic average plate number
N_l	$= (N_2 - N_1)/\ln (N_2/N_1)$, plate number log mean average
N_{ah}	$= 2N_a - N_h$, a plate number second average
N_{gh}	$= (1/N_g + 1/N_h)/2$, a plate number second average
Q	$= A(t)$
R_s	$= (\bar{V}_2 - \bar{V}_1)/w_a$, resolution in terms of peak width arithmetic average
$\bar{R}_s$	$= (\bar{V}_2 - \bar{V}_1)/w_l$, resolution in terms of peak width log average
$R_{s,K}$	resolution according to the Knox equation
$R_{s,P}$	resolution according to the Purnell equation
R_s'	resolution according to the Said equation
t	argument of the error function
V	retention volume
V_1, V_2	any two retention volumes on the chromatogram
$\bar{V}_1$, $\bar{V}_2$	peak maximum retention volumes for Components 1 and 2
V_a	void peak retention volume
V_s	volume of the stationary phase in the column
V_m	volume of the mobile phase in the column
w	peak width at the base
w_1, w_2	peak width at the base for Components 1 and 2
w_a	peak width arithmetic average
w_l	peak width log mean average

Greek Symbols

α	$= k_2/k_1 = K_2/K_1$, distribution coefficient ratio
α'	$= (k_2 + 1)/(k_1 + 1) = \bar{V}_2/\bar{V}_1 = w_2/w_1 = \sigma_2/\sigma_1$, separation factor
β	$= N_2/N_1$, plate number ratio
γ	$= N_{av}/N_a$
σ	standard deviation of the chromatographic peak
σ_1, σ_2	standard deviations of Peaks 1 and 2
η	separation efficiency. It is the fractional impurity when a cut is made at equal fractional impurities on both sides
$\eta_{1:1}$	separation efficiency for two equal peaks

REFERENCES

1. J. H. Purnell, *J. Chem. Soc.*, *1960*, 1268.
2. J. H. Knox, *Ibid.*, *1961*, 433.
3. A. S. Said, *J. Gas Chromatogr.*, *2*, 60 (1964).
4. B. L. Karger, *Advances in Gas Chromatography*, *1967* (A. Zlakkis, ed.), p. 1.
5. L. R. Snyder, *Anal. Chem.*, *39*, 705 (1967).
6. J. C. Giddings, *Ibid.*, *40*, 2144 (1968).
7. H. A. C. Thijssen, *J. Chromatogr.*, *11*, 141 (1963).
8. A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, *35*, 1358 (1941).
9. A. S. Said, *AIChE. J.*, *3*, 477 (1956).
10. J. C. Giddings, *Dynamics of Chromatography*, Part 1, Dekker, New York, 1965.
11. G. Guiochon, *Anal. Chem.*, *38*, 1020 (1966).
12. E. Glueckauf, *Trans. Faraday Soc.*, *51*, 34 (1955).
13. A. S. Said, *J. Gas Chromatogr.*, *1*, 20 (1963).
14. Pearson and Hartley (eds.), *Biometrika Tables for Statisticians*, Vol. 1, 3rd. ed., Cambridge University Press, 1970.
15. J. C. Giddings, *Anal. Chem.*, *39*, 1027 (1967).
16. J. C. Giddings, *Sep. Sci.*, *4*, 181 (1969).
17. E. Grushka, *Anal. Chem.*, *42*, 1142 (1970).
18. R. P. W. Scott, *J. Chromatogr. Sci.*, *9*, 449 (1971).
19. H. Vink, *J. Chromatogr.*, *69*, 237 (1972).
20. J. Tranchant, *Practical Manual of Gas Chromatography*, Elsevier, New York, 1969, p. 218.
21. P. Chovin and G. Guiochon, *Bull. Soc. Chim. Fr.*, *1965*, 2391.
22. P. Chovin and G. Guiochon, *Ibid.*, *1965*, 2396.
23. D. C. Collins and G. F. Freeguard, *Chromatographia*, *6*, 404 (1973).
24. E. Glueckauf, *Trans. Faraday Soc.*, *60*, 729 (1964).
25. A. B. Littlewood, *Gas Chromatography; Principles, Techniques, and Applications*, 2nd ed., Academic, New York, 1970, p. 159.
26. W. R. Supina, *The Packed Column in Gas Chromatography*, Supelco Inc., Bellefonte, Pennsylvania, 1974, p. 15.
27. H. H. Willard, L. L. Merritt, and J. A. Dean, *Instrumental Methods of Analysis*, Van Nostrand, Reinhold, New York, 1968.
28. C. Liteanu, S. Gocan, and E. Horwood, *Gradient Liquid Chromatography*, Wiley, New York, 1974, p. 82.
29. J. A. Dean, *Chemical Separation Methods*, Van Nostrand, Reinhold, New York, 1969, pp. 104 and 244.
30. T. Gäumann, *Ann. Rev. Phys. Chem.*, *6*, 128 (1965).
31. F. Helfferich, *Advances in Chromatography*, Dekker, New York, 1965, p. 44.
32. S. H. Tang and W. E. Harris, *Anal. Chem.*, *45*, 1977 (1973).
33. J. J. Van Deemter, F. J. Zuiderweg, and A. Klinkenberg, *Chem. Eng. Sci.*, *5*, 271 (1956).
34. J. Tranchant, *Practical Manual of Gas Chromatography*, Elsevier, New York, 1969, p. 21.
35. J. R. Conder and J. H. Purnell, *Chem. Eng. Sci.*, *25*, 353 (1970).
36. J. R. Conder and J. H. Purnell, *Chem. Eng. Prog. Symp. Ser.*, *91*, 651 (1969).

37. J. R. Conder, *New Developments in Gas Chromatography*, Vol. 11 (Advances in Analytical Chemistry and Instrumentation, J. H. Purnell, ed.), Wiley-Interscience, New York, 1972, p. 147.
38. R. P. W. Scott, *Contemporary Liquid Chromatography*, Wiley, New York, 1976, p. 84.

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