REVISION OF THE VAN DEEMTER THEORY FOR DIFFUSION AND PRESSURE DROP IN THE GAS PHASE

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INTRODUCTION

It is well known that the system of differential equations (1) in Table I under the assumption of the constant flow rate of mobile phase shown by eqn. (2) was solved rigorously with the conditions (3) and (4) by LAPIDUS AND AMUNDSON[1] resulting in the expressions (5). This equation was later transformed by VAN DEEMTER et al.[2] into the convenient form of Gaussian distribution as given by eqns. (6)–(12).

In gas chromatography, however, because of the pressure drop along the column, these mathematical treatments do not hold strictly, and KAMBARA[3] proposed the corresponding derivation shown by eqns. (13)–(21), in which the diffusion of the sample component in the gas phase is neglected, and succeeded in elucidating the kinetic derivation of the JAMES-MARTIN factor[4]. In the present study it is intended to clear up mathematically the kinetic role of diffusion and pressure drop in gas chromatography.

The most important mathematical expressions are summarized in Table I and the symbols employed are given in Table II.

MATHEMATICAL FORMULATION OF THE PROBLEM

As shown by eqns. (13)–(21), if one ignores the diffusion term, the problem can well be solved. In order to introduce the diffusion term, we will employ the relationship given by eqn. (23), *i.e.* the diffusion constant D_{gas} is inversely proportional to the number of particles in unit volume, *viz.*, to the pressure p, as cited by GLASSTONE[5] and PERRY[6].

Thus, the flux of the sample component is shown by

$$f = -\frac{D^*}{p} \cdot \frac{\partial C}{\partial x} + uC \qquad (27)$$

whence eqn. (22) holds, where D^* is the diffusion constant at unit pressure. The set of differential eqns. (22) is difficult to solve, and so we will assume that the approximate solution thereof could be, in analogy to the VAN DEEMTER theory, rounded into the normal distribution form as shown by eqn. (6) including the variance term σ^2 which consists of two terms, one of which σ_α^2 depends on the rate constant α and the other σ_D^2 on the diffusion constant. If one could rationally determine the σ^2-term, it might

TABLE I

LIST OF IMPORTANT EQUATIONS

System of differential equations	*Exact solution*	*Approximate solution*
LAPIDUS AND AMUNDSON[1]		VAN DEEMTER, ZUIDERWEG AND KLINKENBERG[2]

$$F\frac{\partial C}{\partial t} = FD\frac{\partial^2 C}{\partial x^2} - Fu\frac{\partial C}{\partial x} - \alpha(KC_S - C)$$

$$F_S\frac{\partial C_S}{\partial t} = -\alpha(KC_S - C)$$

$u = $ const.

Initial condition:

$t = 0,\ 0 < x < \infty,\ C_S = 0,\ C = 0$

Boundary condition:

$x = 0\ \begin{cases} 0 < t < t_0,\ C = C_0 \\ \ \end{cases}$

Exact solution:

(1) $\quad C = C_0 t_0 \exp\left(\frac{ux}{2D}\right)\left\{\frac{\partial F_1(x,t)}{F_S} + \frac{\alpha K}{F_S} F_1(x,t)\right\}$

(2) $\quad F_1(x,t) = \exp\left(-\frac{\alpha K t}{F_S}\right)\int_0^t I_0\left\{2\sqrt{\frac{\alpha^2 K}{FF_S}\xi(t-\xi)}\right\} \times$

(3) $\quad \times \frac{x}{2\sqrt{\pi D\xi^3}} \times \exp\left(-\frac{x^2}{4D\xi} - k_1\xi\right)d\xi$

(4) $\quad k_1 = \frac{u^2}{4D} + \frac{\alpha}{F} - \frac{\alpha K}{F_S}$

Approximate solution (Van Deemter, Zuiderweg and Klinkenberg):

$$C(l,t) = \frac{sC_0t_0}{\sqrt{2\pi\sigma^2}}$$

(6) $\quad \exp\left\{\frac{-(t-t_R)^2}{2\sigma^2}\right\}$

(7) $\quad \sigma^2 = \sigma_D^2 + \sigma_a^2$

(8) $\quad \sigma_D^2 = \frac{2Dl}{\beta^2 u^3}$

(9) $\quad \sigma_a^2 = \frac{2F_S^2 l}{\alpha F K^2 u}$

(10) $\quad t_R = \frac{l}{\beta u}$

(11) $\quad \frac{1}{\beta} = 1 + \frac{F_S}{KF}$

(12) $\quad s = 1$

(5)

KAMBARA[8]

$$F\frac{\partial C}{\partial t} = -F\frac{\partial}{\partial x}[uC] + \alpha(KC_S - C) \tag{6}$$

$$F_S\frac{\partial C_S}{\partial t} = -\alpha(KC_S - C)$$

$$u = -w\frac{dp}{dx} = \frac{wm}{2(p_i^2 - mx)^{1/2}} = \frac{wm}{2p} \tag{14}$$

$$m = \frac{2wp}{w} = \frac{p_i^2 - p^2}{x} = \frac{p_i^2 - p_o^2}{l} \tag{15}$$

$$v = qupF = \text{const.}$$

$$C = C_0 t_0 \frac{p}{p_i}\exp\left(-\frac{T_x\alpha}{F}\right)\times \tag{13}$$

$$\times\left[\frac{\partial}{\partial t}[\exp\{-n(t-T_x)\}\, I_0(2\sqrt{k(t-T_x)})] + n\cdot\exp\{-n(t-T_x)\}\, I_0(2\sqrt{k(t-T_x)})\right]$$

$$\left. \right\} \tag{17}$$

$$n = \frac{\alpha K}{F_S}$$

$$T_x = \frac{4}{3m^2 w}(p_i^3 - p^3) = \frac{4l^2(p_i^3 - p^3)}{3w(p_i^2 - p_o^2)^2} \tag{16}$$

Gaussian distribution

$$\sigma_D^2 = 0 \tag{18}$$

$$\sigma_\alpha^2 = \frac{2F_S^2 T_l}{\alpha FK^2} \tag{19}$$

$$t_R = \frac{T_l}{\beta} \tag{20}$$

$$s = \frac{p_o}{p_i} \tag{21}$$

KAMBARA AND OHZEKI (present work)

$$F\frac{\partial C}{\partial t} = -F\frac{\partial}{\partial x}\left[\frac{D^*}{p}\cdot\frac{\partial C}{\partial x} + uC\right] + \alpha(KC_S - C) \tag{6}$$

$$F_S\frac{\partial C_S}{\partial t} = -\alpha(KC_S - C) \left. \right\} \tag{22}$$

$$D_{gas} = \frac{D^*}{p} \tag{23}$$

Gaussian distribution

$$\sigma_D^2 = \frac{D^* l}{p_o\beta^2 u_o^3}\left(\frac{p_i^2 + p_o^2}{p_o^2}\right) \tag{24}$$

$$\sigma_\alpha^2 = \frac{2F_S^2 T_l}{\alpha FK^2} \tag{25}$$

$$s = \frac{p_o}{p_i} \tag{26}$$

TABLE II

LIST OF SYMBOLS

Symbol	Significance	Unit or dimension	Equation
C	concentration in gas phase	mole cm^{-3}	(1), (13), (22)
C_S	same in stationary phase	mole cm^{-3}	(1), (13), (22)
C_0	initial concentration injected	mole cm^{-3}	(4)
D_{gas}	diffusion constant at pressure p	cm^2 sec^{-1}	(23)
D^*	diffusion constant proportionality factor	cm^2 sec^{-1} atm	(23)
F	fraction by volume occupied by mobile phase	dimensionless	(1), (13), (22)
F_S	fraction by volume occupied by stationary phase	dimensionless	(1), (13), (22)
K	distribution coefficient ($= C/C_S$ at equilibrium)	dimensionless	
l	length of packing	cm	(15)
m	$2\,up/w$	atm^2 cm^{-1}	(15), (17)
n	number of theoretical plates	dimensionless	(39)
p	pressure of carrier gas, dependent on x	atm [M L^{-1} T^{-2}]	(14)–(17)
p_i	pressure of carrier gas at column inlet	atm [M L^{-1} T^{-2}]	(14), (15), (17)
p_o	pressure of carrier gas at column outlet	atm [M L^{-1} T^{-2}]	(15), (17)
q	proportionality factor	atm^{-1} mole cm^{-3}	(16)
s	p_o/p_i	dimensionless	(6), (12), (21)
t	time elapsed after sample feed	sec	
t_0	duration of concentration pulse injected	sec	(4)
t_R	retention time of sample component	sec	(10), (20)
T_x	passing time of carrier gas through the column length x	sec	(17), (20), (25)
T_l	passing time of carrier gas through the whole column length l	sec	(17), (20), (25)
u	linear gas velocity, dependent on x	cm sec^{-1}	(2), (14)
u_i	linear gas velocity at column inlet	cm sec^{-1}	
u_o	linear gas velocity at column outlet	cm sec^{-1}	
v	gas flow rate per unit cross section of column	mole cm^{-2} sec^{-1}	(16)
w	permeability coefficient	cm^2 sec^{-1} atm^{-1}	(14), (15)
x	distance from column inlet along the column	cm	
α	rate constant of dissolution or adsorption	sec^{-1}	(1), (13), (33)
β	$1 + (F_S/KF)$	dimensionless	(11)
σ^2	variance of peak	sec^2	(7)
$\sigma_D{}^2$	contribution of diffusion term to variance	sec^2	(8), (18), (24)
$\sigma_\alpha{}^2$	contribution of adsorption rate term to variance	sec^2	(9), (19), (25)

be safe to say that the famous VAN DEEMTER theory could be revised theoretically and successfully for the pressure drop along the column and for the pressure-dependent diffusion in the gas phase.

Elimination of the concentration C_S in the stationary phase from the eqns. (22) gives:

$$G(x,t) = -\frac{\partial^2 C}{\partial t^2} - \frac{\alpha K}{F_S}\cdot\frac{\partial C}{\partial t} + \frac{D^*}{p}\cdot\frac{\partial^2 C}{\partial t\partial x} + \frac{\alpha K}{F_S}\cdot\frac{D^*}{p}\cdot\frac{\partial^2 C}{\partial x^2} - \frac{D^*}{p^2}\frac{dp}{dx}\frac{\partial^2 C}{\partial t\partial x} -$$

$$-\frac{\alpha K}{F_S}\cdot\frac{D^*}{p^2}\cdot\frac{dp}{dx}\cdot\frac{\partial C}{\partial x} - \frac{du}{dx}\cdot\frac{\partial C}{\partial t} - \frac{\alpha K}{F_S}\cdot\frac{du}{dx}C - u\frac{\partial^2 C}{\partial t\partial x} - \frac{\alpha K}{F_S}u\frac{\partial C}{\partial x} -$$

$$-\frac{\alpha}{F}\frac{\partial C}{\partial t} = 0. \tag{28}$$

This equation is difficult to integrate, since p and u depend on x. However, it may be considered that the first-order approximate solution of eqn. (28) is shown by

eqns. (6) and (19), if one neglects the diffusion term. Regarding that the variance σ^2 depends only on x and not on t, one can obtain the derivatives of C from eqn. (6), the insertion of which into eqn. (28) with the assumption:

$$t = t_R = \frac{Tx}{\beta} \tag{29}$$

transforms it into the following form (see Appendix I).

$$H(\sigma,D) = \frac{D^*}{p} \left\{ \frac{pt_R''\sigma - 6\,pt_R'\sigma' + 2\,t_R'p'\sigma}{\sigma^4} \right\} - \frac{D^*}{p^2}\,p'\,\frac{pt_R'}{\sigma^3} - \frac{\alpha K}{Fs}\frac{D^*}{p^2}\,p'\,\frac{p'\sigma - p\sigma'}{\sigma^2}$$

$$+ \frac{\alpha K}{Fs}\frac{D^*}{p} \left\{ \frac{(p''\sigma - p\sigma'')\sigma - 2\,\sigma'(p'\sigma - p\sigma') - (t_R')^2 p}{\sigma^3} \right\} \tag{30}$$

$$H(\sigma,D) + \frac{p}{\sigma^3} - \frac{\alpha K}{Fs}\,u'\,\frac{p}{\sigma} - \frac{upt_R'}{\sigma^3} - \frac{\alpha K}{Fs}\,u\,\frac{p'\sigma - p\sigma'}{\sigma^2} = 0. \tag{31}$$

Here the notation dash implies the differentiation with respect to x. Ignoring $H(\sigma, D)$ and multiplying eqn. (31) by σ^3, one can write:

$$p(ut_R' - 1) + \frac{\alpha K\sigma^2}{Fs}\,(u'p + up') = \frac{\alpha K}{Fs}\,up\sigma\sigma'$$

Since $u = wm/2\,p$ (14) and $t_R' = 2\,p/mw\beta$, it is seen that:

$$ut_R' = \frac{1}{\beta} \gg 1$$

Further, one can derive $u'p + up' = 0$ from eqn. (16), so that eqn. (31) is reduced to:

$$\sigma\sigma' = \frac{Fs}{\alpha K}\,t_R'$$

whence

$$\sigma^2 = \frac{2\,Fs}{\alpha K}\,t_R = \frac{2\,Fs^2 Tl}{\alpha K^2 F} \tag{32}$$

Thus the σ_α^2-term shown by eqns. (7), (18) and (19) is again confirmed in a different manner from that in our previous publication[3], provided that diffusion does not take place.

Now we have to solve the simplified form of eqn. (31), namely:

$$- \sigma^3 H(\sigma,D) + upt_R' = \frac{\alpha K}{Fs}\,up\sigma\sigma' \tag{33}$$

As discussed in Appendix II, under the usual gas chromatographic conditions one may simplify the expression $H(\sigma,D)$, so that one has now to integrate:

$$\frac{\alpha K D^*}{Fs}\,(t_R')^2 + upt_R' = \frac{\alpha K}{Fs}\,up\sigma\sigma'$$

where up = const. and $t_R' = 2\,p/mw\beta$. Hence, the integration of the left-hand side of the above equation yields:

$$\int_0^l (t_R')^2 dx = \frac{4}{m^2 w^2 \beta^2} \int_0^l p^2 \cdot dx = \frac{4}{m^2 w^2 \beta^2} \int_{p_i}^{p_o} \left(\frac{-2\,p^3}{m}\right) \cdot dp = \frac{2}{m^3 w^2 \beta^2} (p_i^4 - p_o^4) \,;$$

$$\int_0^l \frac{dt_R}{dx}\, dx = \int_0^{t_R} dt_R = t_R.$$

The right-hand side is calculated as follows.

$$\int_0^l \sigma\sigma' \cdot dx = \frac{\sigma^2}{2}$$

Thus, it is clear that:

$$C(l,t) = \frac{p_o C_o t_o}{p_i \sqrt{2\,\pi\sigma^2}} \exp\left\{-\frac{(l-t_R)^2}{2\,\sigma^2}\right\} \tag{34}$$

where:

$$\sigma^2 = \frac{2\,F_s^2 T l}{\alpha K^2 F} + \frac{D^* l}{p_o \beta^2 u_o^3} \left(\frac{p_i^2 + p_o^2}{p_o^2}\right) \tag{35}$$

DISCUSSION

If there is no pressure drop and the linear velocity is distributed uniformly along the column, the present theory is reduced to the original VAN DEEMTER theory. Thus, the famous VAN DEEMTER theory is considered to hold as the limiting law and quite legitimate in liquid phase chromatography.

If one integrates the product of concentration and linear velocity with respect to time, the quantity obtained should express the amount of sample component that penetrates a cross section of unit area at an arbitrary position. Thus, it follows that:

$$\int_{-\infty}^{+\infty} C \cdot u \cdot dt = C_o t_o u_t \tag{36}$$

whence the conservation of material is proved.

The above procedure for evaluating the peak variance was also found successful, when it was applied to the derivation of the VAN DEEMTER eqns. (6)–(12) from the LAPIDUS-AMUNDSON system of differential eqns. (1)–(4). This result will be published elsewhere[7].

The expression for the height equivalent to a theoretical plate (H) is easily derived from eqns. (34) and (35), and it is found that it has the same form as shown by:

$$H = A + \frac{B}{u_o} + C u_o \tag{37}$$

However, the three constants A, B and C depend on pressure and have somewhat different meanings from those in the original VAN DEEMTER equation. For the

elucidation of temperature and pressure dependencies of plate number[8], the form of Gaussian distribution seems fundamentally more important and useful, as discussed in our former publications.

APPENDIX I. DERIVATION OF EQUATION (31)

In eqn. (6) p, σ and t_R are functions of x. Expressing the partial differentiation with respect to x by a dash and that with respect to t by a dot, such as $C' = \partial C/\partial x$ and $\dot{C} = \partial C/\partial t$, and putting:

$$k = \frac{C_0 t_0}{p_i (2\pi)^{1/2}} = \text{const.}; \quad f(x) = \frac{p}{\sigma}; \quad g(x,t) = \exp\{h(x,t)\}; \quad h(x,t) = -\frac{(t - t_R)^2}{2\sigma^2};$$

$$t_R = \frac{T_x}{\beta}$$

one easily derives:

$$g' = h'g; \quad \dot{g} = \dot{h}g; \quad \ddot{g} = \{\ddot{h} + (\dot{h})^2\}g; \quad \dot{h} = -\frac{t - t_R}{\sigma^2}; \quad \ddot{h} = -\frac{1}{\sigma^2};$$

$$h' = \frac{(t - t_R)t_R'\sigma + \sigma'(t - t_R)^2}{\sigma^3}; \quad \dot{h}' = \frac{t_R'\sigma + 2\sigma'(t - t_R)}{\sigma^3} \text{ etc.}$$

Since we are interested in the region near the chromatographic peak, we may put $t = t_R$. Then, the result is:

$$h = \dot{h} = h' = 0; \quad \ddot{h} = -\frac{1}{\sigma^2}; \quad h'' = -\frac{(t_R')^2}{\sigma^2}; \quad \dot{h}' = \frac{t_R'}{\sigma^2}; \quad \ddot{h}'' = \frac{t_R''\sigma - 4 t_R'\sigma'}{\sigma^3}$$

$$\text{for } t = t_R.$$

Thus, one obtains:

$$\dot{C}(x,t_R) = kf\dot{h}g = 0; \quad \ddot{C}(x,t_R) = kf\ddot{h}g = -\frac{k}{\sigma^2}fg; \quad C'(x,t_R) = kf'g; \quad C''(x,t_R) =$$

$$= k\left\{f'' - f\frac{(t_R')^2}{\sigma^2}\right\}g; \quad \dot{C}'(x,t_R) = \frac{k}{\sigma^2}t_R'fg$$

$$\dot{C}''(x,t_R) = k\left(\frac{2 t_R'f'}{\sigma^2} + f\frac{t_R''\sigma - 4 t_R'\sigma'}{\sigma^3}\right)g$$

where:

$$f' = \frac{p'\sigma - p\sigma'}{\sigma^2}; \quad f'' = \frac{(p''\sigma - p\sigma'')\sigma - 2\sigma'(p'\sigma - p\sigma')}{\sigma^3}$$

Insertion of the above equations into eqn. (28) yields eqns. (30) and (31).

APPENDIX II. SIMPLIFICATION OF $H(\sigma,D)$ AND DERIVATION OF EQNUATION (33)

The function $H(\sigma,D)$ shown by eqn. (30) can be rearranged by means of the relationships:

$$t_R' = \frac{\alpha K}{F_s}\sigma\sigma'; \quad t_R'' = \frac{\alpha K}{F_s}\{(\sigma')^2 + \sigma\sigma''\}$$

derived from the first-order approximation given by eqn. (32), and the result is:

$$- H(\sigma,D) \frac{F_s p^2 \sigma^3}{\alpha K D^*} = 2 \; (p')^2 \sigma^2 + 3 \; p^2 (\sigma')^2 + (t_R')^2 p^2 \tag{38}$$

The ratio of the third term to the second in the right-hand side of the eqn. (38) is:

$$\frac{(t_R')^2}{3 \; (\sigma')^2} = \frac{4 \; t_R^2}{3 \; \sigma^2} = \frac{4}{3} \, n \tag{39}$$

where n, the number of plates, is much greater than unity. Hence one can neglect the second term.

Next, the ratio of the third term to the first is given by:

$$\frac{p^2 (t_R')^2}{2 \; (p')^2 \sigma^2} = \frac{n p^2 (t_R')^2}{2 \; (p')^2 t_R^2}$$

Employing the equations:

$$n = \frac{t_R^2}{\sigma^2}; \; t_R = \frac{4}{3 \; m^2 w \beta} (p_i{}^3 - p^3); \; t_R' = \frac{4}{m^2 w \beta} (- p^2 p')$$

one derives

$$\frac{p^2 (t_R')^2}{2 \; (p')^2 \sigma^2} = \frac{9 \, n}{2} \left\{ \frac{1}{(p_i/p)^3 - 1} \right\}^2$$

Since n is much greater than unity, it is seen that the first term can legitimately be ignored.

Thus, the function $H(\sigma,D)$ is simplified into:

$$H(\sigma,D) = - \frac{\alpha K D^*}{F_s \sigma^3} (t_R')^2 \tag{40}$$

resulting in eqn. (34).

SUMMARY

Provided that the flow rate of carrier gas in a gas chromatographic column is maintained constant and the pressure and the linear velocity are distributed as shown by eqns. (14)–(16), and also the diffusion coefficient in gas phase is inversely proportional to the pressure, one can formulate the problem by eqns. (3), (4) and (22). Assuming that the solution is shown by a Gaussian distribution as given by eqn. (6), the above problem is converted into the integration of the ordinary differential eqns. (30) and (31) concerning the peak variance. The calculation provides a revised equation for gas chromatographic peak that includes the familiar VAN DEEMTER theory as a limiting law.

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