

## A SUGGESTION FOR THE DEFINITION OF ZONE (OR BOUNDARY) RESOLUTION IN PHYSICO-CHEMICAL SEPARATION TECHNIQUES

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### INTRODUCTION

In optical instrumentation, the resolving power is a strictly defined concept, and mathematical expressions for it can be derived. This is possible because there is a general agreement concerning what shall be implied by a resolution between two overlapping diffraction patterns. Following a suggestion by Lord Rayleigh, the optical images of two adjacent slits are said to be just resolved if the centre of the main diffraction band of one slit coincides with the first diffraction minimum of the other slit. This condition is called the Rayleigh criterion; it has the advantage of giving simple mathematical expressions and has been generally adopted by other workers in optics. For separation corresponding to this criterion, the overlapping main diffraction bands of the two slits display two light intensity maxima and, between them, a minimum which amounts to 81 % of the maxima (see JENKINS AND WHITE<sup>1</sup>).

Because the depth of the minimum pertaining to the Rayleigh criterion is as small as 19 %, the definition of optical resolving power appears rather liberal. This impression is increased on consideration of the fact that the intensity minimum becomes still less pronounced, or disappears altogether, if the two light sources have unequal intensities. An astronomer will find that he can resolve double stars having an angular separation corresponding to the Rayleigh criterion only if the component stars are of about the same brightness. If one component star is, say, 10 times brighter than the other, a larger angular separation is necessary to resolve them with the same telescope.

The Rayleigh criterion cannot be directly translated to physico-chemical separation techniques because there is no correspondence to the intensity minima of diffraction patterns. The concentration course throughout a zone of a pure compound has only one maximum and no minimum. In the ideal case, it is Gaussian in shape, the concentration declining asymptotically to zero toward both sides. The light intensity being zero in the diffraction minima, there is no difficulty whatsoever in defining the extension of the central diffraction band. For a Gaussian concentration distribution, on the other hand, a definition of the zone breadth is necessary. Several such definitions could be suggested and defended, but the most convenient one identifies the zone breadth with the distance between the two inflexion points, which

is twice the standard deviation. The mass contained within these limits amounts to 68.26 % of the total mass content of the zone.

Light sources of unequal brightness correspond completely to material zones of different mass contents. In another respect, however, there is an important difference between diffraction bands and material zones in separation records. In an optical image, the diffraction bands of different objects are equally broad, but in a separation record, the various zones have, in general, unequal zone breadths depending on the differences in the diffusion coefficients. Moreover, deviations from ideal physico-chemical behaviour give rise to zones with non-Gaussian, and often asymmetric, concentration distributions.

The definition of zone resolution is consequently much more complicated than the definition of optical resolution. A definition leading to great mathematical complexity in the calculation of a resolving power is, however, useless. In this article, the resolution between zones of equal mass contents and equal breadths will be considered first; this treatment corresponds most closely to the classical treatment of optical resolution. Subsequently, a generally applicable definition of zone resolution will be attempted, and its implications for equally broad zones of different mass contents will be investigated.

#### AN INTELLIGIBLE DEFINITION OF THE RESOLUTION BETWEEN ADJACENT ZONES OF EQUAL BREADTHS AND EQUAL MASS CONTENTS

The equation for a Gaussian concentration distribution is:

$$C = \frac{m}{q\sigma \sqrt{2\pi}} \exp(-x^2/2\sigma^2) \equiv \frac{m}{q\sigma} \operatorname{erf}(x/\sigma) \quad (1)$$

where  $m$  is the mass content of the zone,  $q$  the cross-sectional area of the column or tube containing the zone,  $\sigma$  the standard deviation (half zone breadth), and  $x$  the coordinate along the column or tube. The sum of two such concentration functions at a mutual distance of  $2\delta$  can thus be written:

$$C = \frac{m}{q\sigma \sqrt{2\pi}} \left( \exp \frac{-(x-\delta)^2}{2\sigma^2} + \exp \frac{-(x+\delta)^2}{2\sigma^2} \right) \quad (2)$$

The two maxima and the minimum (which for symmetry reasons must be situated at  $x = 0$ ) are found by putting the derivative  $dC/dx = 0$ . This leads to the equation:

$$\exp \frac{2\delta x}{\sigma^2} = \frac{\delta + x}{\delta - x} \quad (3)$$

The concentration minimum is obtained by putting  $x = 0$  in eqn. (2):

$$C_{\min} = \frac{2m}{q\sigma \sqrt{2\pi}} \exp(-\delta^2/2\sigma^2) \quad (4)$$

and the concentration maxima are obtained by combination of (3) with (2). By using the relation:

$$\exp \frac{-(x \pm \delta)^2}{2 \sigma^2} \equiv \exp \frac{-x^2}{2 \sigma^2} \exp \frac{-\delta^2}{2 \sigma^2} \exp \frac{\mp \delta x}{\sigma^2} \quad (5)$$

and eqn. (3) for the last factor, one arrives at the result:

$$C_{\max} = \frac{2 \delta m}{q \sigma \sqrt{2 \pi} \sqrt{\delta^2 - x^2}} \exp (-x^2/2 \sigma^2) \exp (-\delta^2/2 \sigma^2) \quad (6)$$

Division of (4) by (6), finally, gives the ratio between the minimum and the maxima:

$$Q = \frac{C_{\min}}{C_{\max}} = \sqrt{1 - (x/\delta)^2} \exp (x^2/2 \sigma^2) \quad (7)$$

In this equation  $x$  means the abscissae for the maxima, defined by eqn. (3). Unfortunately, an analytical elimination of  $x$  is not possible.

At this point, one has to select a certain numerical value of  $Q$  in order to define a just resolved double-zone. If one wants to copy the Rayleigh criterion for optical resolution, one would have to select  $Q = 0.81$ . There is, however, no theoretical reason for such a definition for Gaussian curves, and it has already been pointed out that the Rayleigh criterion leads to a very liberal definition of resolution, especially if zones of different mass contents are also to be considered. A resolution criterion  $Q = 1/2$  is of course both convenient and simple, but it appears to the author as unnecessarily restrictive, and it has no theoretical foundation in the equation for a Gaussian distribution.

The inflexion points in a single Gaussian curve are situated at an ordinate of  $e^{-1/2} = 0.6065$  of the peak height. This fraction, about half-way between the fractions 0.81 and 0.50 discussed above, appears to be very suitable for a definition of a just resolved double-zone. Accepting this definition, one gets the following equation:

$$\sqrt{1 - (x/\delta)^2} \exp (x^2/2 \sigma^2) = \exp (-1/2) \quad (8)$$

The mathematical difficulty now rests in the impossibility of eliminating  $x$  between (3) and (8). Numerically, the equation can be solved in the following way.

Eqn. (3) is first put into the following form:

$$\frac{x}{\delta} = \frac{\exp (\delta x/\sigma^2) - \exp (-\delta x/\sigma^2)}{\exp (\delta x/\sigma^2) + \exp (-\delta x/\sigma^2)} = \tanh (\delta x/\sigma^2)$$

from which the relation:

$$(\delta/\sigma)^2 = (\delta x/\sigma^2) \coth (\delta x/\sigma^2) \quad (9)$$

is easily found. Eqn. (8) can also be transformed into another form:

$$((\delta/\sigma)^2 - (x/\sigma)^2) \exp (1 + x^2/\sigma^2) = (\delta/\sigma)^2 \quad (10)$$

The calculation starts with guessing a value for  $\delta x/\sigma^2$ . This value is inserted in eqn. (9), whereby the corresponding value of  $\delta/\sigma$  is obtained. Division of the value guessed by the latter gives the corresponding value of  $x/\sigma$ . Thereby all three variables in eqn. (10) are known, and consequently this equation can serve as a control of the correctness of the guess. The procedure is repeated until eqn. (10) becomes sufficiently precise. In this way the author has found the following numerical solution for the zone separation:

$$2 \delta = 3.0776 \sigma \quad (11)$$

The concentration distribution throughout the double-zone thus defined is shown in Fig. 1. If the double-zone is cut into two halves through the minimum, each part will contain 93.8% of one component and 6.2% of the other. On first inspection, the two components are thus very well resolved, and condition (11) appears unnecessarily restrictive. This is not the case, however, if the condition is to be extended to component zones of unequal mass contents. This will be evident in the next section.

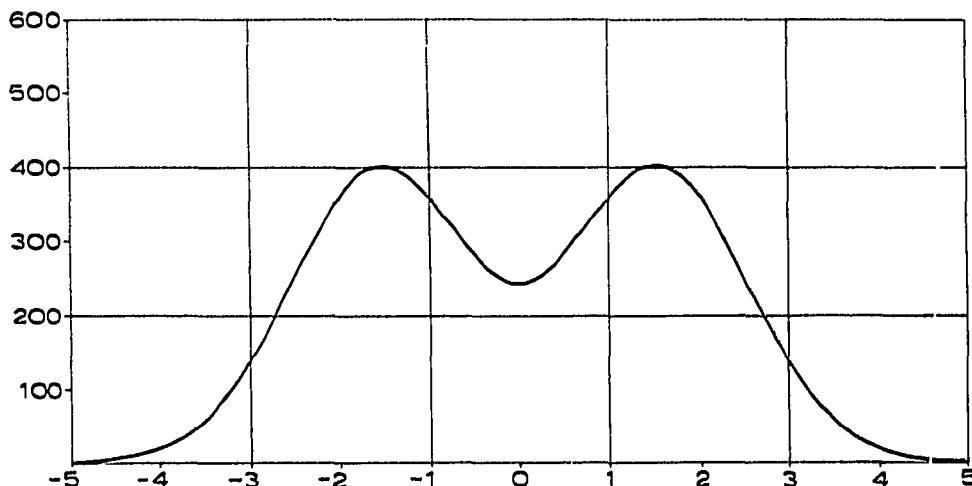


Fig. 1. Just resolved double-zone of mass ratio 1 according to the first definition. The minimum amounts to  $e^{-1/2}$  of the maxima. Zone separation  $3.08 \sigma$ .

#### A POSSIBLE GENERAL DEFINITION OF ZONE RESOLUTION AND ITS IMPLICATIONS FOR COMPONENT ZONES OF EQUAL BREADTHS BUT DIFFERENT MASS CONTENTS

Fig. 2 illustrates a possible general definition for a just resolved double-zone, characterized by an inflexion point with a horizontal tangent in the total concentration course. A mathematical treatment of this condition for component zones of unequal breadths is too complicated to be of any practical value. The treatment will therefore be restricted to component zones of the same breadth,  $2 \sigma$ .

The equation for the total concentration course becomes in this case:

$$C = \frac{1}{q\sigma \sqrt{2\pi}} \left( m_1 \exp \frac{-(x-\delta)^2}{2\sigma^2} + m_2 \exp \frac{-(x+\delta)^2}{2\sigma^2} \right) \quad (12)$$

An inflexion point with a horizontal tangent must satisfy the equation  $dC/dx = 0$ . Again making use of relation (5), one finds that this equation reduces to:

$$\exp \frac{2 \delta x}{\sigma^2} = r \frac{\delta + x}{\delta - x} \quad (13)$$

where  $r$  is the ratio between the masses:

$$r = m_2/m_1 \quad (14)$$

It must also satisfy the equation  $d^2C/dx^2 = 0$ , a condition which is most easily obtained by direct differentiation of eqn. (13). The result is:

$$\exp \frac{2 \delta x}{\sigma^2} = r \frac{\sigma^2}{(\delta - x)^2} \quad (15)$$

The exponential function can now be eliminated between (13) and (15), which leads to the result:

$$\delta^2 = \sigma^2 + x^2 \quad x = \sqrt{\delta^2 - \sigma^2} \quad (16)$$

This expression for  $x$  is finally inserted into (13) or (15), with the result:

$$\sqrt{r} = (y - \sqrt{y^2 - 1}) \exp (y \sqrt{y^2 - 1}) \quad (17)$$

$$y = \delta/\sigma \quad (18)$$

The mass ratio  $r$  as a function of  $y = \delta/\sigma$  is presented in Table I. It is seen that  $r$  varies from unity to about 73 when  $y$  increases from 1 to 2. At the lower end of the table, the minor component is only 1.35 % of the total mass. At the upper end, we have  $r = 1$ , that is, equal masses of the components. In this case, the inflexion point with a horizontal tangent merges with the maximum (compare also Fig. 3).

TABLE I

| $y = \delta/\sigma$ | $r$    |
|---------------------|--------|
| 1.0                 | 1.000  |
| 1.1                 | 1.129  |
| 1.2                 | 1.415  |
| 1.3                 | 1.909  |
| 1.4                 | 2.744  |
| 1.5                 | 4.176  |
| 1.6                 | 6.705  |
| 1.7                 | 11.333 |
| 1.8                 | 20.128 |
| 1.9                 | 37.510 |
| 2.0                 | 73.272 |

#### DISCUSSION

The second suggestion for defining a just resolved double-zone as a zone with a horizontal inflexion would certainly appeal to most chemists in principle. Objections

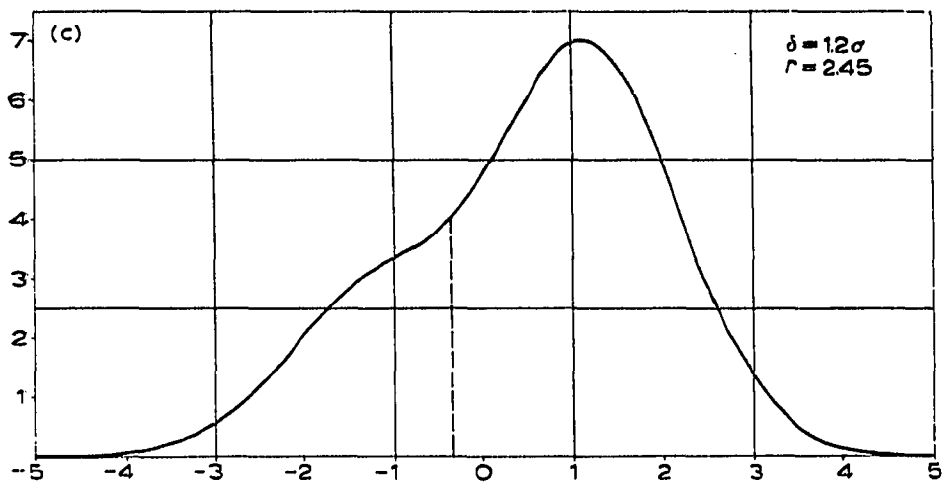
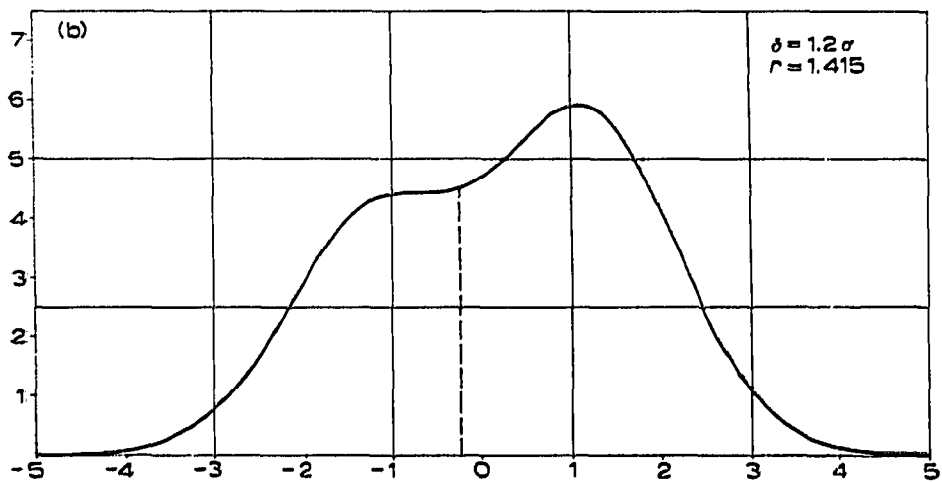
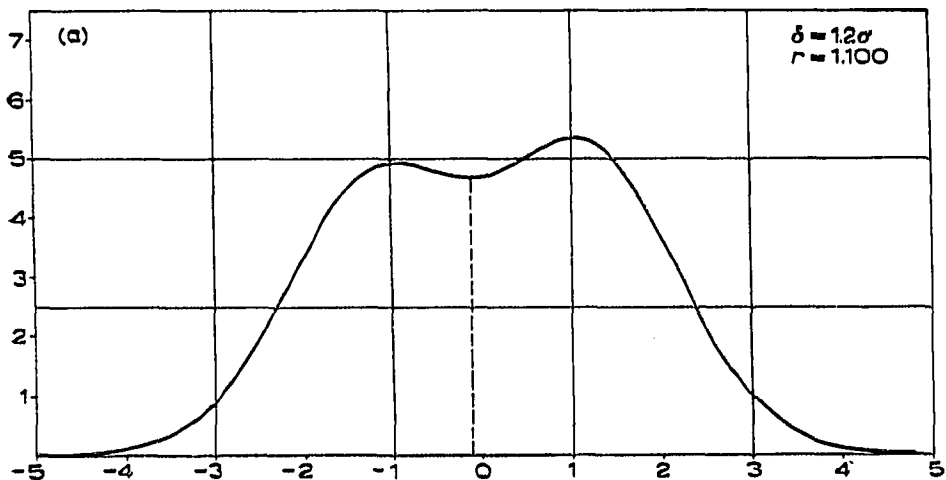


Fig. 2. Illustrating the second definition of zone resolution, according to which zones are said to be resolved if there is a minimum in the concentration course. (a) = Resolved zones; (b) = just resolved zones, concentration course with a horizontal inflexion; (c) = unresolved zones.

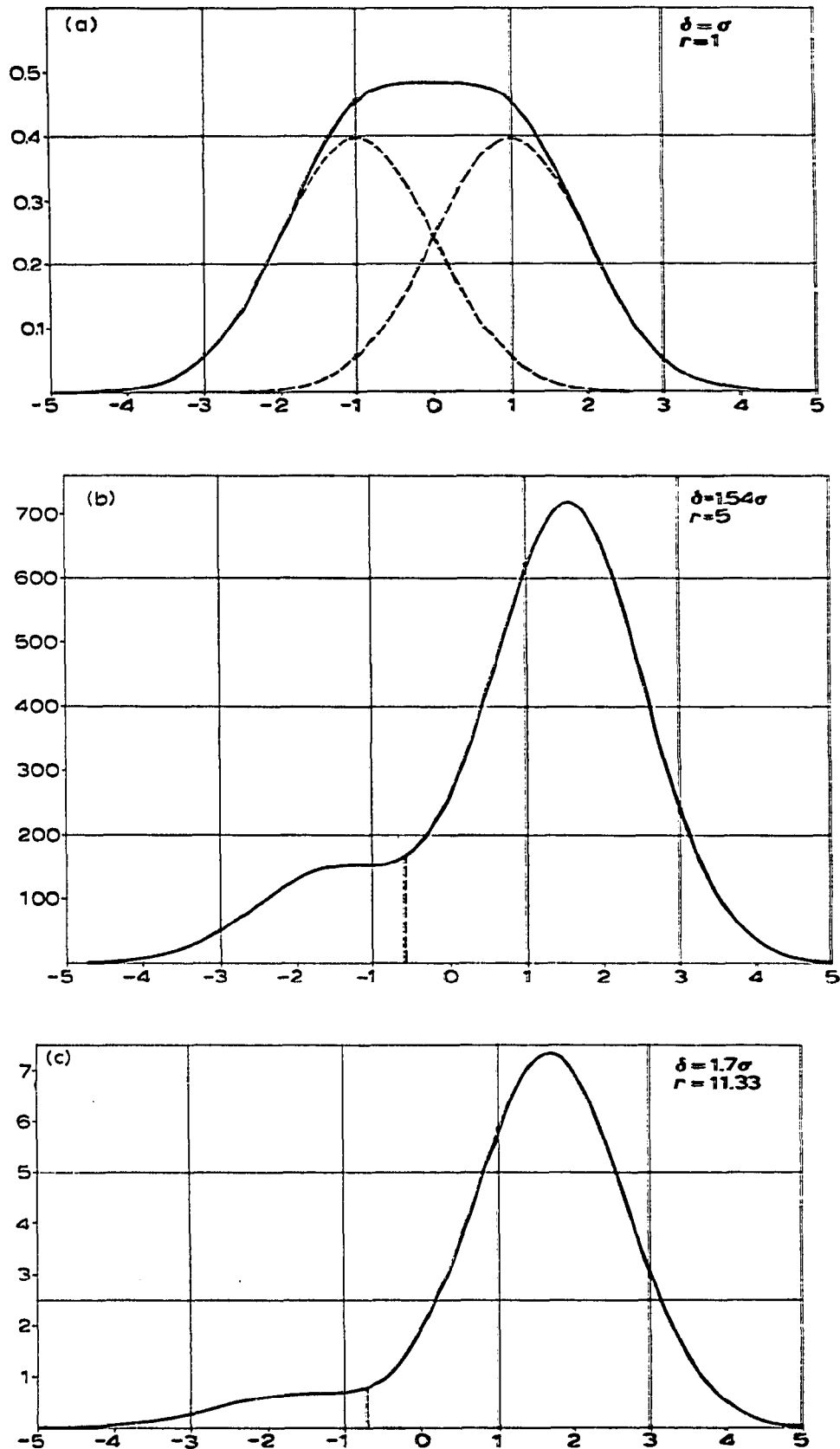


Fig. 3. Illustrating the appearance of just resolved double-zones according to the second definition. (a) Mass ratio 1, zone separation  $2\sigma$  (the horizontal inflexion merges with the maximum); (b) mass ratio 5, zone separation  $3.08\sigma$ , the same as that required by the first definition; (c) mass ratio 11.33, zone separation  $3.4\sigma$ .

can of course be raised against calling the double-zone in Fig. 3a just resolved, but adjacent material zones of exactly the same mass content do not occur very often in experimental practice. The peak separation according to this definition depends, however, on the mass ratio in the way shown by eqn. (17) and Table I. The definition is thus inconvenient in use, especially since eqn. (17) cannot be solved explicitly for  $\gamma$ .

The first suggestion for defining a just resolved double-zone by eqn. (11) has the same simplicity as the Rayleigh criterion in optics, and the same weakness. Thus it fails for widely different mass contents in the component zones. However, since this definition is more restrictive than the Rayleigh criterion, it does not fail until the mass ratio rises above 5 or falls below 0.2. At these limits, there is a double-zone with a horizontal inflexion, and the second definition applies as well. Without much change, the numerical factor in eqn. (11) can be rounded off to 3, and the condition for just resolved adjacent zones would be:

$$2 \delta = 3 \sigma \quad (19)$$

that is, adjacent zones are resolved if the peak separation surpasses three times the standard deviation of the component zones. If their standard deviations are unequal, the arithmetic mean of  $\sigma_1$  and  $\sigma_2$  may be used.

#### SUMMARY

Two possible ways of defining just resolved zones in chromatographic, electrophoretic, etc., separations have been studied. According to one suggestion, two adjacent zones of equal mass contents are said to be just resolved if the minimum between the peaks is  $e^{-1/2} = 0.61$  of the peak heights. This leads to the approximate condition that the peak separation must be greater than three times the standard deviation of the component zones. This condition can then be extended to component zones of unequal mass contents. A minimum still persists for mass ratios between 5 and 0.2. Outside this range, the minor component appears only as a shoulder on the main peak.

Another possibility is to define just resolved zones as double-zones with a horizontal inflexion. Such a definition corresponds, however, to a peak separation that depends on the mass ratio by a rather complicated equation and is thus inconvenient in use.

The definitions discussed for concentration records of free zone systems also apply to concentration gradient records of moving boundary systems.

#### REFERENCE

1 F. A. JENKINS AND H. E. WHITE, *Fundamentals of Optics*, McGraw-Hill, New York, 1957, p. 300.

*J. Chromatog.*, 25 (1966) 266-273