Turbulence and diffusion in the lower atmosphere

which is in excellent agreement with the value of the mean moisture content at Kew Observatory given by Bilham.

I should like to express my thanks to Mr E. Gold for his encouraging interest in this work and to acknowledge my debt to the late Dr F. J. W. Whipple for his help with §3 of this paper.

References

Bilham 1938 Climate of the British Isles.
Brunt 1939 Physical and dynamical meteorology, 2nd ed.
Carruthers 1943 Quart. J.R. Met. Soc. 69, 289.
Ertel 1933 Met. Z. 50, 386.
Goldstén 1938 Modern developments in fluid dynamics.
Sverdrup 1936 Geofys. Publ. 11, no. 7.

Contributions to the theory of chromatography

By E. Glückauf

(Communicated by E. J. Bowen, M.A., F.R.S.—Received 6 June 1945)

A complete analysis has been given of the process of chromatographic separation for two solutes, the adsorption of which follows a Langmuir isotherm. Development of the bands, both with pure solvent and with a solvent containing another solute, has been discussed. Very simple conditions were found to hold for both the volume of solvent and the amount of adsorbent required for complete separation of the two solutes. Provided that the concentrations used are not too low—which is unfavourable—the influence of the initial concentrations is very small. For substances difficult to separate, the minimum amount of adsorbent \( X_0 \) (in g.) is proportional to the quantities to be separated \((m_1 + m_2)\) (in mol.), and inversely to the saturation capacity of the adsorbent \((1/\beta)\) (in mol./g. adsorbent) and to the square of the relative difference of the adsorption coefficients \((a_1, a_2)\) of the solutes

\[
X_0 \approx \frac{\beta(m_1 + m_2)}{(a_2/a_1 - 1)^2}.
\]

The accurate equations are given in the paper.

The main contributions to the theory of chromatography have been made by Wilson (1940), by de Vault (1943) and by Weiss (1943).

Wilson was the first to develop the differential equations governing the process of chromatography, but, as both de Vault and Weiss have shown, these equations are capable of more than one solution. The solution found by Wilson gives correct results only, when the adsorbed amount is strictly proportional to the concentration of solute in the solvent.
Weiss has shown how the properties and positions of a band of a single solute change with progressing chromatographic development, but the case of two or more solutes has so far not been treated beyond the stage of the differential equations. Wilson's deductions have left the impression that the length of column and the amount of pure solvent required for the separation of two substances are inversely proportional to \((a_2 - a_1)/a_1\), where \(a_2\) and \(a_1\) are the adsorption coefficients of the two solutes \((a_2 > a_1)\). As will be shown in this paper this result is by far too optimistic, especially in cases where the differences of adsorption intensities are only slight.

In the following discussion the adsorption isotherms have been assumed to be of the Langmuir type, which is the only isotherm showing the mutual influence of the concentrations on the adsorption isotherms of the components of the system. During formation and development of the bands, the equations of motion for the different parts of the bands have often a form similar to those given by Weiss for a single solute, and frequent comparison will be made with his equations (marked W.). In the following, the subscripts 1 and 2 mark the two bands to be separated while the superscript 0 refers to the original concentrations; letter subscripts refer to the positions in the band as shown in the diagrams. It is assumed that the subscript 1 refers to the faster moving solute.

1. The case of two solutes separated by normal development

As in the case of a single solute, the bands formed originally are of constant intensity throughout, except where they overlap, and the rate of movement of the forward edge of the constant part is given by

\[
x_u = (v + v^0) : c_2^0/(f_2(c_1 c_2) + \alpha c_2^0)
\]

(see figure 1b, also compare with equation W. (11) and de Vault, equation 9), where \(x\) is the distance of the particular point from the top of the column (best expressed in grams of adsorbent),

\(v^0\) is the original volume of solvent in which the solutes of concentration \(c_1^0\) and \(c_2^0\) were contained \((v^0\) in c.c.),

\(v\) is the amount of pure solvent used for developing the chromatogram (in c.c.),

\(c\) concentration of solute in mol./c.c.,

\(\alpha\) is the pore volume of the column per g. of adsorbent.

\(f_2(c_1 c_2) = q_2\) is the equilibrium amount of substance 2 as function of the concentrations \(c_1\) and \(c_2\), adsorbed on a gram of adsorbing material \((q\) in mol./g.).

\((f_2(c_1 c_2) + \alpha c_2)\) thus represents the amount of solute II contained in the space filled by 1 g. of adsorbent, if the local concentrations of solutes in the solvent are \(c_1\) and \(c_2\). The corresponding amount of solute I is \((f_1(c_1 c_2) + \alpha c_1)\). When the development proceeds, regions of varying concentration appear in the chromatogram, as in the case of a single solute. In these regions, the movement of any points of given concentrations proceeds according to

\[
x = v/((\alpha + f_1'(c_1 c_2)) \cdot v/((\alpha + f_2'(c_1 c_2))
\]
where \( f_{1(c_0,c_2)} = dq_1/dc_1 \) and vice versa. * De Vault (1943, equations 19, 20 and 23) has shown that equation (2) results directly from the consideration that the difference between the amounts of solutes entering and leaving a small section of the column must necessarily find their balance in the change of the amount of solutes contained in that section. As pointed out by de Vault, it is not possible to write down a simple solution for the case of multiple solutes, as the dependence of \( c_1 \) and \( c_2 \) can normally not be expressed in general terms. However, equations (1) and (2), together with the Langmuir adsorption isotherms (3, 4) of the two substances, permit of a general solution of all questions affecting the development of the chromatogram. Other isotherms, e.g. that of Freundlich, are quite unsuitable, because the mutual influence of two solvents cannot be formally expressed.

The Langmuir adsorption isotherms in the case of two solutes are

\[
\begin{align*}
\frac{c_1}{c_0} &= \frac{a_1 c_1}{1 + a_1 \beta_1 c_1 + a_2 \beta_2 c_2}, \\
\frac{c_2}{c_0} &= \frac{a_2 c_2}{1 + a_1 \beta_1 c_1 + a_2 \beta_2 c_2},
\end{align*}
\]

where \( a = \) adsorption coefficients (dimension c.c./g. adsorbent) \( a_2 > a_1 \),

\( \beta = \) mol. capacity, i.e. the amount of adsorbent required by 1 mol. of substance if fully covering the adsorbing surface in a mono-molecular layer (dimension g./mol.). For simplicity use is also made of the letters,

\[
\begin{align*}
b &= a \beta, \\
\delta &= (a_2 - a_1)/a_1.
\end{align*}
\]

It follows from equations (3) and (4) that

\[
\begin{align*}
f_{1(c_0,c_2)}' &= a_1 (1 + b_2 c_2 - b_2 c_1 . dc_2/dc_1)/(1 + b_1 c_1 + b_2 c_2)^2, \\
\end{align*}
\]

\[
\begin{align*}
f_{2(c_0,c_2)}' &= a_2 (1 + b_1 c_1 - b_1 c_2 . dc_1/dc_2)/(1 + b_1 c_1 + b_2 c_2)^2.
\end{align*}
\]

From the equality of \( f_1' \) and \( f_2' \) (see equation (2)) at any given point or stage of the chromatogram it is possible to calculate the relation which must exist between any two coexistent concentrations of the two solutes.

Equating (3a) and (4a) results in the differential equation

\[
a_2 - a_1 + a_2 b_1 c_1 - a_1 b_2 c_2 + a_1 b_2 c_2 . dc_2/dc_1 - a_2 b_1 c_2 . dc_1/dc_2 = 0,
\]

the only general solution of which is

\[
a_2 b_1 c_1 = a_1 b_2 c_2 \lambda - (a_2 - a_1) \lambda/(1 + \lambda),
\]

where \( \lambda \) is an integration constant which can be calculated from the boundary conditions applying, e.g.

\[
c_1 = c_1^0, \quad \text{when} \quad c_2 = c_2^0.
\]

* \( f'_{(.-.-)} \) always stands for the complete differential \( df_{(c_1,c_2)}/dc_2 \), the contents of the bracket indicating the values of \( c_1 \) and \( c_2 \) if these are defined; e.g. \( f'_{0(c_1,c_2)} = [df_{0(c_1,c_2)}/dc_2]_{c_1 = 0, c_2 = c_2^0} \). If one of the concentrations is omitted, e.g. \( f'_{(c_1)} \), this means that the missing concentration is zero throughout, thus: \( f_{(c_1)} = [df_{(c_1,c_2)}/dc_2]_{c_1 = 0, c_2 = c_2^0} \). The same applies to the \( f'_{(.-.-)} \)-functions.
which applies to the development of the chromatogram from its beginning if the same solvent is used. Equation (6) is linear for $c_1$ and $c_2$ but quadratic for $\lambda$:

$$\lambda^2 + \lambda \left(1 - a_2 b_1 c_1^0/a_1 b_2 c_2^0 - (a_2 - a_1)/a_1 b_2 c_2^0\right) - a_2 b_1 c_1^0/a_1 b_2 c_2^0 = 0. \quad (8)$$

The positive root $\lambda_1$ (or shortly $\lambda$) of equation (8) is shown in figure 2 as function of $a_2 b_1 c_1^0/a_1 b_2 c_2^0$ and of $\delta/b_2 c_2^0$, and $\lambda_1$ applies to all cases where $dc_1/dc_2$ is positive. The negative root ($\lambda_2$) can be used only for a single point at the frontal edge of the

\[\text{Figure 1a. } v_0 = 100 \text{ c.c., } v = 0.\]

\[\text{Figure 1b. } v = 30 \text{ c.c.}\]

\[\text{Figure 1c. } v_{du} = 57 \text{ c.c.}\]
Contributions to the theory of chromatography

Figure 1d. \( v = 100 \text{ c.c.} \)

Figure 1e. \( V = 174 \text{ c.c.} \)

Figure 1a–e. Development with pure solvent of a band of two solutes \((\delta = 1)\). (a) Band before development. (b) Initial development; original concentrations still preserved in the forward part of the band. (c) Mixed band fully developed, but separated part of band \(I\) still has its original concentration. (d) Further development and spreading of the bands. (e) Separation completed; development of band \(I\) is also completed. Apparent equality of \(q_{1w}\) and \(q_{1s}\) is only a coincidence.

slower band II because, as shown by de Vault, the general solution for the front boundary of the differential equations on which equation (2) is based is unsuitable for this type of adsorption isotherm and has to be replaced by a discontinuity. \(\lambda_2\) does, however, represent correctly the sudden change of \(c_1\) at this discontinuity. No table is given for \(\lambda_2\), as its values follow directly from \(\lambda_1\) and equation (8) as

\[
\lambda_1\lambda_2 = -a_2b_1c_1/a_1b_2c_2.
\]  

It can be seen from figure 2 that for substances very difficult to separate \((\delta \ll 1)\), \(\lambda_1\) is approximately \(c_1^0/e_2^0\), (usually \(\beta_1 = \beta_2\)), while in the event that \(\delta\) is large or \(c_2^0\) is very small, \(\lambda_1 = \delta/b_2c_2^0\). The conditions in the variable parts of the chromatogram can now be given as functions of \(v, x\) and \(c_1\) or \(c_2\) by substituting the differentials and one of the variable concentrations of \((3a)\) and \((4a)\) from equation (6) and using the \(f'\)-functions in equation (2). If \(x\) is neglected, this results in

\[
x = v(1 + B_1c_1)^2/A_1 = v/F'_1(c_1),
\]  

\[
x = v(1 + B_2c_2)^2/A_2 = v/F'_2(c_2)
\]
(compare equation W. (26) for single solute), where

\[ A_1 = \frac{a_1(1 + \lambda)}{1 + \lambda + \delta}, \]
\[ B_1 = \frac{b_1(1 + \lambda)}{\lambda}, \]
\[ A_2 = \frac{a_2(1 + \delta)(1 + \lambda)}{1 + \lambda + \delta}, \]
\[ B_2 = \frac{b_2(1 + \lambda)}{1 + \lambda}. \]

It can be shown easily that the equations (10) and (11) fulfil the fundamental equations for mass conservation (see de Vault equation (19))

\[ \frac{\delta c_i}{\delta x} + \frac{\delta q_i}{\delta v} = 0. \]

2. Formation of Band

If an amount \( v^0 \) of a solvent containing two solutes I and II of the concentrations \( c_1^0 \) and \( c_2^0 \) (where the adsorption intensities are \( a_2 > a_1 \)) is poured on to the chromatographic column, the initial band has the form as shown, e.g. in figure 1a. The pro-
properties of this band with the exception of \( c_{1y} \) can be derived immediately from equations (1), (3) and (4):

\[
x_u = b_2^0 = v_0 c_2^0 (2 \sigma_2^0/2 \sigma_1^0 e_2^0) = v_0 (1 + b_1 c_1^0 + b_2 c_2^0) / a_2.
\]

(12)

\[
q_1^0 = f_1 (e_1 c_1^0) = a_1 c_1^0 / (1 + b_1 c_1^0 + b_2 c_2^0),
\]

\[
q_2^0 = f_2 (e_2 c_2^0) = a_2 c_2^0 / (1 + b_1 c_1^0 + b_2 c_2^0).
\]

(13a, b)

If \( m_1 \) and \( m_2 \) are the total quantities of the solutes (in mol.), the amount of solute I within the length \( l_2 \) is

\[
m_{1,0-u} = m_2 q_1^0 / q_2^0 = m_1 a_1 / a_2.
\]

(14)

while the amount of solute I separated off already during band formation is

\[
m_{1,u-y} = m_1 (a_2 - a_1) / a_2.
\]

(14a)

As predicted already by de Vault the concentration of the less adsorbed solute (I) rises sharply at the discontinuity at \( x_u \) to a value which follows from equation (6) for \( c_2 = 0 \)

\[
c_{1y} = -(a_2 - a_1) \lambda_2 / a_2 (1 + \lambda_2).
\]

(15)

Replacing \( \lambda_2 \) from equation (9) and then \( c_2 \) by means of equation (6), this leads to

\[
c_{1y} = c_1^0 (1 + \lambda_1) / \lambda_1.
\]

(15a)

As can be seen from figure 2, \( c_{1y} \) must have values between \( c_1^0 \) and \( (c_1^0 + c_2^0) \). It also follows from equation (3) that

\[
q_{1y} = a_1 c_{1y} / (1 + b_1 c_{1y}),
\]

(16)

and from equation (1) applied to this case, that the position of the forward edge is

\[
x_y = v_0 (1 + b_1 c_{1y}) / a_1.
\]

(17)

3. Development of the chromatogram

If, after formation of the original chromatogram, a further amount \( v \) of solvent is poured on the column, the bands, dissolving from the top end and travelling down the column, undergo certain changes, some of which are similar to those occurring with a single solute (see figure 1b–d). The first stage in the development is shown in figure 1b. The concentrations in the most forward parts of the column remain unchanged; then follows a part in which both concentrations decrease, the less adsorbed one decreasing to zero; then comes a constant region of pure substance II, followed by a variable region in which this concentration, too, diminishes to zero. Figure 1c shows the end of the first stage, with band II completely developed.

The concentration of the constant region of pure substance II follows directly from equation (6) for \( c_1 = 0 \):

\[
c_{20} = \delta / b_2 (1 + \lambda).
\]

(18)
The other conditions are

\[ x_a = v/\int_{x_2 o}^{x_0} = v/a_2 \quad \text{(see equation W. (23))}, \]

\[ x_b = v/\int_{x_2 o}^{x_0} = v(1 + b_c x_2 o)/a_2 \quad \text{(see equation W. (24))}, \]

\[ x_o = v/F_1(0), \quad \text{(see equation 10)} \]

\[ x_d = v/F_1(x_2 o) = v/F_2(x_2 o), \quad \text{(see equations 10, 11)} \]

\[ x_u = (v + v^0) c_1(x_2 o) = (v + v^0) (1 + b_1 c_1 x_2 o)/a_2, \]

\[ x_y = (v + v^0) c_1 = (v + v^0) (1 + b_1 c_1 x_2 o)/a_1. \]

It is worth while noting that \( x_b \) can never catch up with \( x_o \), as \( x_o/x_b = 1 + \frac{\delta}{1 + \lambda + \delta} \).

It is also interesting that the pure tail fraction between \( x_a \) and \( x_o \) contains the same amount of material, as if the curve of the variable part between \( x_d \) and \( x_o \) would take its uninterrupted course.

The content of the pure tail fraction \( m_2(a-o) \) at any stage of the separation process follows from a very simple consideration:

If the separated band containing \( m_2(a-o) \) were not constantly fed from the tail end of the mixed band, its forward edge would travel at the rate

\[ \frac{\Delta x_{2 o}}{\Delta v} = \frac{c_2 o}{\alpha x_{2 o} + f_{2 o, c_2 o}} \quad \text{(see equation (1))}. \]

Actually \( x_{2 o} \) travels according to

\[ \frac{\Delta x_{2 o}}{\Delta v} = \frac{1}{\alpha + f_{1 o, c_2 o}} \quad \text{(see equation (2) or (21))}. \]

In order to maintain a continuous chromatogram, the amount of solute II introduced by feeding from the mixed band must be

\[ m_2 = (\Delta x_{2 o} - \Delta x_{2 o}) (\alpha x_{2 o} + f_{2 o, c_2 o}), \]

from which follows

\[ m_2(a-o) = \frac{f_{2 o, c_2 o} - c_2 o f_{1 o, c_2 o}}{\alpha + f_{1 o, c_2 o}} v. \]

Neglecting \( \alpha \) and introducing \( c_2 o \) from equation (18) leads to the very simple condition

\[ m_2(a-o) = v c_2 o v^2/b_2 (1 + \lambda). \]

The effect of this equation on the question of complete separation will be shown later.

The contents of the pure head fraction at this stage, i.e. as long as its concentration is constant, is

\[ m_{1, u-y} = (v + v^0) c_1(a_2 - a_1)/a_2. \]

These conditions persist until \( x_d \) overtakes \( x_u \), when development of band II is complete (see figure 1c). This stage is reached when an amount \( v_{du} \) of solvent has been used, which can be obtained by equating equations (22a) and (23):

\[ v_{du} = v^0/b_2 c_2 o (1 + \lambda) = m_2/b_2 (c_2 o)^2 (1 + \lambda). \]
After band II has been fully developed, its frontal concentration $c_{2w}$ (see figure 1d) starts to decrease according to

$$c_{2w} = \sqrt{(m_2/B_2)v} = \sqrt{(m_2/b_2 v(1+\lambda))}$$

in complete analogy to the conditions of a single solute (see equation W. 32). The movement of the frontal edge of band II is given by

$$\sqrt{x_w} = \sqrt{(v/A_2)} + \sqrt{(m_2 B_2/A_2)}$$

(compare equation W. (31)).

The concentration of band I at the forward edge of band II ($c_{1w}$) follows from equations (28) and (6):

$$c_{1w} = \lambda(a_1 b_2/a_2 b_1)\sqrt{(m_2/b_2 v(1+\lambda))} - \lambda(a_2-a_1)/a_2 b_1(1+\lambda).$$

The concentration $c_{1w}'$ at the other side of the discontinuity also follows from equation (6) for $c_{2w} = 0$:

$$c_{1w}' = -\lambda_2'(a_2-a_1)/(1+\lambda_2') a_2 b_1.$$

The boundary condition for determining the integration constant $\lambda_2'$ is in this case no longer $c_1 = c_1^0$ when $c_2 = c_2^0$, but $c_1 = c_{1w}$ when $c_2 = c_{2w}$. This gives the same value of $\lambda_1$, but we obtain now

$$\lambda_2' = -a_2 b_1 c_{1w}/a_1 b_2 c_{2w}.$$

Substituting $\lambda_2'$ into equation (31) results in

$$c_{1w}' = c_{1w}(1+\lambda_1)/\lambda_1.$$

After band II has been fully developed, the head fraction of pure solute I, too, undergoes development. Being a pure solute, a point of given concentration $c_1$ moves forward according to

$$dx = A v(1+b_1 c_1)^2/a_1$$

(see equation (2)), and the boundary conditions are that this movement starts at a point where $c_1 = c_{1w}'$, which occurs according to equation (33) and (30) at

$$v_w = a_1^2 b_2 m_2(1+\lambda)/(a_2 b_1 c_{1w}' + a_2 - a_1)^2$$

and

$$x_w = v(1+b_1 c_{1w}' )^2/A_1,$$

which latter can be shown to be the locus of all points $c_{1w}'$. Combining equations (30), (34), (35) and (36) one obtains for the movement of points between $x_w$ and $x_z$ (where $x_z$ is the most forward part of the head fraction, which has been reached by the development)

$$x = (v-v_w)(1+b_1 c_1)^2/a_1 + x_w,$$

$$x = v(1+b_1 c_1)^2/a_1 + \delta m_2 b_2(1+b_1 c_1)^2/a_1(\delta+b_2 c_1)^2.$$
While equation (37) permits of the calculation of \( c_1 \) at any given \( x \) and \( v \), it seems no longer possible to obtain a simple equation for the end-point \( x_e \) and the frontal concentration \( c_{1_2} \), though these facts are well defined by the condition of mass conservation

\[
\int_{x_1}^{x_2} q_1 \, dx + \int_{x_{1_2}}^{x_2} q_1 \, dx = m_1,
\]

and thus can be constructed in any given numerical case (as has been done in figure 1e).

In some instances, e.g. when only partial separation is required, it may be desirable to know the amount of solute in a particular region for the mixed band.

The amount of solute I between \( x_p \) and \( x_q \) is

\[
m_{1(p-q)} = \int_{x_p}^{x_q} a_1 c/(1 + b_1 c_1 + b_2 c_2) \, dc.
\]

Replacing \( c_2 \) from equation (6) and \( dc_1 \) by \( dx \) from equation (10) this leads to

\[
m_{1(p-q)} = 2vB_1 \int_{x_p}^{x_q} c_1 \, dc_1 = B_1 v(c_{1q}^2 - c_{1p}^2).
\]

Similarly,

\[
m_{2(p-q)} = B_2 v(c_{2q}^2 - c_{2p}^2).
\]

4. Complete separation

Development continues to proceed until the bands separate whereby the frontal concentration in band I becomes continually smaller. The stage of complete separation can be obtained from a number of previous equations, e.g.

(1) from equation (25) by making \( m_{2, a=0} = m_2 \),

(2) by equating \( x_o \) (see equation (21)) and \( x_w \) (see equation (29)),

(3) by making \( c_{1w} \) (equation (30)) or \( c'_{1w} \) (equation (33)) zero.

The result is in all cases that the volume \( V \) required for complete separation is

\[
V = m_2 b_2(1 + \lambda)/\delta^2.
\]

The point of separation of the two bands has a distance from the top of the column which is given by

\[
X_o = V/A_1 = m_2 b_2(1 + \lambda + \delta)/a_1 \delta^2.
\]

The tail end of band II is at

\[
X_a = V/a_2 = m_2 b_2(1 + \lambda)/a_2 \delta^2.
\]

The length of band II at the time of separation is thus

\[
L_2 = m_2 b_2(2 + \lambda + \delta)/a_2 \delta.
\]

In the case of extreme dilution, when \( \delta/b_2 c_2^o \gg 1 \), \( \lambda \) approximately equals \( \delta/b_2 c_2^o \), and we obtain

\[
V = m_2/\delta c_2^o = v^o/\delta,
\]

and, assuming that \( \delta < 1 \),
The length of band II at the point of separation is then

\[ L_2 = m_2/a_2 c_2^0 = 1^2/2, \]

i.e. it has remained unchanged. These are the equations obtained by Wilson (1941) for non-developing bands. At the same time, it can be seen from equations (40)–(42) that this is the most unfavourable condition for a chromatographic separation, as it requires an unnecessarily large amount of both solvent and adsorbent.

The most favourable conditions obviously occur when \( \lambda \) is small. The smallest values of \( \lambda \) usually occur when \( \delta/b_2 c_2^0 < 1 \), i.e. at moderately high adsorption intensities.* As can be seen from table 2, optimum conditions can be defined as

\[ b_2 c_2^0 > \delta \sqrt{(10 c_2^0/c_1^0)} \quad \text{or} \quad b_2 \sqrt{(c_1^0/c_2^0)} > 3\delta, \]

which condition obtains below the dotted line in figure 2.

Under these optimum conditions, where \( \lambda = \text{approx.} \ m_1/m_2 \), equations (40) and (41) change into

\[ V = b_2(m_1 + m_2)/\delta^2, \]

and

\[ X_0 = \beta(m_1 + m_2)(1 + \delta)/\delta^2 \]

which means that within this region both the amount of solvent and the weight of adsorbent required for the complete separation are independent of the original concentrations used, and depend only on the total quantity of solutes to be separated.

In this connexion it may be noted that \( X_0 \) is the necessary amount of adsorbent in the chromatographic tube up to the point of separation and that consequently, as long as the effect of diffusion is neglected, a short column of large diameter will serve equally well as a long and narrow one.

5. Pore space of the adsorbent

In most of the preceding calculations the question of pore space has not been considered for reasons of simplicity. It may, however, be worth while to consider its effect on the volume of solvent and the length of column required for complete separation. It follows from equation (25) that

\[ V_a = m_2(\alpha + f'_1(0,c_2)/f_2(0,c_3) - c_2, f'_1(0,c_2)); \]

eliminating \( c_2 \), this results in

\[ V_a = V \left( \alpha(1 + \lambda + \delta) \right) \]

Further, it follows from equations (44) and (2) that

\[ X_a = m_2(f_2(0,c_2) - c_2, f'_1(0,c_2)) = X_0. \]

This shows that while a correction is required for the volume of solvent, the amount of adsorbent is not influenced by the pore space of the chromatographic column.

* According to the theoretical interpretation of the Langmuir equation, \( b_2 c_2 \) represents the ratio of active surface covered by solute II to surface not covered by this solute.
6. Development with a solvent containing another solute

A. Development of band of single solute

The subscript 3 is used here for the properties of the developing solute, and the index 2 for the band. According to the concentrations employed and to the adsorption intensities involved, different conditions arise as regards the effect of the developing solute.

Case 1.

\[ f'_{2(0)} \leq f_{3(c_3^0)} \quad \text{or} \quad \alpha_2 \leq \alpha_3/(1 + b_3 c_3^0). \]

In this case the developing solution acts like a pure solvent, as all the solute III is adsorbed before it makes contact with band II. This is obvious, as the forward edge of solute III advances according to

\[ x = v c_3^0 f_{3(c_3^0)} \]

while the rear of band II progresses with

\[ x = v f'_{2(0)}. \]

Case 2.

\[ f_{3(c_3^0)} / c_3^0 \leq f'_{2(0)} \leq f_{3(c_3^0)} \quad \text{or} \quad a_3/(1 + b_3 c_3^0) < \alpha_2 \leq \alpha_3. \]

In this case, band II undergoes only partial development (see figure 3a). The concentration \( c_{2o} \) is given by the condition

\[ f_{3(c_3^0)} / c_3^0 = f_{2(c_2^0)} / c_{2o}, \]

in the case of the Langmuir isotherm by

\[ c_{2o} = c_3^0 \alpha_2 b_3 / \alpha_3 b_2 + (\alpha_2 - \alpha_3) / \alpha_3 b_2. \]

With progressing development band II eventually assumes the form shown by the dotted line. This condition also applies, if \( c_2^0 < c_{2o} \). In this case a discontinuous development results (see figure 3b) which, after completion, leaves band II in the form shown by the dotted line. Once the development of band II has been completed, no further change in the length or concentration of band II occurs.

Figure 3a, b. Development of a band containing one solute with a solvent containing a solute which is more strongly adsorbed. (a) Small concentration of developing solute. (b) Large concentration of developing solute.
Case 3. \( f'(0) > f'(0) \) or \( a_2 > a_3 \).

In this case development results in the formation of a mixed band of variable concentration, the conditions of which can only be calculated for the Langmuir equation.

In the variable part equations (2)-(6) apply again, but the boundary condition for the determination of \( \lambda \) is in this case

\[
c_2 = 0 \quad \text{when} \quad c_3 = c_3^0.
\]

By applying this condition to equation (6),

\[
\lambda = \frac{-a_2 b_3 c_3^0}{a_2 - a_3 + a_2 b_3 c_3^0}.
\]

Thus

\[
c_3 = c_3^0 \left(1 - \frac{a_2 b_3 c_2}{a_2 - a_3 + a_2 b_3 c_3^0}\right).
\]

The conditions in the variable part can now be given as functions of \( v \), \( x \) and \( c_2 \), by substituting \( c_3 \) in the equation of the type (4a) from equation (50), and by using the \( f' \)-function in equation (2). This results in

\[
x = v(1 + B_2 c_2^0)^2/A_2,
\]

where

\[
A_2 = a_2/(1 + b_3 c_3^0) \quad \text{(51a)}
\]

and

\[
B_2 = b_3(a_2 - a_3)/(a_2 - a_3 + a_2 b_3 c_3^0). \quad \text{(51b)}
\]

**Figure 4a.** \( v_0 = 200, v = 0 \).

**Figure 4b.** \( v = 50 \).

**Figure 4c.** \( v = 200 \).

**Figure 4d.** \( v = 600 \).

**Figure 4a–d.** Development of a band containing one solute with a solvent containing a solute which is less adsorbed. (a) Band before development. (b) Initial development, beginning with the compression of the band (if \( q_3^0 \) is large enough). (c) Compression completed, development not quite finished. (d) Development of band completed; solute III has overtaken band II.
The various conditions which arise during development are shown in figure 4a–d. Eventually band III completely envelopes band II, its frontal concentration being $c_3$. Band II continues to develop according to equation (51) and it is of interest to note that the spreading of the band after travelling a given distance $x$ is considerably smaller than it would have been, if pure solvent had been used.

B. Development of a band of two solutes

The indices of the two solutes are chosen so that the faster moving solute has the index 1 and the slower one the index 2. As before, the developing solute has the index 3.

Again we have several cases:

Case 1. $f'(1(0) < f_2(0) \leq f_3(c_2)/c_3$, where the solute III has no influence on the separation.

Case 2. $f'(1(0) < f_3(c_2)/c_3 < f_2(0) < f_3'(0)$, where the solute III has only little influence on the separation.

Case 3. $f_3(c_2)/c_3 < f'(1(0) < f_2(0) < f_3'(0)$ and

Case 4. $f'(2(0) < f_1(0) < f_3(0)$.

Both cases 3 and 4 will be discussed in detail.

Case 3

Only the case will be dealt with, where solute III is present in sufficiently high concentration to result in a development corresponding to that in figure 3b, as this appears to be of more practical importance.

During the development the band passes through the stages shown in figure 5a–d. The original band (figure 5a) is compressed during the development to concentrations which are determined by the concentration of the developing solute. At the same time the process of separation starts, so that a moderately complicated system (figure 5b) results, which persists until the original concentrations $c_1$, $c_2$, and $c_3$ have disappeared (figure 5c). Thereafter the separation continues until it is complete (figure 5d).

Apart from the initial compression development, it will be noticed that conditions here are similar to those considered by Wilson, as the concentrations of the bands remain constant during the whole process of separation.

The original concentrations $c_1$ and $c_2$ are in this case of no influence on the separation, as this depends only on the value of $c_3$ which itself depends on $c_3$. This also concerns the final concentrations $c_{2o}$ and $c_{1z}$, which, as the bands must be able to move with the same velocity as the forward edge of solute III, adjust themselves to concentrations which are determined by

$$\Delta x/\Delta v = c_3/\Delta y_2(0) = c_{2o}/c_{2o} = c_{1z}/c_{1z},$$

or, in the case of the Langmuir equation,

$$\Delta x/\Delta v = (1 + b_3 c_3)/a_3 = (1 + b_2 c_{2o})/a_2 = (1 + b_1 c_{1z})/a_1.$$
If the difference between the adsorption factors of the two solutes to be separated is only small, then—with negligible error—

\[ \frac{c_1^{0'}}{f_1(c_1^{0'}c_2^{0'},c_2^{0})} = \frac{c_2^{0'}}{f_2(c_1^{0'},c_2^{0})} \]  

(53)

and

\[ (1 + b_1 c_1^{0'} + b_2 c_2^{0'})/a_1 = (1 + b_0 c_2^{0})/a_0. \]  

(53a)

Figure 5a. \( v_0 = 100, v = 0 \).

Figure 5b. \( v = 50 \).

Figure 5c. \( v = 300 \).

Figure 5d. \( v = 550 \).

Figure 5a–d. Development of a band containing two solutes with a solvent containing a stronger adsorbed solute. (a) Band before development. (b) Compression of band and start of separation. (c) Compression completed; separation further advanced. (d) Separation completed. Both boundaries are sharp and the band has not spread.

Equation (53a), together with the condition

\[ \frac{c_1^{0'}}{c_2^{0'}} = \frac{c_1^{0}}{c_2^{0}} = m_1/m_2, \]  

(54)

results in

\[ c_2^{0'} = \frac{b_2 c_2^{0} - a_3 - a_1}{a_1} a_3 \]  

\[ b_1 m_1/m_2 + b_2. \]  

(55)*

* The correct deduction leads to a similar expression in which \( b_2 \) is replaced by \( b_2 \phi \), where \( \phi = a_1 b_1 c_{12}/(a_2 - a_1 + a_3 b_1 c_{12}) \) and where \( c_{12} \) can be replaced by \( c_2^{0} \) by means of equation (52a). If \( a_1 \) and \( a_3 \) differ only little, \( \phi \) is, under normal working conditions, almost unity.

Vol. 186. A.
The volume of solvent $V$ required for complete separation of the bands I and II is (see equation (25a))

$$V = \frac{m_2 a_1}{c_3^0 (a_2 - a_1)} = \frac{b_1 m_1 + a_1 b_2 m_2 \phi}{a_3 - a_1} \left( b_3 c_3^0 - \frac{a_3 - a_1}{a_1} \right).$$

(56)

The minimum amount of adsorbent required for a complete separation is then (see equation (2))

$$X_0 = \frac{V c_1^0}{f_1^{(e^0 c_1^0 + b_2 c_2^0)} / a_1.}$$

(57)

Again use may be made of the simplifying approximation (53a), leading to

$$X_0 = \frac{V (1 + b_3 c_3^0)}{a_3},$$

$$X_0 = \frac{a_2 - a_1}{a_1} \left( \frac{b_3 c_3^0 - \frac{a_3 - a_1}{a_1}}{a_1} \right).$$

(58)

A close scrutiny of the meaning of this equation shows that it is almost identical with Wilson's equation

$$X_0 = l_0 \frac{a_2 - a_1}{a_1},$$

only that in this case $l_0$ does not represent the length of the band after formation, but after compression in the course of development by the more strongly adsorbed solute III.

If the process of development is conducted with a sufficiently high concentration of the developing solute, i.e.:

$$1 \ll b_3 c_3^0 \gg (a_3 - a_1)/a_1,$$

equation (58) can be simplified into

$$X_0 = \frac{(b_1 m_1 + a_1 b_2 m_2 \phi)}{a_3 (1 + \phi)}.$$  

(59)

If one compares this with the value obtained for development with pure solvent

$$X_0 = \frac{(m_1 + m_2) b_2}{a_1 \delta^2} \quad \text{(see (41a))},$$

the advantage of developing with a solute is very obvious, if $\delta$ is very much smaller than unity. It must, however, be borne in mind that this method leads only to a separation into two adjoining, but not completely isolated bands, because, as has been pointed out, the final concentrations adjust themselves in such a way, that their speed of travel along the chromatographic column is equal. Complete separation into isolated bands can take place only when a method of development resulting in variable concentrations is employed.

**Case 4**

In this case development takes place similar to that produced by a pure solvent. But, as has been shown before in the case of a single solute, the developed band spreads very much less, especially if solute III is only slightly less adsorbed than the...
Contributions to the theory of chromatography

solute to be separated. In this case the amount of adsorbent required for complete separation may be only little more than that required in case 3, and it provides the possibility for the separation of the solutes I and II into completely isolated bands. As the eventually separated bands I and II will contain substantial amounts of solute III which has to be removed separately afterwards, it is obvious that this procedure only offers advantages for very difficult separations, or, if the substance III can be removed easily by a different process, e.g. by chemical separation or by chromatography with a different adsorbent.

As the general equations, even in the case of the Langmuir isotherm, are fairly cumbersome, a solution will be produced only for the case \((a_2 - a_1) / a_1 < 1\) and \(c_3 > c_1 + c_2\), which assumptions permit considerable simplifications. Equations which have been simplified in this way, will be marked with the letter ‘s’.

The fundamental equations governing the relations between coexisting concentrations of \(c_1\), \(c_2\) and \(c_3\) are again (see equation (2))

\[
v \frac{dx}{x} = f_1(c_1, c_2, c_3) = f_2(c_1, c_2, c_3) = f_3(c_1, c_2, c_3),
\]

where

\[
f_{i}(c_1, c_2, c_3) = a_1 c_1 / (1 + b_1 c_1 + b_2 c_2 + b_3 c_3)
\]

and vice versa. Complete differentiation results in the two equations

\[
\begin{align*}
\frac{dc_2}{dx} & = a_1 c_1 c_2 c_3 / (a_3 + a_2 b_3 c_2 c_3 - a_1 b_2 c_1 c_3) \frac{dc_3}{dx} \\
\frac{dc_3}{dx} & = a_3 c_1 c_2 c_3 / (a_2 - a_3 + a_1 b_3 c_1 c_3) \frac{dc_2}{dx}
\end{align*}
\]

The solutions of these differential equations are

\[
c_2 = \alpha c_1 + c_{20},
\]

and

\[
c_3 = \gamma c_1 + c_{30}.
\]

For indices see figure 6. The values of these four constants—\(\alpha, \gamma, c_{20}\), and \(c_{30}\)—can be calculated exactly from the two equations obtained by the substitution of \(c_2\) and \(c_3\) into equations (62) and (63) (which process removes \(c_1\) as well):

\[
\begin{align*}
a_1 (1 + b_2 c_{20} + b_3 c_{30}) & = a_2 (1 + b_2 c_{20} - b_1 c_{20} / \alpha - b_3 c_{20} / \gamma), \\
& = a_3 (1 + b_2 c_{20} - b_1 c_{30} / \gamma - b_2 c_{30} / \alpha)
\end{align*}
\]

(66)

(67)

together with the boundary conditions applied to equations (64) and (65):

\[
\begin{align*}
c_{2d} & = \alpha c_{1d} + c_{20}, \\
c_{3d} & = \gamma c_{1d} + c_{30}, \\
c_{1d} / c_{2d} & = m_1 / m_2.
\end{align*}
\]

(68)

(69)

(70)

Further, \(c_{20}\) and \(c_{30}\) are connected by the single-solute equation (50) which for the respective indices assumes the form

\[
c_{30} = c_{30}^{0} - \epsilon c_{20}^{0},
\]

where

\[
\epsilon = \frac{a_3 b_2 c_{30}^{0}}{a_2 - a_3 + a_2 b_3 c_{30}^{0}}.
\]

(71)
Equations (66)-(71) permit the calculation of $c_{20}$ which is required for the facts about the complete separation of the bands I and II (see equations (25) and (25a)). The final equation for $c_{20}$ after elimination of the other unknown factors is, however, too complicated to give an impression of what is happening, unless numerical examples are used. For this reason a few simplifying assumptions are made, which do not affect the general result. It is assumed that \( \frac{a_2 - a_1}{a_1} = \delta \ll 1 \). This permits us to consider \( c_{1d} + c_{2d} \) as the concentration of a single substance, the value of which could then be obtained from equation (50) for $c_3 = 0$:

\[
c_{1d} + c_{2d} = \frac{c_2^0}{\delta}.
\]  

(72a)

This additional equation can replace the much more complicated equation (66).
Elimination of \(c_{1d}\) and \(c_{2d}\) from equations (68)–(72) leads to

\[
c_{3o}/\gamma = -m_{1}c_{d}^{3}/(m_{1} + m_{2})e
\]

and

\[
c_{3o}\alpha/\gamma = c_{2o} - m_{2}c_{d}^{3}/(m_{1} + m_{2})e.
\]

Substitution of \(c_{3o}\), \(\alpha\) and \(\gamma\) by means of equations (71), (73), (74) in (67) results in

\[
a_{1}(1 + b_{2}c_{2o} + b_{3}c_{d}^{0} - b_{3}c_{c2o}) = a_{3}\left(1 + \frac{b_{1}m_{1}c_{d}^{3}}{(m_{1} + m_{2})e} + \frac{b_{2}m_{2}c_{d}^{3}}{(m_{1} + m_{2})e}\right). \tag{75s}
\]

The resulting expression for \(c_{2o}\) can be very greatly simplified by making the assumption that

\[
b_{1}/a_{1} = b_{2}/a_{2} = b_{3}/a_{3} = \beta,
\]

which, in the interpretation of the Langmuir equation, means that the surface requirements per mol. of the three solutes are equal. Then

\[
c_{2o} = c_{d}^{3}\frac{b_{2}[(a_{2} - a_{1})/a_{1}][1 + b_{2}c_{d}^{0}m_{2}/(m_{1} + m_{2})]}{b_{2}[(a_{2} - a_{3})/a_{3}][1 + b_{3}c_{d}^{0}]} = c_{d}^{3}\frac{b_{2}\delta_{21}\eta}{b_{3}\delta_{23}}, \tag{76s}
\]

where \(\eta\) is likely to have values between 0.5 and 1. The volume \(V\) of developing solution required for reaching complete separation of the solutes I and II then follows from equation (25a):

\[
V = \frac{b_{2}m_{2}\delta_{25}}{b_{3}c_{d}^{0}(\delta_{21})^{3/2}\eta} \tag{77s}
\]

To reach this state requires a minimum quantity of adsorbent

\[
X_{o} = V(1 + b_{2}c_{2o} + b_{3}c_{3o})^{2}/a_{1}
\]

= approximately \(V(1 + b_{2}c_{d}^{0})^{2}/a_{3}\) (see equation (53a)).

Thus

\[
X_{o} = \frac{b_{3}m_{2}\delta_{25}(1 + b_{3}c_{d}^{0})^{2}}{a_{1}\eta(\delta_{21})^{3/2}b_{3}\delta_{23}c_{d}^{0}}. \tag{78s}
\]

To get a minimum value for \(X_{o}\), the concentration of the developing solute should be chosen so that \(b_{3}c_{d}^{0} = 1\), i.e. half of the adsorbing capacity is filled by substance III. Comparison with the separation conditions obtained without a solute in the developing solvent (see equation (40b)) shows that, apart from the factor

\[
m_{2}/(m_{1} + m_{2}) \eta b_{3}c_{d}^{0},
\]

which has little influence unless \(m_{2}/m_{1}\) is very small, the decisive improvement in equation (77) is contained in the additional factor \((a_{2} - a_{3})/a_{3}\). This shows that the use of an extra solute which is less adsorbed than the substances to be separated is only worth while if the adsorption properties of this solute are closely similar to those of the substances to be separated, i.e. if \((a_{2} - a_{3})/a_{3} \ll 1\).

The physical reason why the development with another solute gives a faster separation with less adsorbing material, is that the presence of the other solute impedes the developmental spreading of the bands. The fact that, if the concentration of the developing solute is high, the band first undergoes a contraction, is
only of a secondary importance; this can be seen from the fact that, in the case of
pure solvent development, an initially high concentration of the solutes makes little
difference to the complete separation. The decisive fact which emerges clearly from
these calculations is that the concentration \( (c_{20}) \) of the band II at the point where
separation takes place \( (x_v) \) is higher, if the solvent contains a solute which is either
more (case 3) or only a little less adsorbed than the substances to be separated.

7. The case of other isotherms

It is fully realized that the Langmuir isotherm does not often occur in the case of
adsorptions on liquid-solid phase boundaries. This is most probably due to the fact
that the adsorbents used do not consist of uniformly adsorbing surfaces, but of a
large number of different types of adsorbing centres. Even if every type conforms
to a Langmuir equation this would result in an isotherm of the form

\[
q_1 = \sum_1^n \frac{a_n c_1}{1 + b_n c_1 + b'_n c_2},
\]

and, as has been pointed out by Hinshelwood, a number \( n \) as small as 2 can already
produce a form of curve similar to that of a Freundlich isotherm.

It is apparent that under such conditions where the curvature of the isotherm
towards the \( c \)-axis is due to saturation of the active centres, the process of chromato­
graphic separation cannot differ greatly from the case of the ideal Langmuir isotherm.
The only substantial difference will occur, where the total concentration is very low,
i.e. at the trailing end of band II, which will approach zero only asymptotically.
However, no exact calculations are possible as the interdependence of the con­
centrations cannot be determined without solving the differential equation

\[
f'_1(c_1c_2) = f'_2(c_1c_2),
\]

which in all cases of \( n > 1 \) leads to differential equations of higher orders. Nor was
a solution found possible for any conceivable mixed isotherm apart from the linear
Langmuir isotherm. It must therefore be considered as a piece of extremely good
fortune, that the only simple isotherm which has a theoretical backing, is capable
of a solution and thus gives some insight into the process of chromatographic
separation; by way of analogy, this may be useful also for cases where the conditions
do not permit of a straightforward solution.

It is, however, of interest to consider the behaviour during a chromatographic
separation of substances following an adsorption isotherm which is convex against
the \( c \)-axis. Such an isotherm would be obtained, for example, under conditions
where not only single molecules are adsorbed, but also double molecules of all
combinations. Assuming that the adsorbent is far from saturated, this would result
in an isotherm of the type

\[
q_1 = k_1 c_1 + k_2 c_1^2 + k_3 c_1 c_2. \quad (79)
\]
The differential equation (2) cannot be solved for type (79), but, writing this equation

\[ q_1 = k_1 c_1(1 + k_2 c_1/k_1 + k_3 c_2/k_1), \]

its form, for \( k_2 c_1/k_1 < 1 > k_3 c_2/k_1 \), becomes very similar to

\[ q_1 = \frac{k_1 c_1}{1 - k_2 c_1/k_1 - k_3 c_2/k_1} = \frac{a_1 c_1}{1 - b_1 c_1 - b_2 c_2}, \]  

i.e. equation (3) with negative values of the constants \( b_1, b_2 \). Here the differential equation (2) can be solved.

As shown by de Vault in his treatment of a single solute, an isotherm convex against the c-axis results in a band with a sharp rear boundary and a diffuse front. In this case the separation condition which can be calculated in a similar way as for a Langmuir equation, leads to a distribution as shown in figure 7.

![Figure 7. Developed band of two solutes with adsorption isotherms which are convex against the c-axis (see equation (80)). The development is almost exactly the reverse of that obtaining in the case of a Langmuir isotherm.](http://rspa.royalsocietypublishing.org/)

**Figure 7.** Developed band of two solutes with adsorption isotherms which are convex against the c-axis (see equation (80)). The development is almost exactly the reverse of that obtaining in the case of a Langmuir isotherm.

Complete separation is reached, when

\[ V + v_0 = \frac{b_1 m_1}{(a_2 - a_1)^2} \frac{1 + \lambda}{\lambda} = \text{approx.} \, \frac{b_1 (m_1 + m_2)}{(a_2 - a_1)^2}. \]  

(81)

The minimum amount of adsorbent required for complete separation is

\[ X_0 = \frac{b_1 m_1}{a_1} \frac{(1 + \lambda + \delta)}{\lambda} = \text{approx.} \, \frac{b_1 (m_1 + m_2)}{(a_2 - a_1)^2}. \]  

(82)

In equations (81) and (82), \( \lambda \) is defined by equation (3), but with a negative value of \( b_2 \).

It is of interest to note that here, too, the amount of adsorbent and solvent required for complete separation depends on \( (m_1 + m_2) \) and on \( \delta^2 \) and not, as might be inferred from Wilson's deductions, on \( \delta \) and \( m_2 \) only.

I wish to express my thanks to the Department of Scientific and Industrial Research for permission to publish these investigations, and to Dr A. E. Green, Lecturer in Mathematics at Durham, for solving the differential equation (5) and for discussions concerning the possible use of other adsorption isotherms.
Other general equations for the chromatogram of two solutes formed by normal development

Since this paper went to press, a new fundamental equation of mass conservation has been found for multiple chromatograms (see Glückauf 1945), which makes it possible to give general solutions for most of the equations previously derived for the Langmuir isotherm only, where this has not already been done. These equations still require that the relations between \( c_1 \) and \( c_2 \) within the mixed band are known, and thus demand the solution of equation 2 by calculation or graphical evaluation.

In the following general equations (marked g) which, for the sake of brevity, are given without deduction and under the same number as the corresponding Langmuir relationships, \( F_1(c_1) \) and \( F_2(c_2) \) (see equations 10 and 11) are given the wider meaning

\[
F_1(c_1) = f_1(c_1, c_2) \quad \text{and} \quad F_2(c_2) = f_2(c_1, c_2),
\]

the mathematical connexion being supplied by equation (2), which requires that \( c_1 \) is a function of \( c_2 \).

The fundamental equations are:

\[
m_1(o-x) = x f_1(c_1, c_2) + v c_1 - w c_1
\]

\[
m_2(o-x) = x f_2(c_1, c_2) + v c_2 - w c_2
\]

where \( c_1 \) and \( c_2 \) are the concentrations at the point \( x \), and where

\[ x_0 < x < x_d \text{ or } x_w. \]

The additional general equations are:

For \( c_{2w} \) as function of \( v \) (can also be used for \( v_{du} \) if \( v_{du} = c_{2w}^0 \))

\[
v = m_2 \frac{F'(c_{2w})}{F_2(c_{2w}) - c_{2w} F'(c_{2w})},
\]

for \( x_w \) as function of \( c_{2w} \)

\[ x_w = m_2 / (F_2(c_{2w}) - c_{2w} F'(c_{2w})). \]

For \( c_{1w} \) and \( c_{2w} \)

\[
\frac{c_{1w} - c_{1w}^0}{c_{2w}^0} = \frac{F_1(c_{1w}) - F_1(c_{1w}^0)}{F_2(c_{2w}^0)},
\]

for the movement of the fully developed frontal band I:

\[
x = \frac{v}{f_1(c_1)} + \frac{m_1(f'(c_1) - F'(c_{2w}^0))}{f_1'(c_1) (F_2(c_{2w}^0) - c_{2w} F'(c_{2w}^0))},
\]
Contributions to the theory of chromatography

\( c_{1w}^* \) is a function of \( c_1 \); it is defined by equation (g 33) with a value of \( c_{1w} \) as following from equation (2) and with \( c_{1w}' = c_1 \), for the contents of any section of the mixed band:

\[
m_{1(p-q)} = \nu \left[ \frac{F_1(c_1) - c_1 F'_1(c_1)}{F'_1(c_1)} \right]^{c_2},
\]

and vice versa for \( m_{2(p-q)} \).

If the pore space is to be taken into account, the corresponding \( \alpha \) has to be added to every function, and \( \alpha \) has to be added to every differentiated function.

References

Glückauf, E. 1945 Nature, 156, 748.

The plastic deformation of non-cubic metals by heating and cooling

By W. Boas and R. W. K. Honeycombe, Council for Scientific and Industrial Research, Lubricants and Bearings Section, Melbourne

(Communicated by Sir David Rivett, F.R.S.—Received 1 September 1944)

Several pure metals were subjected to cyclic thermal treatment between 30 and 150°C. Specimens of zinc, cadmium and tin showed signs of plastic deformation which were evident after a small number of cycles, and which became more pronounced as the number of cycles increased. On the other hand, the phenomenon was not observed in lead. Evidence is brought forward to show that this deformation is due to the anisotropy of thermal expansion in the crystals of non-cubic metals. The persistence of the lattice distortions is shown by X-ray photographs, and also by recrystallization subsequent to the cyclic treatment. In certain metals, grain boundary migration is associated with the deformation. The implications of the phenomenon are particularly exemplified in a comparison of certain tin-base and lead-base bearing alloys. Some possible theoretical and practical implications of the phenomenon are discussed.

1. Introduction

In the course of a comparative study of the properties of tin-base and lead-base bearing alloys, marked differences were observed between the two types of alloy. Small steel cylinders coated on the inside with these bearing alloys were alternately