81. *On the Theory of Chromatography.*

By Joseph Weiss.

A general theory for the formation of a chromatogram in an absorption column from a single substance and the process of development by a solvent is given and discussed for several adsorption isotherms (Langmuir, Freundlich, linear isotherm).

The structure and shape of the band and the process of elution are discussed in general for the case of complete equilibrium between the solution and the adsorbed state, but some reference is also made to non-equilibrium conditions.

In the following paper an attempt is made to correlate the theory with experimental results.

THE method of chromatographic adsorption analysis, discovered by Tswett, is now used mainly for the separation of organic compounds. In its simplest form, a mixture of the compounds in a suitable solvent is allowed to run through a vertical column of a suitable, finely powdered adsorbent. The mixture is separated into a series of bands (chromatogram), which are obvious in the case of coloured substances, and often show fluorescence in U.V. light if they are normally colourless. The separation of these bands can be completed by the process of " development " : after the original chromatogram is formed, one passes a suitable solvent through the column, thereby washing the bands down at different rates and thus effecting their separation. By cutting the column, the bands can be extracted separately, or they can be removed by fractional desorption (elution) with suitable solvents.

It is obvious that for any of these processes the structure of the bands (*e.g.*, width, concentration) is of great interest, for on this must depend primarily the possibility of a separation of two or more substances. Only two published papers deal with the theory of chromatography.* Wilson (*J. Amer. Chem. Soc.*, 1940, **62**, 1583) gives the correct differential equation for the case of complete equilibrium between the solution and the adsorbent, but in the solution of this differential equation and in its physical interpretation he has overlooked various important points, and he therefore obtains the result that the adsorption band—even after development by a solvent—remains always of the same width, depending only on the initial concentration of the solution. Actually, as is well known, the adsorption band broadens out, and also the concentration of the eluate is not in agreement with this theory. Wilson, who was aware of these difficulties, attributed them to secondary effects (finite rate of adsorption and desorption, etc.).

The second paper (Martin and Synge, *Biochem. J.*, 1941, **35**, 1358) only takes into consideration a linear adsorption isotherm, in an adaptation of the theory of the fractionating column.

I. The following theoretical treatment is also based on the assumption of practically instantaneous equilibrium between the solution and the absorbent. The chromatogram of a solution containing a single solute will be discussed first, for this is an essential preliminary to the understanding of the chromatogram of mixtures.

The differential equation governing the adsorption process is given by the conservation condition, *viz.*, that the amount of substance disappearing from a solution of volume dv and concentration c—changing to $(c - dc)$—in passing through an adsorption column of length dx is equal to $-(\partial c/\partial x)dx \,.\, dv$, and this must appear in the quantity adsorbed in the length dx from the volume dv, *i.e.*, $(\partial q/\partial v)dv \,.\, dx$, q being the amount of substance adsorbed per unit of length of the column. Therefore

$$- (\partial c/\partial x)dv \,.\, dx = (\partial q/\partial v)dv \,.\, dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In general,

$$q = A\mathrm{f}(c) \text{ (adsorption isotherm)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where A is the amount of adsorbent per unit of length of the column, and

$$\partial q/\partial v = (\partial q/\partial c)(\partial c/\partial v) = A\mathrm{f}'(c)(\partial c/\partial v) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Finally, from (1), (2), and (3) we obtain

$$(\partial c/\partial x) + A\mathrm{f}'(c)(\partial c/\partial v) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The solution of this equation is given by

$$c = \phi\{v - xA\mathrm{f}'(c)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where ϕ is an arbitrary function to be determined by the initial conditions. The full mathematical discussion of equation (5) is given in the Appendix, and we give here only the results there obtained.

II. We consider two operations : (i) When a solution of a given concentration is poured on an adsorption column, and (ii) when pure solvent of volume v is poured on the chromatogram formed according to (i).

(i) According to this theory, the adsorption band formed from a solution of initial concentration c_0 and volume v_0 is of uniform concentration. The amount adsorbed per unit of length (see equation 2) is given by

$$q_0 = A\mathrm{f}(c_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

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* (Note added in proof.) After this paper had gone to press another paper (de Vault, *J. Amer. Chem. Soc.*, 1943, **65**, 532) appeared in which, as far as the same problems are treated, the author arrives at substantially the same conclusions as those reported here.

The width of the adsorption band extending from $x = 0$ to $x = x_0 = l$ is given by

$$v_0 c_0 / A \mathrm{f}(c_0) = l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

(see Fig. 1) (Appendix, equation A7).

FIG. 1.

Original adsorption band, extending from
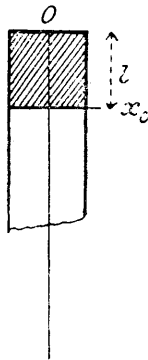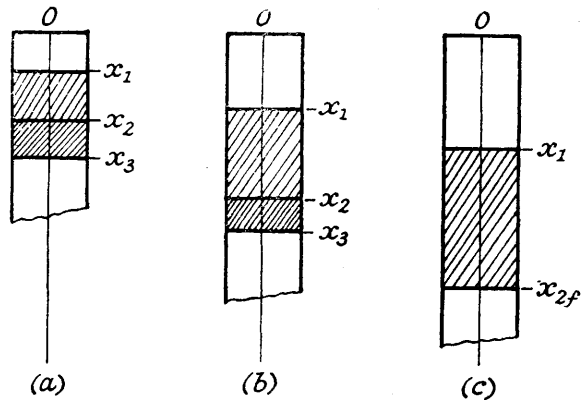x = 0 to x = x₀ = 1 (the positive x-
axis pointing downward).

FIG. 2.

Schematical representation of the various stages of develop-
ment of a single band by a pure solvent.

(a)   (b)   (c)

(ii) The theory shows that in general the band formed originally goes successively through the stages shown schematically by Fig. 2 (a), (b), (c), which follow the stage shown by Fig. 1. When pure solvent is poured on, the band begins to move down and to broaden, "dissolving" from the top end. The band is then, in general, represented by two regions (Fig. 2a), viz., the lower region ($x_2 x_3$), where there is still the original concentration present as given by equation (6), and the upper region ($x_1 x_2$) with a variable concentration (c) which is given, in general, as a function of (v/x), viz. (see Appendix, equation A16),

$$v/x = A \mathrm{f}'(c) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

With increasing v, the region of the original concentration in the lower part gradually diminishes (Fig. 2b) and eventually disappears (Fig. 2c). The various levels are given by the equations (Appendix, equations A14, A18, A20) :

$$x_1 = v/(A \mathrm{f}'(0)) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$
$$x_2 = v/A \mathrm{f}'(c_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$
$$x_3 = v c_0 / A \mathrm{f}(c_0) + \underbrace{v_0 c_0 / A \mathrm{f}(c_0)}_{l} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The minimum volume (v_m) of pure solvent to make the lower region of initial concentration just disappear is given by the condition

$$x_2 = x_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Substituting from (10) and (11), we obtain

$$v_m = v_0 \{ c_0 \mathrm{f}'(c_0) / [\mathrm{f}(c_0) - c_0 \mathrm{f}'(c_0)] \} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

III. We shall now discuss the above theory for the known adsorption isotherms.

(a) *Linear adsorption isotherm :*

$$q = A \mathrm{f}(c) = ac \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$
$$A \mathrm{f}'(0) = A \mathrm{f}'(c_0) = a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$
$$x_1 = x_2 = v/a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$
$$x_3 = v/a + l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The width of the band is given by

$$l = v_0/a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

depending only on the initial volume (v_0) and independent of the initial concentration (c_0). In the development, the band moves down unchanged at the constant rate (per unit of volume) :

$$x/v = 1/a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

In practice, the case of the linear adsorption isotherm is of little importance. We have discussed this only because, for this special case, our results are identical with those of Wilson (*loc. cit.*).

(b) *Langmuir adsorption isotherm :*

$$q = A \mathrm{f}(c) = ac/(1 + bc) \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$
$$A \mathrm{f}'(c_0) = a/(1 + bc_0)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$
$$A \mathrm{f}'(0) = a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$
$$x_1 = v/a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$
$$x_2 = v(1 + bc_0)^2/a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$
$$x_3 = v(1 + bc_0)/a + l \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

The equilibrium concentration of the solute in the variable part $(x_1 x_2)$ as derived from equation (8) is given by $A f'(c) = v/x = a/(1 + bc)^2$, i.e.,

$$c = (\sqrt{ax/v} - 1)/b \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (26)$$

The amount of adsorbed matter (m) in any interval $(x_u x_l)$ of the variable part is given by

$$A \int_{x_l}^{x_u} f(c) dx = m \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (27)$$

Combining this with (26), we have

$$m = a(x_u - x_l)/b - 2\sqrt{av}(\sqrt{x_u} - \sqrt{x_l})/b \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (28)$$

If $(x_u x_l)$ represents the whole of the variable interval, i.e., if $x_u = x_2$ and $x_l = x_1$, and if we introduce their values from (23) and (24) into (28), we obtain

$$A \int_{x_1}^{x_2} f(c) dx = vbc_0^2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (29)$$

We can also calculate the total width of the band when all the adsorbed matter present, m_0 (i.e., the total amount), is present in the variable part (i.e., when the lower region has disappeared).

The lower level $x_u = x_{2f}$ can then be obtained from the equations (27) and (28) by introducing the value for x_1 from (23) and we obtain

$$bm_0 = (\sqrt{ax_{2f}} - \sqrt{v})^2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (30)$$

and

$$\sqrt{x_{2f}} = \sqrt{v/a} + \sqrt{bm_0/a} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (31)$$

The maximum equilibrium concentration (c_{2f}) at the front edge of the band corresponding to the level x_{2f} is then obtained from equations (26) and (31) as

$$c_{2f}(x_{2f}, v) = \sqrt{m_0/bv} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (32)$$

v being the volume of the pure solvent that has passed.

(c) *Freundlich adsorption isotherm :*

$$q = A f(c) = Bc^a; \quad 0 < \alpha < 1 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (33)$$
$$A f'(c_0) = \alpha B c_0^{(a-1)} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (34)$$
$$A f'(0) = \infty \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (35)$$
$$x_1 = 0 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (36)$$
$$x_2 = v/\alpha B c_0^{(a-1)} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (37)$$
$$x_3 = v/B c_0^{(a-1)} + l \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (38)$$

The fact that $x_1 = 0$ means that in this case the upper edge of the band never moves completely away from the top of the column. The equilibrium concentration of the solute in the variable part $(x_1 x_2)$ is again given by equation (8) as

$$c = (\alpha B x/v)^{1/(1-a)} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (39)$$

The amount of adsorbed matter in any interval of the variable part can be calculated from (27) and (39).

The total width of the band, when all the adsorbed matter (m_0) is present in the variable part of the band, can be calculated from the equation

$$A \int_0^{x_2} f(c) dx = m_0 = \frac{B^{1/(1-a)} \alpha^{a/(1-a)} (1-\alpha)}{v^{a/(1-a)}} x_2^{1/(1-a)} \qquad . \qquad . \qquad . \qquad (40)$$

and

$$x_{2f} = \frac{(1-\alpha)^{(1-a)} v^a}{\alpha^a} \frac{v^a}{B} m_0^{(1-a)} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (41)$$

The maximum equilibrium concentration (c_{2f}) at the front edge of the band corresponding to the level x_{2f} is then obtained from equations (39) and (41) :

$$c_{2f} = (1-\alpha)\alpha m_0/v \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (42)$$

IV. We will now consider the process of elution of the chromatogram of a single substance. If we add pure solvent to the original band, then for any volume greater than v_m (equation 13) the original band is completely " washed out " (except in the case of the linear isotherm, in which the band remains unchanged). This volume v_m is given for the two cases discussed above by

$$\text{(Langmuir)} \quad v_m \gg v_0/bc_0 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (43)$$

$$\text{(Freundlich)} \quad v_m \gg v_0\alpha/(1-\alpha) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (44)$$

If we continue to add pure solvent, eventually the lower edge of the band reaches the bottom of the adsorption column; until then no solute will have appeared in the eluate.

We shall call the volume of solvent required to shift the adsorption band to the end of the adsorption column

(of total length x_t) the " threshold " volume v_t, and $V_t = v_t + v_0$. The volume v_t is given by the following expressions, obtained from (17), (31), and (41) for $x = x_t$ and by solving for $v = v_t$:

$$\text{(Linear isotherm) } v_t = a(x_t - l) = ax_t - v_0 \qquad \ldots \quad \ldots \quad (45)$$

$$\text{(Langmuir) } v_t = (\sqrt{ax_t} - \sqrt{bm_0})^2 \qquad \ldots \quad \ldots \quad \ldots \quad (46)$$

$$\text{(Freundlich) } v_t = \frac{\alpha}{(1 - \alpha)^{(1-a)/a}} \frac{(Bx_t)^{(1-a)}}{m_0^{(1-a)/a}} = \frac{ks^{1/a}}{m_0^{(1-a)/a}} \qquad \ldots \quad \ldots \quad (47)$$

s is the total amount of adsorbent in the column $= Ax_t \propto Bx_t$.

Equations (46) and (47) are only valid for fully developed bands (*i.e.*, $v_t \gg v_m$) ; whereas for partly developed bands one obtains

$$v_t' = [x_t A \mathrm{f}(c_0)/c_0] - v_0 \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (48)$$

The mean concentration of the substance in the eluate ($\bar{c}_e$) for any volume (v) in excess of v_t is given (corresponding to equation 27) by the expression

$$\bar{c}_e = \frac{m}{v} = \frac{A}{v} \int_{v_t}^{v_t + v} \mathrm{f}(c) \cdot \mathrm{d}x \qquad \ldots \quad \ldots \quad \ldots \quad (49)$$

after substituting for $\mathrm{f}(c)$ for the different adsorption isotherms [*e.g.*, (20) and (26) or (33) and (39)] and using the relations between v_t and x_t (equations 31 and 41).

We give here only the result for the Freundlich isotherm, which has been verified by experiment and is given by

$$\text{(Freundlich) } \bar{c}_e = (m_0/v)\{1 - [v_t/(v_t + v)]^{a/(1-a)}\} \qquad \ldots \quad \ldots \quad \ldots \quad (50)$$

From this equation the mean concentration in the eluate after passage of, *e.g.*, the volume αv_t is then given by the expression

$$\bar{c}_{e(a v_t)} = (m_0/\alpha v_t)\{1 - [1/(1 + \alpha)]^{a/(1-a)}\} \qquad \ldots \quad \ldots \quad \ldots \quad (51)$$

For the (differential) concentration in a small volume Δv, collected after the passage of a volume v, one obtains

$$c_e = \frac{\Delta m}{\Delta v} = \frac{m_0}{\Delta v}\left[\left(\frac{v_t}{v_t + v}\right)^{a/(1-a)} - \left(\frac{v_t}{v_t + v + \Delta v}\right)^{a/(1-a)}\right] \qquad \ldots \quad \ldots \quad (52)$$

V. The concentration of the eluate as given by (49) or (50) is directly related to that of the adsorbed matter within the band, and the differential concentration of the eluate gives us directly a picture of the " shape " of the band. We shall consider briefly the resultant " shapes " of the bands after development with a solvent for the various adsorption isotherms.

Generally, the amount adsorbed per unit of length of the band is given by $q(x, v)$; and for the variable part (tail) of the band :

$$\partial q/\partial x = A\partial \mathrm{f}(c)/\partial x = A\mathrm{f}'(c)\partial c/\partial x = (v/x)(\partial c/\partial x) \quad (53)$$

For the Langmuir isotherm this gives

$$\partial q/\partial x = (2\sqrt{a}/b)(v^{1/2}/x^{3/2}) \text{ (for } x \gg v/a) \quad (54)$$

$$q = 0 \qquad \qquad \text{(for } x \ll v/a)$$

This is schematically represented in Fig. 3.
For the Freundlich isotherm we obtain :

Schematic representation of the shape of the band for the Langmuir adsorption isotherm (1, partly developed; 2, fully developed).

Quantity adsorbed (q).

q_0

1

2

0   x_l x_l'

Length of column, x.

$$\frac{\partial q}{\partial x} = \frac{(\alpha B)^{1/(1-a)}}{(1-\alpha)v^{a/(1-a)}} x^{(2a-1)/(1-a)}, \text{ for } \alpha > \tfrac{1}{2} \text{ (Fig. 4a)}. \quad \ldots \quad \ldots \quad (55)$$

$$\frac{\partial q}{\partial x} = \frac{(\alpha B)^{1/(1-a)}}{(1-\alpha)v^{a/(1-a)}} \frac{1}{x^{(1-2a)/(1-a)}}, \text{ for } \alpha < \tfrac{1}{2} \text{ (Fig. 4b)}. \quad \ldots \quad \ldots \quad (56)$$

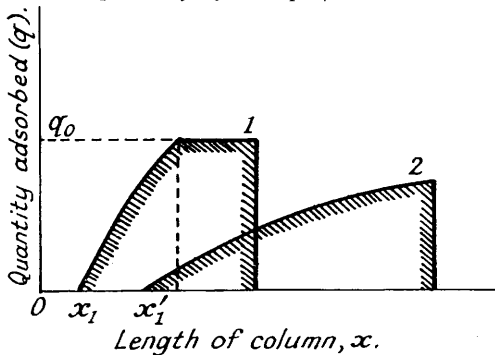The actual amount of substance in the variable (tail) part of the band (m_{tl}) is given by the expressions

$$\text{(Langmuir) } m_{tl} = bc_0^2 v \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (57)$$

$$\text{(Freundlich) } m_{tl} = [(1 - \alpha)/\alpha^2]c_0 v \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (58)$$

and so for small α it is large, and as $\alpha \longrightarrow 1$ it tends to become zero.

In all the above cases we have a sharp frontal edge and the band "dissolves" from the top end. This result is always obtained on the basis of the "equilibrium theory" if f'(c) is a decreasing function of c (see Appendix). Actually, the frontal edge of the band, although often fairly sharp, generally shows some diffuseness, which becomes more marked if there is a strong dependence of the amount adsorbed on the concentration, *e.g.*, in the case where α approaches unity, as for the linear adsorption isotherm. In this case we might expect a deviation from the equilibrium theory at the frontal edge where the concentration is a maximum.

FIG. 4.

Shape of the adsorption band in the case of the Freundlich isotherm (1, partly developed; 2, fully developed).
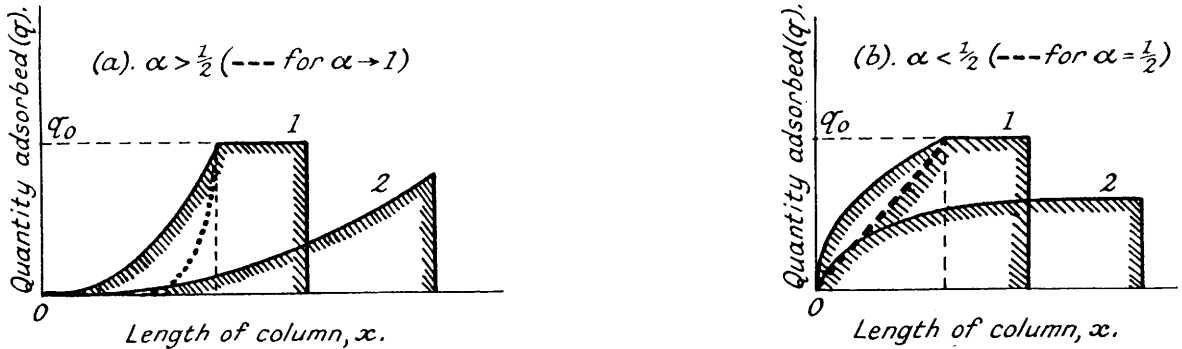
FIG. 4a.—$\alpha > \frac{1}{2}$. The broken line represents the change in the form if α approaches unity.
FIG. 4b.—$\alpha < \frac{1}{2}$. The broken line shows the band for $\alpha = \frac{1}{2}$.

A detailed theory of this effect cannot be given without some assumptions about the kinetics of the processes involved, but the following remarks serve to illustrate this point. In the case of a linear isotherm, the amount adsorbed (per unit of length) is given by $q = ac$ (equation 14). For higher concentrations, if equilibrium is not fully reached, the simple isotherm may be replaced by an equation of the form

$$q = A\mathrm{f}(c) = b_1c + b_2(b_1c)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

Here, $b_1 < a$, and the equation must have the property that for sufficiently small c, $b_1 \longrightarrow a$, and the second term disappears. However, at the frontal edge where c is large, we must apply equation (59). This gives

$$q = A\mathrm{f}'(c) = b_1 + (2b_2b_1{}^2)c \quad . \quad . \quad . \quad (60)$$

In this case f'(c) is an increasing function of c and the concentration in the variable part is given (from the general equation 8) by :

$$c = [(v/x) - b_1]/2b_2b_1{}^2 \quad . \quad . \quad . \quad . \quad (61)$$

and

$$\partial q/\partial x = - v^2/2b_2b_1{}^2x^3 \quad . \quad . \quad . \quad . \quad (62)$$

The frontal edge of the adsorption band is schematically represented by Fig. 5.

The theory was worked out at first to explain certain preliminary results in chromatographic experiments obtained by Weil-Malherbe. There can be no doubt that the assumption of a complete and instantaneous equilibrium and of the absence of all other factors, such as finite rate of adsorption and desorption, hydrodynamic effects, etc., is never completely fulfilled in practice. However, in this treatment only a minimum number of assumptions is necessary and it is of interest to see how far this simple theory does represent the experimental facts. This experimental test is communicated in the following paper.

FIG. 5.
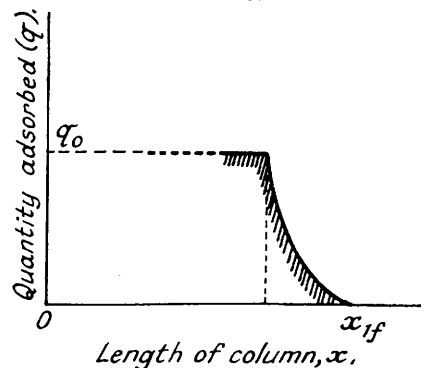
Schematical representation of the "diffuse" frontal edge of an adsorption band for certain non-equilibrium conditions.

Appendix.

(1) *Formation of the Chromatogram.*—For equation (5) we have initially

$$\left.\begin{array}{ll} c(x, 0) = 0 & . \quad . \quad . \quad . \quad . \quad x > 0 \ (v = 0) \\ c(0, v) = c_0 & . \quad . \quad . \quad . \quad . \quad v > 0 \ (x = 0) \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (A1)$$

Hence, denoting $v - xA\mathrm{f}'(c)$ by ξ, the function $\phi(\xi)$ is defined by

$$\phi(\xi) = \begin{cases} 0 & . \quad . \quad . \quad . \quad . \quad \xi < 0 \\ c_0 & . \quad . \quad . \quad . \quad . \quad \xi > 0 \end{cases} \quad . \quad . \quad . \quad . \quad . \quad (A2)$$

Now $\xi < 0$ if $v - xAf'(0) < 0$, i.e.,

$$v < xAf'(0) \qquad \qquad \qquad \text{(A3)}$$

and,$\xi > 0$ if $v - xAf'(c_0) > 0$, i.e.,

$$v > xAf'(c_0) \qquad \qquad \qquad \text{(A4)}$$

We shall suppose (as is actually the case) that $f'(c)$ is a decreasing function of c, i.e., the amount of adsorbed matter increases with c, but the rate of increase decreases with c. Now since $f'(c)$ is decreasing :

$$\left. \begin{array}{l} f'(c_0) < f'(0) \\ xAf'(0) > xAf'(c_0) \end{array} \right\} \qquad \qquad \text{(A5)}$$

and so there is a range of values of v in which both inequalities (A3) and (A4) are satisfied. We infer that for a given value of $v = v_0$

$$c = c_0 \text{ for } x \leqslant x_0$$

and

$$c = 0 \text{ for } x > x_0$$

where x_0 satisfies the inequality

$$v_0/Af'(0) \leqslant x_0 \leqslant v_0/Af'(c_0) \qquad \qquad \text{(A6)}$$

To determine x_0 we must have additional information; this is provided by the fact that the total amount of matter adsorbed is $c_0 v_0 = x_0 Af(c_0)$, i.e., the width of the band is

$$x_0 = c_0 v_0/Af(c_0) = l \qquad \qquad \text{(A7)}$$

The solution is, therefore

$$c(x, v) = \begin{cases} c_0 & \qquad x \leqslant c_0 v_0/Af(c_0) \text{ or } v_0 \geqslant xAf(c_0)/c_0 \\ 0 & \qquad x > c_0 v_0/Af(c_0) \text{ or } v_0 < xAf(c_0)/c_0 \end{cases} \Bigg\} \qquad \text{(A8)}$$

We have also

$$q(x, v) = \begin{cases} Af(c_0) & \qquad v_0 \geqslant xAf(c_0)/c_0 \\ 0 & \qquad v_0 < xAf(c_0)/c_0 \end{cases} \Bigg\} \qquad \text{(A9)}$$

(ii) *Development of the Chromatogram with a Solvent.*—Since equations (1) and (2) remain true, the solution is again given by equation (5) with, of course, a different function $\phi(\xi)$. Let us suppose that initially

$$q_0(x, v) = \begin{cases} Af(c_0), & \qquad x < l \qquad \text{i.e., for } 0 \leqslant x \leqslant l \\ 0, & \qquad x > l \end{cases}$$

i.e., the adsorption column has a band of uniformly adsorbed matter $[q_0 = Af(c_0)$ per unit length] of width l; $c(0, v) = 0$ for all values of $v > 0$; therefore $\phi(v) = 0$, $v > 0$, where $\phi(\xi)$ is defined by

$$\phi(\xi) = \begin{cases} 0 & \qquad \xi > 0 \\ c_0 & \qquad -lAf'(0) < \xi < 0 \\ 0 & \qquad \xi < -lAf'(c_0) \end{cases} \qquad \text{(A10)}$$

Now $\xi > 0$ if $v - xAf'(0) > 0$, i.e.,

$$v > xAf'(0) \qquad \qquad \qquad \text{(A11)}$$

and $\xi < 0$ if $v - xAf'(c_0) < 0$, i.e.,

$$v < xAf'(c_0) \qquad \qquad \qquad \text{(A12)}$$

but again $f'(0) > f'(c_0)$, and so there is a gap, $xAf'(c_0) < v < xAf'(0)$, in which the function $\phi(\xi)$ is not defined. This is due to our taking a discontinuous function for $\phi(\xi)$ and can be overcome by taking a $\phi(\xi)$ which is continuous at $\xi = 0$. From a physical point of view it is obvious that a discontinuous solution is impossible as there exist in any case certain phenomena (diffusion and convection processes, etc.) which will remove the discontinuity. For our purposes we can avoid the discontinuity by approximating the function in the region (2δ) between the two discontinuous solutions by a linear function, e.g., by the straight line $\phi(\xi) = R_0 \xi + \frac{1}{2}c_0$. We then obtain

$$\phi(\xi) = \begin{cases} 0 & \qquad \xi \geqslant \delta > 0 \\ R_0 \xi + \frac{1}{2}c_0 & \qquad -\delta \leqslant \xi \leqslant \delta, \ R_0 = -c_0/2\delta \\ c_0 & \qquad -lAf'(c_0) < \xi \leqslant -\delta \\ 0 & \qquad \xi < -lAf'(0) \end{cases} \Bigg\} \qquad \text{(A13)}$$

We can take the region δ as small as we please, so R_0 can be taken as large as we please. From the first equality we get

$$c(x, v) = 0 \text{ if } v > xAf'(0) + \delta \qquad \qquad \text{(A14)}$$

From the second equality

$$c(x, v) = R_0\{v - xAf'(c)\} + \frac{1}{2}c_0 \qquad \qquad \text{(A15)}$$

which is an equation for c. Dividing by R_0, we get $xAf'(c) = v + c_0/2R_0 - c/R_0$, where R_0 may be taken as large as we please. In the limit the terms with R_0 disappear and we get the solution

$$Af'(c) = v/x \qquad \qquad \qquad \text{(A16)}$$

where $0 \leqslant c \leqslant c_0$. As δ is arbitrary, equation (A16) holds for

$$Af'(c_0) \leqslant v/x \leqslant Af'(0) \qquad \qquad \text{(A17)}$$

The third equality gives

$$c = c_0 \text{ for } \beta \ll v/x \ll A\mathrm{f}'(c_0) \qquad \text{(A18)}$$

and the fourth equality

$$c = 0 \text{ for } v/x < \beta \qquad \text{(A19)}$$

The lower edge moves down at the same rate as before (as long as there is still some of the original band left), given by

$$v/\beta = vc_0/A\mathrm{f}(c_0) + l(= x_3) \qquad \text{(A20)}$$

which also defines the value of β introduced in (A18).