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## MASS TRANSFER TERMS IN POROUS LAYERS AND PARTICLES

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## SUMMARY

Mobile phase mass transfer terms are derived or rederived for various geometries of porous material in which the mobile phase is stagnant. The results are tabulated and compared with those of other workers in Table I. A new, simpler and more rigorous equation is given for plate height in a porous layer open tubular column. Stationary phase mass transfer terms are increased by a factor,  $f$ , when the stationary phase must be reached through stagnant fluid. In these circumstances the mobile phase mass transfer term for the moving stream of mobile phase is also changed so that where the relative sample velocity  $R$  occurs in such terms it must be replaced by  $\phi R$  or, equivalently, the column capacity ratio  $k$  must be replaced by GOLAY'S "virtual  $k$ ",  $k_v$  given by  $k_v = (1 + k - \phi)/\phi$ .

GIDDINGS' non-equilibrium theory<sup>1</sup> will derive the mass transfer  $C$  term in the equation for "plate height",  $H$ , for almost any stationary phase or combination of stationary phases. It has been used to derive a great many. The purpose of this paper is to use these solutions to derive the  $C$  terms for stationary portions of the mobile phase; that is, for stagnant mobile phase in porous layers and particles such as porous layer open tubular columns, porous layer beads, porous particles impermeable to flow and gel filtration media. This will confirm some equations obtained by other routes and establish the limitations of others.

The general expression for stationary phase mass transfer in bodies of liquid stationary phase is (ref. 1, p. 146-149):

$$C_1 \bar{v} = \frac{qR(1-R)d_1^2 \bar{v}}{D_1} \quad (1)$$

where  $\bar{v}$  is the mobile phase velocity averaged over the entire mobile phase, stagnant or moving,  $R$  is the fraction of the sample in the mobile phase,  $q$  is a geometrical factor describing the shape of the liquid phase,  $d_1$  is the depth of the liquid phase at its deepest point, and  $D_1$  is the diffusivity of the sample in the liquid.

When applying this to a porous mass containing stagnant mobile phase, the porous mass is considered to be the stationary phase analogous to the liquid phase in eqn. 1. Thus the velocity must be the velocity outside the porous mass (*i.e.*, the

interparticle velocity for a column of porous particles),  $v_i$ , and the sample fraction,  $R$ , must be the fraction of the sample outside the porous mass,  $R_i$ . Hence:

$$C_m \bar{v} = \frac{qR_i(1 - R_i)d^2v_i}{D_p} \quad (2)$$

where  $C_m$  is the mass transfer coefficient for a mobile phase,  $d$  is now the depth of the porous mass at its deepest point and  $D_p$  is the diffusivity of the sample in the porous mass. If velocities are measured using an unretained sample and dividing the column length by its elution time, the result is the mean velocity,  $\bar{v}$ , averaged over all the mobile phase, moving or stagnant (except in the case of gel filtration as discussed later). If the fraction of the mobile phase which is outside the porous mass is called  $\phi$ , then this average is  $\bar{v}_i\phi = \bar{v}$ . Similarly  $R_i/R = \phi$  and the  $R_i$  in eqn. 2 may be replaced by the more measurable  $\phi R$  and the  $v_i$  by  $\bar{v}/\phi$ .

The diffusivity in the porous mass,  $D_p$ , must be replaced by more available constants. These may be obtained by applying Fick's law for flux,  $J$ , of sample through a plane of unit area:

$$J = -D_p \frac{\partial c_p}{\partial z} \quad (3)$$

where  $c_p$  is the concentration in the porous mass at a distance  $z$  from the surface. Diffusion actually takes place only in the mobile phase and we may thus re-write this for a unit plane of pure mobile phase:

$$\frac{J}{\varepsilon_p} = -D_m \frac{\partial c_m}{\partial z} \quad (4)$$

where  $\varepsilon_p$  is the void fraction in the porous layer and  $c_m$  is the concentration in the mobile phase at a depth  $z$  within the layer. Equating eqns. 3 and 4 gives:

$$D_p \frac{\partial c_p}{\partial z} = D_m \varepsilon_p \frac{\partial c_m}{\partial z} \quad (5)$$

Now:

$$c_p = c_m \varepsilon_p + c_s(1 - \varepsilon_p) \quad (6)$$

where  $c_s$  is the concentration in the stationary phase (mass/volume) including any solid support. Putting  $c_s = c_m K$  where  $K$  is the partition coefficient, this may be rearranged and differentiated to give:

$$\frac{\partial c_p}{\partial z} = [\varepsilon_p + K(1 - \varepsilon_p)] \frac{\partial c_m}{\partial z} \quad (7)$$

and inserting this into eqn. 5 gives:

$$D_p = \frac{D_m}{1 + K(1 - \varepsilon_p)/\varepsilon_p} \quad (8)$$

This equation can be put into a number of other forms to show equivalence to treatments of the problem by other authors. Thus:

$$K \frac{(1 - \varepsilon_p)}{\varepsilon_p} = K \frac{v_s}{v_{mp}} = \frac{w_s}{v_s} \frac{v_{mp}}{w_{mp}} \frac{v_s}{v_{mp}} = \frac{w_s}{w_{mp}} \quad (9)$$

where  $v_s$  and  $v_{mp}$  are the volumes of adsorbent and of mobile phase within the porous mass and  $w_s$  and  $w_{mp}$  are the masses of sample adsorbed and in the mobile phase within the porous mass. This leads to CRANK's solution<sup>2</sup>:

$$D_p = \frac{D_m}{1 + w_s/w_{mp}} \quad (10)$$

although it is not equivalent to the equation given in ref. 3 as an interpretation of CRANK, which I have been unable to rederive.

It is equivalent to GOLAY's expression<sup>4</sup>  $D_p = D_m/K_{eff}$  (though misprinted  $D_1/K_{eff}$ ) only if, as GOLAY assumes, the volume of the true stationary phase is a negligible fraction of the total volume of the sorbent bed, *i.e.*,  $\varepsilon_p = 1.0$ . This may be shown by writing:

$$K_{eff} = \frac{\text{concn. in total sorbent}}{\text{concn. in gas}} = \frac{w_s + w_{mp}}{v_s + v_{mp}} \bigg/ \frac{w_{mp}}{v_{mp}} \approx \frac{w_s + w_{mp}}{w_{mp}} = 1 + \frac{w_s}{w_{mp}}$$

which is the equivalent of eqn. 10.

It is useful to put these expressions into a form where the retention is expressed as  $k$  rather than  $K$  so as to make them directly applicable to all forms of sorption and not merely to adsorbents. Thus putting

$$K \frac{(1 - \varepsilon_p)}{\varepsilon_p} = K \frac{v_s}{v_{mp}} = k \frac{v_m}{v_s} \frac{v_s}{v_{mp}} = \frac{k}{1 - \phi} \quad (11)$$

into eqn. 8 and rearranging gives:

$$D_p = \frac{(1 - \phi)D_m}{1 - \phi + k} \equiv \frac{R(1 - \phi)D_m}{1 - \phi R} \quad (12)$$

In these two forms the equation is true not only for solid adsorbents but for supported adsorbents or stationary liquids, since the extent of partition is specified only by relative retention times. They need, however, to be multiplied by an obstruction factor,  $\gamma_p$ , to allow for the tortuous and constricted path by which the sample must diffuse a unit distance into the porous mass. Thus finally:

$$D_p = \frac{(1 - \phi)\gamma_p D_m}{1 - \phi + k} \equiv \frac{R(1 - \phi)\gamma_p D_m}{1 - \phi R} \quad (13)$$

This is the same equation as derived by HAWKES<sup>5</sup> by a more questionable method. Substituting eqn. 13 into eqn. 2 and putting  $v_t = \bar{v}/\phi$  and  $R_t = \phi R$  as shown above yields the general equation for  $C_m$  in terms of experimental parameters:

$$C_m = \frac{q(1 - \phi R)^2 d^2}{(1 - \phi)\gamma_p D_m} \quad (14)$$

For spherical globules of stationary phase GIDDINGS has shown (ref. 1, p. 147) that  $q = 1/30$  and entering this value yields GIDDINGS' equation (ref. 1, p. 158 and ref. 6) for mass transfer in the mobile phase of porous spherical particles:

$$C_m = \frac{(1 - \phi R)^2 d_p^2}{30(1 - \phi)\gamma_p D_m} \quad (15)$$

SIE AND RIJNDERS' form<sup>7</sup> is readily derived from this by putting  $R = 1/(1 + k)$ .

#### MASS TRANSFER IN THE TRUE STATIONARY PHASE

These results are unaffected if there is significant resistance to mass transfer in or on the true stationary phase (that is the adsorbent surface or stationary liquid). This may be shown using GIDDINGS' treatment (ref. 1, p. 169) for a sphere of stationary phase (paralleling our stagnant mobile phase) with adsorption sites uniformly distributed within it. The mass transfer at the adsorption sites appears as a separate additive term while the liquid stationary phase term appears as:

$$C_1 = \frac{R(1 - R)d_p^2}{30(1 - f)D_1} \quad (16)$$

where  $f$  is the fraction of the sample molecules in the porous mass which are held on the true stationary phase. The quantity  $(1 - f)$  is thus  $w_{mp}/(w_{mp} + w_s) = 1/(1 + w_s/w_{mp})$  and eqn. 16 is thus identical with that obtained using the treatment described here starting with eqn. 10. Clearly a different geometry cannot affect this conclusion and hence it is universally true that mass transfer at the sorbent does not affect the equation for mass transfer in the stagnant fluid.

However, the reverse is not true. Mass transfer at the sorbent is affected by passage through the stagnant mobile phase. GIDDINGS (ref. 1, p. 169) deals with this term for the same particular case of mass transfer at adsorption sites within a sphere of stationary liquid phase. The resulting expression is exactly  $f$  times the regular expression for adsorption kinetics where there is no intervening fluid to complicate matters, where  $f$  is the fraction of those sample molecules in the porous medium that are actually sorbed.

To determine whether this is a general rule it was necessary to review GIDDINGS' arguments, particularly with respect to liquid stationary phase dispersed in the porous mass and with respect to stationary phase which is non-uniformly dispersed. GIDDINGS (ref. 1, p. 128-129) deals with the general case of transfer among three states (in our case the mobile, stagnant, and stationary phases) and derives a stationary phase expression (ref. 1, p. 129, eqn. 4.2-48) which may be rearranged to  $H = 2R(1 - R)fv/k_{3,2}$  where  $k_{3,2}$  is the rate constant for desorption from the third (stationary) to the second (stagnant) state. This is exactly  $f$  times the exactly analogous expression (ref. 1, p. 126, eqn. 4.2-37) derived specifically for adsorption on surfaces in contact with the mobile phase. However,  $k_{3,2}$  is a general expression independent of the nature of the stationary phase. In the case of a liquid stationary phase  $k_{3,2}$  is diffusion controlled but the form of the equation is still the same (*i.e.*, it is dependent on  $R(1 - R)v$  as has been shown many times) and the analogy is complete. Since the factor  $f$  is thus shown to apply to the general case and has been shown to apply specifically

to adsorption at the bottom of a liquid stationary phase (ref. 1, p. 129) and to uniformly distributed adsorption sites (ref. 1, p. 169) it is presumably applicable to any mode of distribution of sorptive sites.

This produces the theorem, "The expression for resistance to mass transfer in or on a stationary sorbent phase must be multiplied by  $f$  whenever the sorbent phase must be reached through a stationary fluid, whether this is a liquid stationary phase or merely stagnant mobile phase".

Fortunately  $f$  is usually near unity so that there is little error in ignoring it, as is usual, except at low values of  $k$  (i.e., for most purposes, when  $k < 2$ ).

#### EFFECT ON MASS TRANSFER IN THE FLOW STREAM

Where the  $C_m$  term for mass transfer in the flow stream is retention dependent, the unadsorbed fraction  $R$  must be replaced by  $\phi R$  as before. This is equivalent to GOLAY's<sup>4</sup> "virtual  $k$ ",  $k_v$ , given by  $(1 + k)/(1 + k_v) = \phi$ .

The open tubular column has the only known equation for  $C_m$  in a flow stream with a well understood retention dependence. Thus for a porous layer open tubular column the flow stream mass transfer is:

$$C_m = (6\phi^2 R^2 - 16\phi R + 11) (r - d)^2 / 24 D_m \quad (17)$$

#### UNIFORM POROUS LAYERS

In porous layer open tubular columns and in columns of porous layer beads, there is a more or less uniform porous layer which may be treated by this method putting  $q = 2/3$  so that:

$$C_m = \frac{2(1 - \phi R)^2 d^2}{3(1 - \phi) \gamma_p D_m} \quad (18)$$

This is also identical with an equation previously derived by HAWKES<sup>5</sup> more questionable procedure. It is not identical with those derived by GOLAY<sup>4,8</sup> since GOLAY used approximations which prevent algebraic identity and create error when  $d/r$  is significant. They can be compared by writing the full equations from both treatments and correcting the misprint  $ru/D_g$  to  $r^2u/D_g$  in GOLAY's eqn. 6 (ref. 8).

$$\frac{C_m D_m}{r^2} = \frac{(6\phi^2 R^2 - 16\phi R + 11)}{24} + \frac{2(1 - \phi R)^2 d^2 / r^2}{3(1 - \phi) \gamma_p} \quad (19)$$

$$\frac{C_m D_m}{r^2} = \left\{ \frac{1 + 6k + 11k^2}{(1 + k)^2} + \frac{8 + 32k}{(1 + k)^2} \frac{\varepsilon_p d}{r} + \frac{8k^2}{(1 + k)^2} \frac{d}{r \varepsilon_p \gamma_p} \right\} \frac{1}{24} \quad (20)$$

where  $r$  is the radius of the flowpath, not of the column as a whole. It is readily shown by putting  $R = 1/(1 + k)$  that when  $d = 0$  these are identical. Otherwise some simplifying assumptions are needed. Putting  $1 - \phi = (2d\varepsilon_p/r)/(1 + 2d\varepsilon_p/r) \approx 2d\varepsilon_p/r$  (i.e., assuming  $2d\varepsilon_p/r \ll 1$ ), separating the first term of eqn. 19 into two terms,  $(6R^2 - 16R + 11)/24 + [6(1 - \phi^2)R^2 - 16(1 - \phi)k]/24$ , assuming  $1 + \phi \approx 2$ , putting  $R = 1/(1 + k)$ , and ignoring terms in  $d^2/r^2$  in the expansion of the last term, eqn. 20

follows from eqn. 19. As eqn. 19 involves none of these assumptions and is also simpler in form it is to be preferred, although the simplicity is reduced when  $\phi$  is substituted by  $1/(1 + 2d\varepsilon_p/r)$ . Putting  $\varepsilon_p = \gamma_p = 1$  into eqn. 20 produces GOLAY'S simplified equation<sup>4</sup>.

The full equation for plate height in an open tubular column is thus:

$$H = \frac{2D_m}{v} + \left\{ \frac{(6\phi^2 R^2 - 16\phi R + 11)(r-d)^2}{24D_m} + \frac{2(1-\phi R)d^2}{3(1-\phi)\gamma_p D_m} + \frac{q_1 R(1-R)fd_1^2 r^2}{D_1} \right\} v \quad (21)$$

#### LIQUID-LIQUID CHROMATOGRAPHY WITH POROUS PARTICLES

GIDDINGS has shown (ref. 1, p. 181) that the optimum stationary phase loading in liquid-liquid chromatography is one which completely saturates the particle. In this case eqn. 1 applies with only the addition of the tortuosity factor,  $\gamma_p$ . For spherical particles it is thus:

$$C_1 = \frac{R(1-R)d_p^2}{30\gamma_p D_1} \quad (22)$$

and for porous layer beads it is:

$$C_1 = \frac{2R(1-R)d^2}{3\gamma_p D_1} \quad (23)$$

#### EXCLUSION CHROMATOGRAPHY WITHOUT ADSORPTION

The following argument will assume that the diffusion coefficient  $D_m$  is constant throughout a particle of exclusant. There will be some error here for at the limits of its penetration the sample molecule may be in a space with dimensions less than its mean free path. It is assumed that it will rarely be in such places so that the effect is small, but there is a possibility that this is wholly untrue. In this case a much more complex theory of zone broadening will be needed. A different theory will also be needed for non-rigid gels if it is true that diffusion is hindered by the molecular strands of the gel which must be moved aside for the sample to penetrate.

Unlike other systems considered in this paper, the velocity of an unretained sample is  $v_i$  because such samples have large molecules that will not enter the particle. Hence  $\bar{v} = v_i$  and similarly  $R = R_i$ . Since there is no adsorption,  $D_p = \gamma_p D_m$ . Applying these to eqn. 2 and putting  $q = 1/30$  gives the  $C_m$  term for spherical particles as:

$$C_m = \frac{R_i(1-R_i)d_p^2}{30\gamma_p D_m} \quad (24)$$

which is identical with the equation given by GIDDINGS<sup>9</sup>.

#### EXCLUSION CHROMATOGRAPHY WITH ADSORPTION

It has been shown<sup>10,11</sup> that the exclusion mechanism is often complicated by adsorption. This also complicates the  $C_m$  term. Since the large-molecule sample used

to determine  $\bar{v}$  is presumably insignificantly adsorbed, it remains true that  $v_i = \bar{v}$  and  $R_i = R$ . However,  $D_p$  must be recalculated starting from eqn. 8 which is unaffected. We may also use the relation  $K(1-\epsilon_p)/\epsilon_p = k'/(1-\phi)$  providing we define  $k'$  as the ratio of mass of sample adsorbed to mass unadsorbed without any reference to ratios of elution times. No experimental method of quantitatively determining  $k'$  with any confidence or of relating it to  $R_i$  has yet occurred to the author so the formula cannot be expressed in terms of available experimental quantities and it is left as:

$$D_p = \frac{D_m}{1 + k'/(1 - \phi)} \quad (25)$$

and hence:

$$C_m = \frac{R_i(1 - R_i) [1 + k'/(1 - \phi)] d_f^2}{3\sigma\gamma_p D_m} \quad (26)$$

Thus if adsorption is substantial  $C_m \propto k'$  and the degree of adsorption has a direct effect on the zone spreading.

TABLE I  
SUMMARY OF EQUATIONS OBTAINED

Medium	Equation	Agreement with references
Porous layer open tube	$C_m = \frac{(6\phi^3 R^2 - 16\phi R + 11)(r-d)^2}{24D_m} + \frac{2(1-\phi R)^2 d^2}{3(1-\phi)\gamma_p r D_m}$	4, 7—moderate
Porous layer spherical particles	$C_m = \frac{2(1-\phi R)^2 d^2}{3(1-\phi)\gamma_p D_m}$	5—precise
Porous spherical particles containing mainly stagnant mobile phase	$C_m = \frac{(1-\phi R)^2 d_p^2}{3\sigma(1-\phi)\gamma_p D_m}$	6—precise 3—disagrees
Non-adsorbing spherical gel filter particles	$C_m = \frac{R(1-R)d_p^2}{3\sigma\gamma_p D_m}$	7—precise
Adsorbing spherical gel filter particles	$C_m = \frac{R_i(1-R_i)[1 + k'/(1-\phi)]d_p^2}{3\sigma\gamma_p D_m}$	—
Porous spherical particles filled completely with stationary phase	$C_1 = \frac{R(1-R)d_p^2}{3\sigma\gamma_p D_1}$	—

#### SYMBOLS

- $c_p$  concentration in the porous mass  
 $c_m$  concentration in the mobile phase  
 $c_s$  concentration in the stationary phase  
 $C$  mass transfer coefficient  
 $C_1$  liquid phase mass transfer coefficient  
 $C_m$  mass transfer coefficient for mobile phase  
 $d$  depth of porous mass at its deepest point  
 $d_1$  depth of liquid phase at its deepest point

$d_p$	particle diameter
$D_1$	diffusivity of sample in liquid phase
$D_m$	diffusivity of sample in mobile phase
$D_p$	diffusivity of sample in the porous mass
$f$	fraction of the part of the sample within the porous bed which is held by the true stationary phase
$H$	zone dispersion rate ("plate height")
$J$	mass diffusing through a unit plane in unit time
$k$	column capacity ratio, mass sample sorbed/mass sample in mobile phase
$k'$	mass sample adsorbed on gel matrix/mass unadsorbed
$K$	partition coefficient, mass sample per ml of sorbent/mass sample per ml of mobile phase
$q$	geometrical factor
$q_1$	geometrical factor for a liquid stationary phase within the porous bed
$r$	radius of open tubular column
$R$	fraction of sample in the mobile phase, stagnant or moving
$R_t$	fraction of sample outside the porous mass
$v$	mobile phase velocity
$\bar{v}$	mobile phase velocity averaged over the entire mobile phase
$v_i$	interstitial velocity or average mobile phase velocity outside the porous mass
$v_s$	volume of solid adsorbent
$v_{mp}$	volume of (stagnant) mobile phase within the porous mass
$w_s$	weight of sample held to the true stationary phase
$w_{mp}$	weight of sample held in the mobile phase within the porous mass
$z$	distance from the surface of the porous bed
$\alpha$	ratio of bed depth to radius of open tubular column
$\gamma_p$	obstruction factor for diffusion in the porous mass
$\epsilon_p$	fraction of the volume of the porous bed occupied by (stagnant) mobile phase
$\phi$	fraction of the mobile phase which is outside the porous bed

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