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J. Calvin Giddings[a]
[a] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH

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Basic Approaches to Separation: Steady-State Zones and Layers

J. CALVIN GIDDINGS

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF UTAH
SALT LAKE CITY, UTAH
SALT LAKE CITY, UTAH 84112

Abstract

The physical and mathematical basis of steady-state zones in chemical separation systems is outlined. With certain assumptions, the general equation for steady-state concentration profiles can be reduced to a single explicit expression of wide applicability. This expression is then used to describe zones and layers in ten different separation techniques divided into three classes of separation systems: (a) isoelectric focusing, isopycnic sedimentation, elutriation (steady-state zones in free space); (b) field-flow fractionation, equilibrium sedimentation, thermogravitational columns (solute layers formed at impermeable barriers); (c) ultrafiltration, reverse osmosis, pressure dialysis, zone melting (solute layers formed by influx to a semipermeable barrier). The zones in Class (a) are all found to be Gaussian while those in (b) and (c) are exponential. In all cases, zone dimensions are related to underlying transport parameters, and common features of the different methods are pointed out.

INTRODUCTION

It was shown in a preceding paper that the basic mass transport equations combined with the profile in chemical potential and the orientation in flow provides a logical framework on which to classify and unify the field of separations (*1*). The present paper expands on that theme by showing that the zones and layers of solute developed in many separation processes have much in common in both form and significance, and are subject to the same general mathematical description.

Some common features of systems which have zones in steady translation (chromatography, electrophoresis, rate-zonal centrifugation) were demonstrated in the previous paper (*1*). However, there is a large class of separation systems where steady-state zones or layers are formed or approached. In some of these systems (isoelectric focusing, isopycnic sedimentation, some types of elutriation), solute or particle zones form a steady-state distribution, each centered around a characteristic point along the continuum of the separation path. In other systems (field-flow fractionation, equilibrium sedimentation, thermogravitational columns), solute samples are forced into narrow steady-state layers against a wall. In still other systems (zone melting, filtration, ultrafiltration, reverse osmosis, pressure dialysis) there is a tendency to form steady-state layers in which a constant influx of solute to the layer is matched (or can be so approximated) by the leakage of solute through a barrier or interface. In all the above cases the efficacy of separation depends on the concentration profile of solute in the steady-state zones and layers.

It is worth reflecting on the physical origin of steady-state conditions in separative transport. Any narrow pulse of solute will tend to diffuse outward, and its profile can only be maintained in a steady-state condition if some transport process exactly balances diffusion. Such transport may be induced by flow or external fields. The transport, in effect, tends to focus solute toward a given point, keeping the solute compressed as a narrow zone around that point.

We should note that solutes also approach a stationary distribution across the interface of two-phase separation systems such as chromatography, countercurrent distribution, and simple extraction. These distributions are generally governed by simple equilibrium relationships. This subject has been widely explored in the literature (*2*, *3*). We need deal with it no further here.

THEORY

We define a steady-state zone or layer as one in which concentration c remains constant with time

$$\partial c/\partial t = 0 \tag{1}$$

Another expression for $\partial c/\partial t$ arises from the equation of continuity (*4*, *5*)

$$\partial c/\partial t = -\nabla \cdot J \tag{2}$$

where J is the flux density. All the methods under discussion involve transport that can be approximated as one-dimensional. We therefore take the axis of transport as coordinate x. The equation of continuity then becomes

$$\partial c/\partial t = -\partial J/\partial x = 0 \tag{3}$$

This equation requires that J must equal the constant J_0 at all points along the x axis, although J can in theory vary with time.

The two contributions to J—translation and diffusion—can be expressed by the general transport Eq. (1):

$$J = Wc - D_T\, \partial c/\partial x \tag{4}$$

in which translational velocity W is equal to the sum of velocity U induced by external fields and flow velocity v:

$$W = U + v \tag{5}$$

Coefficient D_T represents the sum of all contributions to effective diffusion. When J_0 is substituted for J in Eq. (4) and the latter rearranged, we obtain the form

$$c - (J_0/W) = (D_T/W)\, \partial c/\partial x \tag{6}$$

This is a linear differential equation of first order which admits of a formal solution, which we show in the Appendix. The solution, unfortunately, consists of integrals that can acquire some complexity when J_0 is finite and D_T and W vary in an arbitrary way with x. Under most circumstances it is physically reasonable to impose certain restrictions (below) on J_0, D_T, and W for simplification. Under these circumstances a simpler (and more physically direct) approach is available which yields the principal results and thus demonstrates the essential similarities between the separation methods.

We first define a new concentration scale

$$c' = c - J_0/W \tag{7}$$

such that c' equals the left-hand side of Eq. (6). The derivative of c' with respect to x is simply

$$\partial c'/\partial x = \partial c/\partial x \tag{8}$$

providing $\partial(J_0/W)/\partial x = 0$. The latter is valid either when

$$J_0 = 0 \tag{9}$$

or (since J_0, if finite, is constant with respect to x, Eq. 4),

$$W = \text{constant} \tag{10}$$

When Eqs. (7) and (8) are substituted into Eq. (6) we get

$$c' = (D_T/W)\,\partial c'/\partial x \tag{11}$$

When the variables are separated and the resulting equation integrated between 0 and x we obtain the equation

$$\ln (c'/c_0') = \int_0^x (W/D_T)\,dx \tag{12}$$

in which c' and c_0' are the newly defined concentrations at positions x and zero, respectively. When these concentration terms are replaced by the corresponding terms c and c_0 using Eq. (7), we obtain the following explicit equation for concentration:

$$\ln [(c - J_0/W)/(c_0 - J_0/W)] = \int_0^x (W/D_T)\,dx \tag{13}$$

It should be noted that this equation is based on the separation of variables in Eq. (11) in which it is assumed that the ratio W/D_T may be a function of x but not of c'. For high concentrations this assumption may fail and a more involved integration may be required. In this light, Eq. (13) must be regarded as a limiting equation valid at low concentrations.

Equation (13) is the solution sought to Eq. (6). This solution is subject only to the two conditions that J_0/W is a constant (Eqs. 9 and 10) and W/D_T is independent of c.

We now assume, for simplicity, that D_T is a constant independent of x. This leaves W as the sole variable in the integrand of Eq. (13). We can proceed generally by expanding W in a (Taylor's) series around $x = 0$:

$$W = a_0 + a_1 x + a_2 x^2 + \cdots \tag{14}$$

Depending on circumstances (detailed later), we find the terms of either zeroth or first order dropping out. Higher order terms can be reasonably neglected. Thus in all cases transport velocity W can be written in the simple form

$$W = -ax^n \tag{15}$$

where $n = 0$ or 1. Equation (15) is written in such a way (consistent with the steady state) that all the transport described by W is directed toward the position $x = 0$. The negative sign reflects the focusing motion which brings solute back toward $x = 0$ whenever $x > 0$. We note that the need to keep J_0/W constant requires either $J_0 = 0$ or $n = 0$, the latter so that W is a constant, Eq. (10).

With Eq. (15) and the assumption of constant diffusivity D_T, the integral of Eq. (13) acquires the form $-ax^{n+1}/D_T(n+1)$. When this form is substituted back into Eq. (13) and the latter rearranged, we get

$$\frac{c - J_0/W}{c_0 - J_0/W} = \exp\left(-\frac{ax^{n+1}}{D_T(n+1)}\right) \tag{16}$$

which leads us to the result that steady-state zones tend to acquire some kind of exponential distribution, the form depending on whether $n = 0$ (simple exponential) or $n = 1$ (Gaussian). The Gaussian of the latter case is largely unrelated to the Gaussians formed in uniform translation, as in chromatography and electrophoresis.

APPLICATIONS

There are three classes of separations in which steady-state zones are described to a good approximation by Eq. (16). These are discussed briefly below.

Isoelectric Focusing, Isopycnic Sedimentation, Elutriation (Steady-State Zones in Free Space). These are methods in which the different solutes are each forced toward a unique position along the coordinate axis of the system (*6*). Even after solute has accumulated in the designated region, it continues to diffuse outward in opposition to the focusing force, establishing a steady state (see Fig. 1). For steady-state conditions we can write $J_0 = 0$ because no solute enters or leaves the zone after its formation.

Generally, for such zones we can assume D_T = constant. Furthermore, for each zone we need retain only the first-order term of the series expansion, and we thus write $W = -ax$, which is equivalent to Eq. (15) with $n = 1$ (*6*). The linearity of the expression $W = -ax$ suggests that a linear restoring force or its equivalent is acting on the solute molecules or particles to force them toward the origin, $x = 0$. The origin and nature of this force for particular methods has been discussed (*6*).

The above conditions reduce Eq. (16) to the form

$$\frac{c}{c_0} = \exp\left(-\frac{ax^2}{2D_T}\right) \tag{17}$$

which is a Gaussian profile with variance

$$\sigma^2 = D_T/a \tag{18}$$

The constants D_T and a can usually be estimated on physicochemical

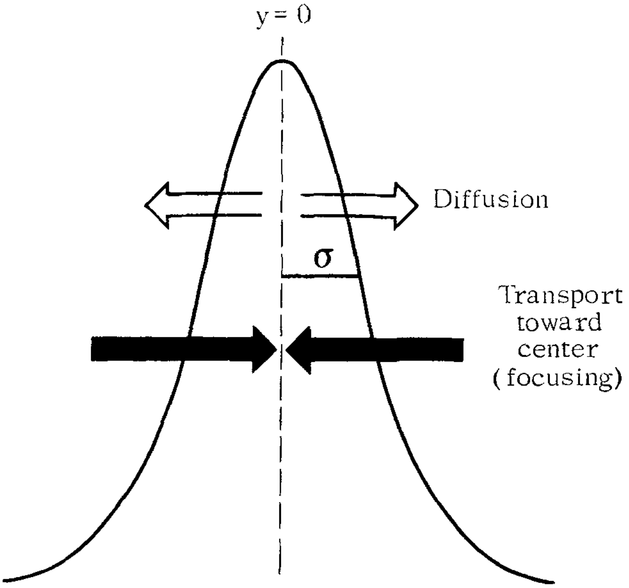

FIG. 1. Steady-state Gaussian zone formed in isoelectric focusing, isopycnic sedimentation, and elutriation by the opposing interplay of a focusing force and diffusion. Different components focus at separate locations to give separation.

grounds. Thus zone width can be calculated, and resolution parameters estimated (*6*).

Expressions equivalent to Eqs. (17) and (18) have been obtained for isoelectric focusing and density gradient centrifugation (along with several hypothetical steady-state methods) (*6*). However, the earlier treatment did not include a generalization to systems such as elutriation with finite flows. In this light, the scope of Eqs. (17) and (18) is rather broad. It is not nearly as broad as the precursor expressions, Eqs. (13) and (16), because the latter can be applied to many other separation processes as well. Most importantly, Eq. (16) can be applied to those cases in which solute accumulates in a steady-state layer against a wall or barrier. These are considered in the two categories below.

Field-Flow Fractionation, Equilibrium Sedimentation, Thermogravitational Columns (Solute Layers Formed at Impermeable Barriers). The field or gradient applied laterally to a field-flow fractionation (FFF) channel forces solute toward a wall which the solute molecules cannot penetrate. The solute is confined to a narrow region adjacent to the wall by the wall's surface, which it cannot pass, and the focusing force, which prevents its escape toward the center of the channel. The solute soon establishes a steady-state layer (polarization layer) in which outward diffusion balances the steady inward drift due to the field. The structure and dimensions of this layer determine the behavior and resolution characteristics of the solute in the separation process (*7*, *8*). (As with other methods, the steady-state in FFF is a condition closely approached but never reached. In FFF, a small but systematic departure from equilibrium is responsible for zone spreading.)

Similar layers are formed in thermogravitational columns and at the bottom wall of a centrifuge tube when the sedimentation process is allowed to approach equilibrium (providing pelleting does not occur).

For the above cases the appropriate assumptions are $J_0 = 0$, D_T = molecular diffusion coefficient D (usually a constant), and $W = -|W|$ (a constant). Quantity W is written in its absolute value form because it is negative: displacement occurs along the negative coordinate axis toward the wall. Since W is constant, the exponent n of Eqs. (15) and (16) is zero, and the resulting distribution is a simple exponential rather than a Gaussian. Equation (16) yields the form

$$\frac{c}{c_0} = \exp\left(\frac{-|W|x}{D}\right) = \exp\left(\frac{-x}{l}\right) \tag{19}$$

where the effective mean layer thickness l is given by

$$l = \frac{D}{|W|} = \frac{D}{|U + v|} \tag{20}$$

Thus the solute layer is characterized by quantity l, and the magnitude of l controls component migration and column efficiency in FFF (*8*). Equation (20) covers most forms of FFF in which an external field yields a finite U and a zero v, and flow FFF in which v is finite and $U = 0$, and any possible combination of the two.

Ultrafiltration, Reverse Osmosis, Pressure Dialysis, Zone Melting (Solute Layers Formed by Influx to a Semipermeable Barrier). In the filtration-type methods (the first three techniques listed above), solute accumulates in a thin polarization layer at a barrier or membrane in much the same way as it does in FFF or equilibrium centrifugation. However, there are several complications. First, fresh solute is constantly brought into the layer by the flow of liquid toward and through the filter. This steady influx of solute can be described by a finite flux density term J_0. Second, solute can be removed from the outer reaches of the layer by stirring or by transverse flow in a thin-cell device (*9*). Third, the membrane or barrier may be leaky and allow the transmission of a portion of the solute, profoundly affecting the attempted separation. In fact, one reason for the importance of the solute layer structure is that membrane leakiness depends on the magnitude of the solute buildup at the membrane surface.

A similar situation exists in zone melting where a molten zone passes through a solid bar gathering up the solid's impurities (*10*). The trailing solid–liquid interface acts like a filter in differentially rejecting part of the impurities or solutes. The rejected solute load then accumulates in a thin layer next to the advancing interface. The amount of solute material eventually recaptured and refrozen into the solid (equivalent to the leakage of a membrane)—and thus the residual impurity content of the recrystallized solid—depends again on solute buildup.

(It makes no important difference in filtration or zone melting whether the solute-rejecting surface advances on a stationary liquid solution, or whether liquid advances on a stationary surface, since only the relative motion is important. Usually, in zone melting, the zone and thus the interface is stationary, and the solid bar and the molten liquid are in translation.)

With the initiation of the filtration or zone melting process, solute begins to accumulate at the barrier and continues to build up in the solution until one of several things happens: precipitation or gelation occurs, the procedure is stopped, or stirring, leakage, or transverse flow removes solute as rapidly as it arrives. It is not our object to describe all of these special cases here. Instead, we will discuss a limiting steady-state model in which solute removal occurs at the same rate as solute influx. The layer structure calculated on this basis is a reasonable approximation for the layers formed when removal is negligible or when removal occurs by different mechanisms. Every aspect of the separation—from plausible operating conditions (flow rate, duration, pressure, stirring methods, cell geometry) to the resulting level of concentration or purification—depends on the nature and form of this layer.

The limiting equations applicable at low concentrations are obtained by assuming a finite but negative J_0 which we write as $-|J_0|$, where $|J_0|$ is the influx, D_T is a constant (which equals molecular diffusion coefficient D if there is no stirring), and $W = -|v|$, another constant equal to the velocity of the liquid relative to the surface. The absolute value forms are used to allow the positive coordinate axis to point into the flow from the barrier or interface to which we assign coordinate position $x = 0$.

With the above assumptions, Eq. (16) becomes applicable and yields

$$\frac{c - |J_0|/|v|}{c_0 - |J_0|/|v|} = \exp\left(-\frac{|v|x}{D_T}\right) \tag{21}$$

Writing ($|J_0|/|v|$) as J_0/v (both terms are negative and the ratio is therefore positive) and rearranging, we get

$$c = \frac{J_0}{v} + \left(c_0 - \frac{J_0}{v}\right) \exp\left(-\frac{vx}{D_T}\right) \tag{22}$$

We note that the resultant concentration profile is a simple exponential superimposed on the constant background concentration of the incoming solute, J_0/v (see Fig. 2). (The background concentration, of course, can remain constant only so long as the supply of the solute–solvent mixture lasts. In practice the duration of the supply is finite, but typically this duration will greatly exceed the time constant for forming the steady-state layer, and Eq. 22 will be little disturbed.) The effective thickness of the exponential component, $l = D_T/|v|$, is seen to be identical in form to that found for FFF, Eq. (20).

The amount of excess solute E (measured in moles per unit area) that can accumulate in the polarization layer is simply the excess concentration above that of the background solution, $c - J_0/v$, integrated over

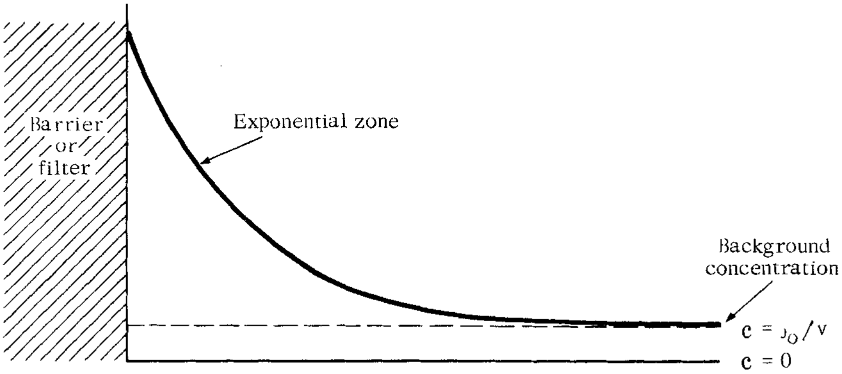

FIG. 2. Formation of exponential zone superimposed on a background of constant concentration for solute piling up behind a partially rejecting barrier like a membrane.

coordinate x:

$$E = \int_0^\infty (c - J_0/v)\, dx \tag{23}$$

With the substitution of Eq. (22) for c and integration, Eq. (23) yields

$$E = \frac{D_T}{|v|}\left(c_0 - \frac{J_0}{v}\right) \tag{24}$$

Usually the separation is effective in proportion to E because E represents either the amount of contaminant removed if the rejected solute is undesirable, or the amount of product concentrated if the solute is desirable. However, the degree to which the concentration at the interface c_0 can be increased to gain higher E values is limited because high c_0 values augment leakage, resistance to flow, and the risk of precipitation. Consequently, to increase E, efforts are generally made to increase effective diffusivity D_T, best done through stirring or convective processes. Thus these processes become important considerations to effective operation.

We note that different removal mechanisms will tend to deplete solute from different regions of the solute layer, thus disturbing the steady-state profile in different ways. Continuing solute influx also upsets the steady state. The degree to which steady-state conditions are maintained depends on how rapidly the layer repairs itself after being disturbed. The "relaxation time" for repair is approximately the time needed for transport by either diffusion or flow over distance l: $\sim D/v^2$. Usually the relaxation time is short and the steady-state approximation is satisfactory for all practical purposes. The same considerations apply to FFF where, once again, steady-state conditions are closely approached by virtue of the rapid relaxation to the steady-state profile.

The disturbance of the steady state and other topics common to the separation methods discussed above could be pursued at much greater length. However, the pursuit of detail is beyond the scope of this paper, where our purpose is limited to showing the close relationship of diverse methods.

CONCLUSIONS

The approach developed in this paper applies to 10 or so different steady-state separation methods. A single expression, Eq. (16), approximates the solute profile in all these methods. All the solute layers reduce to only two forms: Gaussian and exponential. The variance of all the Gaussians is given by a single general expression, Eq. (18). The effective thickness l of the exponential layers is also given by a single expression, Eq. (20). The near-identity in the mass transport equations for these various techniques and the remarkable resemblance of the results emphasizes the deep unity that runs through the separations field. This unity is not commonly recognized. There is good reason to believe that the plight of the separation scientist and technologist confronting so many seemingly unrelated techniques and subtechniques would be considerably relieved by the recognition and use of the common thread running through such large groups of methods.

APPENDIX

Equation (6) can be written in the form

$$\frac{dc}{dx} - \frac{W}{D_T}c = -\frac{J_0}{D_T} \tag{A-1}$$

If W/D_T and J_0/D_T are functions of x but not of c, we can use the integrating factor

$$e^{-\int (W/D_T)dx} \tag{A-2}$$

which leads to the general solution

$$c = e^{\int (W/D_T)dx}\left[\int \frac{-J_0}{D_T} e^{-\int (W/D_T)dx} dx + k\right] \tag{A-3}$$

where k is an integration constant. If W is constant, the integral inside the square brackets reduces to

$$\int \frac{-J_0}{D_T} e^{-(W/D_T)dx} dx = (J_0/W) e^{-W\int dx/D_T} \tag{A-4}$$

Since this integral reduces to zero when $J_0 = 0$, we can broaden our assumption in which W was assumed constant to one requiring only that the ratio J_0/W be constant. The latter is fulfilled either by $J_0 = 0$ or $W =$ constant (Eqs. 9 and 10), corresponding to our earlier assumption.

With the substitution of Eq. (A-4) into Eq. (A-3), the latter can be rearranged to

$$c = \left(\frac{J_0}{W}\right) e^{\int (W/D_T)dx} e^{-W\int dx/D_T} + ke^{\int (W/D_T)dx} \tag{A-5}$$

The first term on the right reduces to zero if $J_0 = 0$, and to J_0/W if $W =$

constant: in either case it can be written as J_0/W. Thus Eq. (A-5) becomes

$$c - \frac{J_0}{W} = k e^{\int (W/D_T) dx} \tag{A-6}$$

If the integral is written as the definite integral, $\int_0^x (W/D_T)\,dx$, this integral will vanish at $x = 0$, at which point we write for concentration $c = c_0$. Equation (A-6) thus reduces to $c_0 - (J_0/W) = k$ at this point, which establishes the value of k. The substitution of this k back into Eq. (A-6) leads to

$$\frac{(c - J_0/W)}{(c_0 - J_0/W)} = e^{\int_0^x (W/D_T) dx} \tag{A-7}$$

which is the same as Eq. (13).

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