687. *Theory of Chromatography. Part VI. Precision Measurements of Adsorption and Exchange Isotherms from Column-elution Data.*

By E. Glueckauf.

An investigation is reported into how far it is permissible to use elution data from chromatographic columns for the calculation of adsorption isotherms, in view of the necessarily non-ideal conditions of any experiment. The conclusion is that diffusion and non-equilibrium phenomena do not greatly affect the form of the rear boundary of a chromatogram, if sufficient precautions are taken. An equation is deduced which permits the determination of accurate adsorption equilibria from chromatographic-elution data, under conditions of moderate boundary disturbance.

Symbols :

v = volume of solvent used for elution of solutes (in c.c.).
x = distance from top of column (in g. of sorbent).
$\bar{x}$ = length of column (in g. of sorbent).
c = concentration of solute in the solvent (milliequiv./c.c.).
$f^*(c)$ = amount of solute adsorbed by 1 g. of sorbent in equilibrium with the concentration c (in milliequiv. per g. of sorbent).
$f(c) = f^*(c) + \alpha c$ = amount of solute taken up by 1 g. of sorbent (including the pore space α c.c. per g. of sorbent).
μ = amount of solute which remains in the column after development with pure solvent, when the concentration in the eluate has reached the value c (in milliequiv.).
$N = \bar{x}/2k$ = number of " theoretical units " in the whole column.
$2k$ = height of theoretical unit (in g. of sorbent).

Under ideal conditions, *i.e.*, in the absence of diffusion and non-equilibrium phenomena, and with an infinitely small grain size, the movement of a solute of concentration c inside an adsorption or ion-exchange column is governed by the differential equation :

$$\left(\frac{\partial f(c)}{\partial v}\right)_x + \left(\frac{\partial c}{\partial x}\right)_v = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

This is derived, as has been shown by Wilson (*J. Amer. Chem. Soc.*, 1940, **62**, 1583), de Vault (*ibid.*, 1943, **65**, 532), and Weiss (*J.*, 1943, 297), by the conditions that in any section of the column the change in adsorbed solute must be equalled by the balance of the inflowing and the outflowing solute.

For the movement of points of constant concentration c, equation (1) leads to :

$$\left(\frac{\partial v}{\partial x}\right)_c = \frac{\mathrm{d}f(c)}{\mathrm{d}c} = f'(c) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In the case of the rear boundary, formed by development with pure solvent, the boundary conditions are :

$$c = c^0 \text{ at } v = 0 \text{ for } x > 0$$

and

$$c = 0 \text{ at } x = 0 \text{ for } v > 0$$

which results in

$$\left(\frac{\partial v}{\partial x}\right)_c = \left(\frac{v}{x}\right)_c = f'(c) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which describes the movement of a point of constant concentration c.

As pointed out first by de Vault (*loc. cit.*), equation (3) permits the calculation of adsorption-equilibrium data from the diffuse rear boundary of an elution curve :

$$f(\bar{c}) = \frac{1}{\bar{x}}\int_{c=0}^{c=\bar{c}} v \, \mathrm{d}c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which can be written in the form (see Glueckauf, *J.*, 1947, 1308, and *Nature*, 1945, **156**, 748)

$$f^*(\bar{c}) = [\mu + (v - a\bar{x})\bar{c}]/\bar{x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where μ is the amount of solute which remains in a column containing x g. of sorbent, after development with a volume v.

Equation (5) has been used to some extent in the study of ion-exchange equilibria. Though these investigations have been carried out under conditions guaranteeing a minimum of disturbing effects by use of a grain size of 250 mesh ($\sim$0·007 cm.) or less, and flow rates sufficiently low to reach almost complete equilibrium ($1{\cdot}75 \times 10^{-3}$ cm./sec.), it is still necessary to investigate how far the adsorption or exchange isotherms obtained from equation (5) are affected by the necessarily non-ideal conditions of any real experiment.

In these circumstances equation (1) requires the addition of further terms which, in the case of diffusion and grain-size effects, have the form $-\,k\left(\frac{\partial^2 c}{\partial x^2}\right)_v$, whilst, in the case of non-equilibrium, this term has the, in practice not greatly different, form $k'\left(\frac{\partial^2 c}{\partial x \partial v}\right)$. As can be easily shown, $2k$ represents the height of a "theoretical unit" in the same dimensions as x. We shall consider in detail the former case, giving the complete equation of mass conservation :

$$\frac{\partial f(c)}{\partial v} + \frac{\partial c}{\partial x} - k \, . \, \frac{\partial^2 c}{\partial x^2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The equation can be integrated in the case of a linear adsorption isotherm :

$$f(c) = a/c \text{ (for details see Appendix A).}$$

If we take the case of a column, which was originally saturated with a solution of concentration c^0, being eluted with pure solvent, we obtain an elution curve where c is given as function of $a\bar{x}/v$ and $\bar{x}/k$. Writing $\bar{x}/k = 2N$, we have

$$c = \frac{c^0}{2}\left[\operatorname{erfc}\frac{a\bar{x} - v}{2v}\left(\frac{v}{ak}\right)^{\frac{1}{2}} + \mathrm{e}^{2N} \, . \operatorname{erfc}\frac{ax + v}{2v}\left(\frac{v}{ak}\right)^{\frac{1}{2}}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where erfc n is the error function complement of the argument n.

For large values of N, *i.e.*, after the passage of a large number of " theoretical units," when $(a\bar{x} - v)$ becomes small compared with v, the second term in the bracket can be neglected and equation (7) can be simplified to

$$c = \frac{c^0}{2}\operatorname{erfc}\left(\frac{v - \bar{v}}{2\sqrt{(v\bar{v})}}\sqrt{2N}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $\bar{v} = a\bar{x}$ gives the position of the centre of the boundary ($c = c^0/2$) in the elution curve.

Equations (7) and (8) result in almost symmetrical S-shaped boundaries which according to the values of the parameters $v/\bar{v}$ and N are more or less sloping (see figure 2; experimental ^{24}Na–^{23}Na curve).

A relationship similar to equation (5) which takes account of the disturbing effects represented by equation (6), can be obtained for a linear isotherm. In this case

$$f^*(c) = \frac{1}{\bar{x}}\left[\mu + (v - a\bar{x})c + \frac{v^2}{N}\left(\frac{\partial c}{\partial v}\right)_x\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

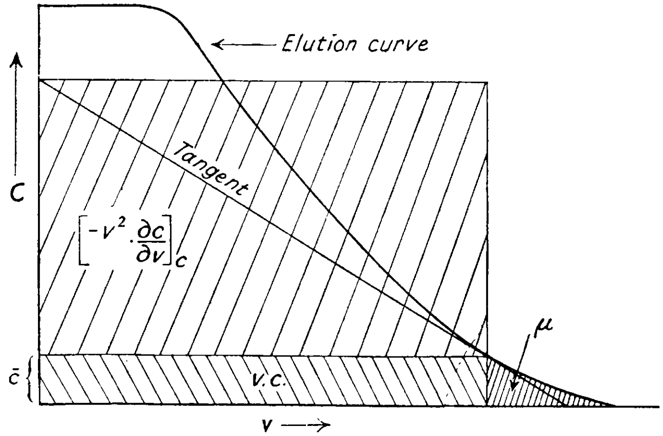
(for calculation see Appendix B).

Here all the data on the right-hand side, apart from N are obtainable from the elution curve of the substance studied.

On the other hand, equation (6) cannot be solved directly for non-linear isotherms and it is necessary to make a few approximations. If we subtract from the left-hand side of equation (6) the very small quantity

$$\left(\frac{\partial f(c)}{\partial x}\right)_v\left[\left(\frac{x}{v}\right)_c - \left(\frac{\partial x}{\partial v}\right)_c\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

FIG. 1.



which is zero in the ideal case when $N = \infty$ (see equation 3), and is negligible if the isotherm is strongly curved, and if N is very large, we can integrate equation (6) by $(\partial x)_v$ and obtain

$$\mu = f^*(c) \, . \, \bar{x} - (v - a\bar{x})c + \frac{\bar{x}}{2N} \cdot \frac{\partial c}{\partial x} \cdot v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or

$$f^*(c) = \frac{1}{\bar{x}}\left[\mu + (v - a\bar{x})c + \frac{\varepsilon}{2N} \, . \, v^2 \, . \left(\frac{\partial c}{\partial v}\right)_x\right] \text{ where } \varepsilon = 1 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Thus we can calculate $f(c)$ for the two extreme types, with equation (9) for the linear isotherm, and with equation (12) for strongly curved isotherms. The difference is expressed by the factor $\varepsilon = 2$ in the case of the linear isotherm. As the curvature of the isotherm is roughly inverse to $(\partial c/\partial \ln v)_{c,x}$ of the elution curve, one might expect that for mildly curved isotherms the factor ε of the correction term would approximate to

$$\varepsilon \simeq 1 + \frac{\partial c/c^0}{\partial \ln v} \bigg/ \left(\frac{\partial c/c^0}{\partial \ln v}\right)_{\text{linear isotherm}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

which can be assessed experimentally. This represents an approximate interpolation between the two extremes, which takes into account both the curvature of the isotherms and the value of N. Whilst this is mentioned for the sake of completeness, it should be noted that equation (12) is usually quite adequate for the calculation of $f(c)$ from the elution data, as most adsorption isotherms have a fair degree of curvature.

Both the terms $(\mu + vc)$ and $v^2(-\partial c/\partial v)$ can be easily evaluated from the elution diagram (see Figure 1).

Thus the only unknown terms are N (representing the total number of " theoretical units " in the column), and the factor ε, which at any rate must lie between 1 and 2. N is obtained by determining, with the same column, the elution curve of a substance with linear adsorption or exchange isotherm. For this one can use the replacement of one solute by an isotopic solute.

From such an elution curve, N can be obtained by a simple relationship from the gradient dc/dv at the centre ($\bar{v}$) of the eluted boundary where $c = c^0/2$:

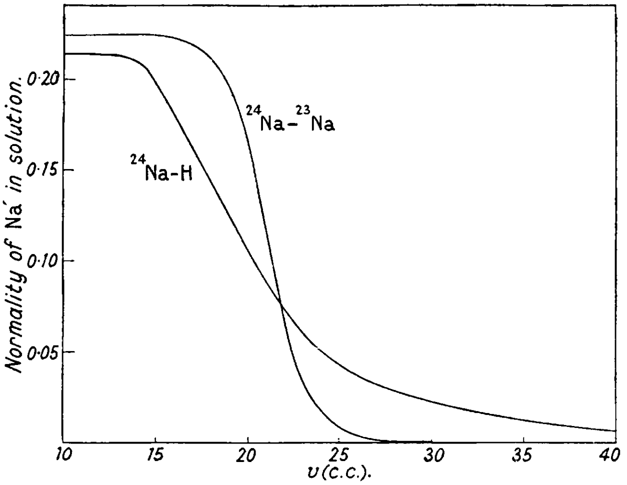
$$N = 2\pi\left[\frac{v}{c^0}\cdot\left(\frac{\partial c}{\partial v}\right)_{x,\bar{v}}\right]^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

which follows from the differentiation of equation (7).

From the same experimental data can also be obtained the value of ε.

If sufficient precautions are taken to ensure a large value of N the last term in equation (12) need not as a rule affect the calculation of $f(c)$ to more than 1%. There are, however, instances—especially in the case of ion exchange—where, owing to the slow rate of exchange at room temperature, a larger correction may become operative. This applies particularly to the case of the Na–H ion-exchange at room temperature on the slow-acting " Dowex 50 " as, owing to the near-linear exchange isotherm and the resulting high values of dc/dv, the correction term is no longer negligible.

FIG. 2.



Application of the Method under Most Unfavourable Conditions (Na–H *Exchange on Dowex* 50 *at Room Temperature*).—A column of 1·07 g. of Na-" Dowex 50 " was eluted with 0·2N-hydrochloric acid, and the concentrations in the eluate were measured as a function of the elution volume v (see Fig. 2, curve A). For the determination of N the same column of Na-" Dowex 50 " containing ^{24}Na as tracer was eluted with 0·2N-^{23}NaCl solution. From the experimental values of $\bar{v} = 21{\cdot}1$ c.c. and $d(c/c^0)/dv = 0{\cdot}21$, the value of N becomes 123. The simultaneous plot of the ^{24}Na–^{23}Na and the Na–H elution curve (see Fig. 2) shows that the relative gradient of the former is about 3 times that of the latter. One would, therefore, according to equation (14) expect a value of $\varepsilon \simeq 1 + \frac{1}{3} \simeq 1{\cdot}33$.

We thus obtain for the calculation of the exchange isotherm $f(c)$ the equation

$$f(c_{\mathrm{Na}}) = [\mu + (v - a\bar{x})c_{\mathrm{Na}} - 0{\cdot}0054v^2(-\partial c/\partial v)]/\bar{x} \quad . \; . \; . \; . \; . \; . \quad (14)$$

The data are given in the table.

$x_{\mathrm{Na_R}}$.	$v' =$ $v - a\bar{x}$.	$\mu + v'c$.	$-0{\cdot}0054$ $v^2\partial c/\partial v$.	$\bar{x}\,.\,f_{\mathrm{Na}}$.	$X_{\mathrm{Na_R}}$.	K_c (calc.).	K_c (by other method).
0·214	12·1	4·607	0·000	4·607	1·00	—	—
0·186	15·8	4·197	0·027	4·170	0·90	1·44	1·40
0·161	17·1	3·787	0·032	3·755	0·86	1·45	—
0·138	18·3	3·391	0·036	3·355	0·73	1·47	1·49
0·114	19·6	2·937	0·038	2·899	0·63	1·48	—
0·072	22·1	2·062	0·038	2·024	0·44	1·54	1·54
0·046	24·6	1·454	0·022	1·432	0·31	1·64	—
0·033	27·1	1·118	0·017	1·098	0·24	1·71	1·65
0·024	29·6	0·863	0·013	0·850	0·18	1·78	—
0·018	32·1	0·678	0·010	0·668	0·14	1·83	1·77

The table shows the application of equation (14) to the calculation of equilibrium values (column 5) and mass-action factors (column 7) at different molar fractions ($X_{\mathrm{Na_R}}$) of sodium on the resin (column 6), and a comparison with values of K_c obtained by an independent method (column 8). $\bar{x} = 1{\cdot}07$ g. of " Dowex 50 "; the eluting solution was 0·214N-hydrochloric acid. Measurements (columns 1 and 2 and 8) were by Dr. J. F. Duncan.

It can be seen that the correction term (column 4) affects the calculated adsorption or exchange function to a noticeable extent only at the lowest molecular ratios, but it affects K_c also at the highest molecular ratios because of the smallness of $[f(c^0) - f(c)]$.

There are few methods which are sufficiently accurate to be used for testing the mass-action factor K_c obtained from equation (14). One such method is based on the determination of the break-through volume in an adsorption or exchange column. This method, however, without being more accurate than equation (14), requires a separate experiment for every concentration point.

A comparison of the two methods is given in column 8.

The agreement shows conclusively that, even if boundary disturbances occur in the column, as, *e.g.*, in the above example, reliable adsorption data can be obtained by using equation (12).

At the same time, the investigation shows clearly that the disturbance of the rear boundary by diffusion and non-equilibrium phenomena is, even in this very unfavourable case, almost negligible. It follows from this that for experiments with faster-acting resins or adsorbents, or at higher temperatures, completely satisfactory data will be obtained by the use of equation (4) or (5) without any correction term, provided that comparable flow rates are being used.

APPENDIX A.

[By J. H. TAIT].

Solution of Equation (A.1) (see equation 6).

$$a\,\partial c/\partial v + \partial c/\partial x - k\partial^2 c/\partial x^2 = 0 \quad \ldots \ldots \quad (A.1)$$

Let

$$c = g\,.\exp\left(\frac{2ax - v}{4ak}\right) \quad \ldots \ldots \quad (A.2)$$

Then equation (A.1) becomes

$$\frac{\partial g}{\partial v} = \frac{k}{a}\cdot\frac{\partial^2 g}{\partial v^2} \quad \ldots \ldots \quad (A.3)$$

The boundary conditions for the case of a solution of constant concentration c^0 entering an empty column are :

$$c = 0 \text{ when } v = 0, \text{ and } c = c^0 \text{ when } x = 0$$

or

$$g = 0 \text{ when } v = 0, \text{ and } g = c^0\,.\exp(v/4ak) \text{ when } x = 0.$$

The solution to this problem is given on page 44 of Carslaw and Jaeger (" Conduction of Heat in Solids," 1947).

$$g = \frac{2c^0}{\sqrt{\pi}}\int_{x/\sqrt{4kv/a}}^{\infty}\exp\left(\frac{v}{4ak} - \frac{x^2}{16k^2\theta^2} - \theta^2\right)d\theta \quad \ldots \ldots \quad (A.4)$$

$$g = \frac{c^0}{2}\,.\,e^{v/4ak}\left\{e^{-x/2k}.\,\mathrm{erfc}\left[\frac{x}{2\sqrt{(kv/a)}} - \sqrt{(v/4ak)}\right] + e^{x/2k}\,.\,\mathrm{erfc}\left[\frac{x}{2\sqrt{(kv/a)}} + \sqrt{(v/4ak)}\right]\right\} \quad (A.5)$$

Substituting g from (A.2) gives

$$c = \frac{c^0}{2}\left[\mathrm{erfc}\,\frac{ax - v}{2v}\left(\frac{v}{ak}\right)^{\frac{1}{2}} + e^{x/k}\,\mathrm{erfc}\,\frac{ax + v}{2v}\left(\frac{v}{ak}\right)^{\frac{1}{2}}\right] \quad \ldots \ldots \quad (A.6)$$

If $(ax - v)$ is small compared with ax, *i.e.*, for large values of x/k, the second term can be neglected. Replacing ax by $\bar{v} = v(c^0/2)$, we can write

$$c = \frac{c^0}{2}\,\mathrm{erfc}\left(\frac{\bar{v} - v}{2\sqrt{(v\bar{v})}}\,.\,\sqrt{(x/k)}\right) \approx \frac{c^0}{2}\,\mathrm{erfc}\left(\frac{\bar{v} - v}{2\bar{v}}\,.\,\sqrt{(x/k)}\right) \quad \ldots \ldots \quad (A.7)$$

(If the pore space is taken into consideration, v and $\bar{v}$ should be replaced by $(v - \alpha x)$ and $(\bar{v} - \alpha x)$ respectively.) If equations (A.6) and (A.7) are applied to the elution of a band, x becomes $\bar{x}$.

APPENDIX B.

Linear isotherm $f(c) = ac$.

Neglecting the second term in equation (A.6) we obtain by differentiation at constant c

$$\left(\frac{\partial x}{dv}\right)_c = \frac{1}{2}\left[\left(\frac{x}{v}\right)_c + \frac{1}{a}\right] = \frac{1}{2}\left[\left(\frac{x}{v}\right)_c + \frac{dc}{df(c)}\right] \quad \ldots \ldots \quad (B.1)$$

Multiplying (B.1) by $2[\partial f(c)/\partial x]_v$ and then replacing $[\partial f(c)/\partial v]_x$ from equation (6) gives

$$\frac{x}{v}\left(\frac{\partial f(c)}{\partial x}\right)_v + 2k\,.\left(\frac{\partial^2 c}{\partial x^2}\right)_v - \left(\frac{\partial c}{\partial x}\right)_v = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B.2)$$

Multiplying by $v\,.\,\partial x$ and integrating for constant v between $c = 0$ and c, we obtain

$$x\,.\,f(c) - \int_{c=0}^{c=c} f(c)\,.\,\mathrm{d}x + 2kv\left(\frac{\partial c}{\partial x}\right)_v - cv = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (B.3)$$

Replacing the integral by μ, and

$$(\partial c/\partial x)_v \text{ by } -\left(\frac{\partial c}{\partial v}\right)_x \left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)_c,$$

and then $\mathrm{d}v/\mathrm{d}x$ from equation (B.1) by

$$(2av/(ax + v) = 2v\bar{v}/[x(v + \bar{v})],$$

we obtain for elution

$$\mu = x\,.\,f(c) - vc - [4\bar{v}kv^2/(\bar{v} + v)\bar{x}](\partial c/\partial v)_x. \quad . \quad . \quad . \quad . \quad . \quad . \quad (B.4)$$

or, as for large values of $\bar{x}/k = 2N$, $v \gtrsim \bar{v}$, we have

$$\mu = \bar{x}f(c) - vc - \frac{v^2}{N}\,.\left(\frac{\partial c}{\partial v}\right)_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B.5)$$

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