

298. *The Behaviour of Charcoal Columns in the Adsorption and Desorption of Acetic Acid in Aqueous Solution.*

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Studies of the adsorption on charcoal columns of acetic acid from a stream of aqueous solution and of its subsequent desorption into pure water are directly relevant to a number of practical problems.

The initial penetration ("breakdown") phenomena of the column can be interpreted in terms of a general theory of adsorption (based on the assumption that the rate of diffusion of the adsorbate to the adsorbing surface is fast relative to the rate of flow of the carrier stream). Theoretical predictions of the effect on the breakdown time of a column of (*a*) column length, (*b*) flow-rate of the stream, (*c*) initial concentration of the stream, and (*d*) granule size of the charcoal are compared with experimental results.

The distribution of the adsorbate on the column depends on the precise shape of the adsorption isotherm. The distribution can be calculated from the experimentally determined isotherm if it is assumed that equilibrium between the stream and the charcoal is attained

rapidly relative to the rate of flow of the stream. This theoretical treatment gives results in good accord with those determined experimentally. It can be applied to distribution during adsorption and during desorption by a stream of pure solvent, both for uniform and for non-uniform initial distribution of adsorbate.

THE preceding paper confirmed the view that the adsorption on charcoal of acetic acid from aqueous solution takes place through the undissociated molecule only. This work referred to adsorption under conditions of strict equilibrium, whereas the present paper considers the phenomena arising from the adsorption of acetic acid from solutions flowing through packed columns of granular charcoal, *viz.*, "breakdown" phenomena, and the distribution of adsorbate during both adsorption and desorption. This work has a direct bearing on numerous practical problems of recovery and purification of both solutes and solvents.

The corresponding case for gaseous adsorbates has been described in two papers (Danby, Davoud, Everett, Hinshelwood, and Lodge, *J.*, 1946, 918; Barrow, Danby, Davoud, Hinshelwood, and Staveley: *J.*, 1947, 401), which form the basis of this comparison. The mathematical treatments presented in these papers were developed with reference to the general problem of adsorption from flowing streams, with no assumptions limiting their application particularly to the gaseous phase. In outline, therefore, they form the theoretical background of the present work.

The general problem of the passage of an adsorbate carried in an inert stream through a column of granular adsorbent can be given a strict mathematical treatment, but this leads to a differential equation which is, in general, intractable. By the use of approximations, however, it is possible to derive equations which can be compared directly with experimental results. These approximations depend upon one or other of the following assumptions: either (a) that, for substances which are strongly adsorbed, adsorption can be treated as an irreversible process of definite rate, or (b) that in any adsorption or desorption process, equilibrium is established at a rate fast compared with the rate of flow of the adsorbate through the column.

The first assumption is applicable to the initial breakdown phenomena of reacting columns (*i.e.*, to phenomena connected with the first appearance of detectable traces of the adsorbate in the stream leaving the column). The second assumption relates to the distribution of reactant or adsorbate along the column as a function of time, both in adsorption and desorption. In both cases the shape of the adsorption isotherm is of fundamental importance. We shall consider these in turn in relation to the adsorption of acetic acid on charcoal from aqueous solution.

Breakdown Phenomena.

Assumption (a) above is applicable to the treatment of the initial breakdown of columns. It applies when the shape of the adsorption isotherm is such that the total capacity of the charcoal for the adsorbate is very large. Adsorption then takes place very readily, while desorption, under normal conditions of flow, is very slow, so that the former can be regarded, to a first approximation, as an irreversible process.

The successful application of this approximate treatment to the adsorption of acetic acid depends on: (i) the shape of its adsorption isotherm, (ii) its rate of adsorption. The shape of the adsorption isotherm of acetic acid on charcoal justifies the use of the approximation that adsorption is effectively an irreversible process *under these conditions* (*i.e.*, a steady flow of solution through the column), provided that the solutions used be not very weak.

A preliminary investigation of the rate of adsorption showed it to be fast relative to the rates of percolation used. Thus, for charcoals of the kind used in these experiments, but in the coarser grading of 8—18 mesh B.S.S., 80% of the total adsorption took place within 15 minutes. The rate appeared to be faster for more active charcoals, and a faster rate would be expected if finer grading were used.

The mathematical treatment of the general problem has been given in full by Danby, Davoud, Everett, Hinshelwood, and Lodge (*loc. cit.*). The basic equation relating the breakdown time, τ , of a column of length λ is:

$$\tau = \frac{1}{kc_0} \cdot [\ln(e^{kN_0\lambda/L} - 1) - \ln(c_0/c' - 1)]$$

where c_0 is the concentration of adsorbate entering the column,

c' is the concentration of adsorbate leaving the column at breakdown,

L is the linear flow rate of the solution,

N_0 is the number of active centres of unit activity per c.c. of material,

and k is a constant, except under certain conditions, specified below.

If, as proves to be the case in practice, $e^{kN_0\lambda/L}$ is much greater than 1, we can re-write this equation as

$$\tau = \frac{1}{kc_0} \cdot \left[\frac{kN_0\lambda}{L} - \ln (c_0/c' - 1) \right] \dots \dots \dots (1)$$

From this equation relations can be derived for the effect of each variable on the behaviour of the column.

Effect of column length. A linear relation is deduced :

$$\tau + \tau_0 = N_0\lambda/c_0L \dots \dots \dots (2)$$

where

$$\tau_0 = [\ln (c_0/c' - 1)]/kc_0$$

Effect of flow rate. The fundamental property of charcoal columns, rather than the breakdown time, is the breakdown volume, Y . This is the volume of solution which passes through the column before breakdown is reached. It is related to the breakdown time by the equation

$$Y = F\tau$$

where F is the total flow rate of the solution through the column and is related to the linear flow-rate by the equation

$$F = AL$$

where A is the cross-sectional area of the column.

Equation (1) can now be re-written in the form

$$F \cdot \ln (c_0/c' - 1) = -kc_0Y + kAN_0\lambda \dots \dots \dots (3)$$

Rates of diffusion are slower in solution than in the vapour phase and it is therefore necessary to use the modified rate constant for adsorption, k_D , in equation (3), where :

$$k = k_D L^{\frac{1}{2}} \dots \dots \dots (4)$$

This gives

$$F \cdot \ln (c_0/c' - 1) = -k_D L^{\frac{1}{2}} c_0 Y + k_D L^{\frac{1}{2}} AN_0\lambda$$

Hence

$$Y = \frac{AN_0\lambda}{c_0} - \frac{F^{\frac{1}{2}} A^{\frac{1}{2}} \cdot \ln (c_0/c' - 1)}{k_D c_0}$$

which can be re-written in the form :

$$Y = Y_0 - KF^{\frac{1}{2}} \dots \dots \dots (5)$$

where Y_0 and K are constants.

Effect of initial concentration of solution. The effect of variation of breakdown time with initial concentration cannot be expressed in any simpler form than that of equation (1). From this we see that a plot of τ against $1/c_0$ should give a straight line when c_0 is small [*i.e.*, when $\ln (c_0/c' - 1)$ is much less than $kN_0\lambda/L$], falling off towards the $1/c_0$ axis as c_0 increases, *i.e.*, towards the origin.

Effect of granule size. Reduction of granule diameter increases the accessibility of the adsorption sites, although the number of active centres per c.c. remains unchanged. Accessibility might be expressed approximately as the ratio

$$\frac{\text{external surface of granule}}{\text{mass of granule}} = \frac{\pi d^2}{1/6\pi d^3} = \frac{6}{d}$$

Hence we can write k^*/d for k in equation (1), which becomes

$$\tau = \frac{N_0\lambda}{c_0L} - \frac{d \cdot \ln (c_0/c' - 1)}{k^*c_0}$$

which is of the form

$$\tau = \tau_0' - k_1 d \dots \dots \dots (6)$$

where τ_0' and k_1 are constants.

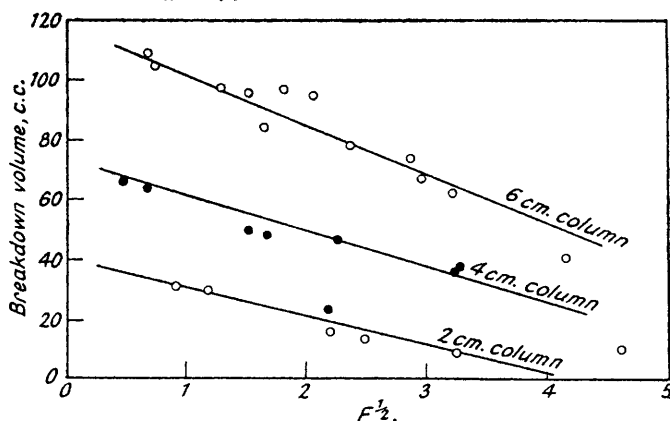
Note. The equations used throughout refer to a breakdown criterion based on the concentration of solute in the effluent. The experimental breakdown criterion depends on the total amount of solute penetrating the column. Slightly more complicated equations apply to this case, but differ from those given only in the value of some of the constants. The difference is small and does not affect the form of the equations.

Experimental.—The experiments were carried out with columns of steam-activated nutshell charcoal and unbuffered solutions of acetic acid. The columns were supported on a sintered-glass plate in a tube 16 mm. in diameter. The charcoals were carefully graded before use and then well washed with distilled water to remove fine particles. The columns were formed from the wet charcoal, which was packed to maximum density. Solutions from a reservoir were allowed to percolate through the columns at controlled rates. The criterion of breakdown was neutralisation by the effluent stream of 1 c.c. of $N/100$ -sodium hydroxide, with phenolphthalein as indicator. The final volume was measured after breakdown.

The following conditions applied throughout except where otherwise stated: Grading of charcoal: 40–80 mesh B.S.S. Flow-rate of solution: 2 c.c./min. Column length: 4 cm. Concentration of acetic acid: $N/10$.

FIG. 1.

Effect of flow rate on breakdown volume.

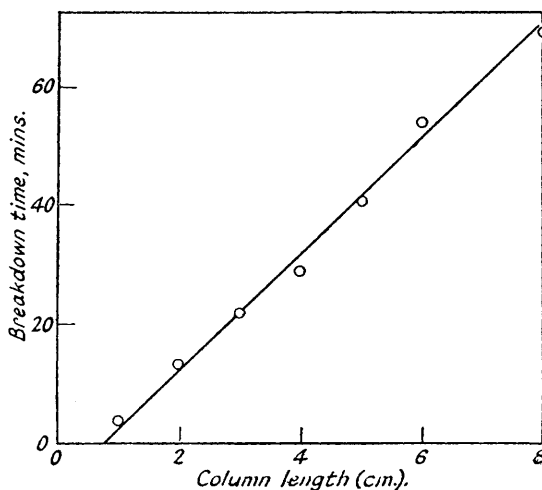


Results.—Effect of flow rate. The effect of flow rate on breakdown volume was determined for columns of different lengths. It was found that a plot of Y against F does not give the linear relation required by equation (3). A plot of Y against $F^{1/2}$ (Fig. 1) gives a close approximation to the linear relation required by equation (5). It is therefore clear that rate of diffusion is important.

Effect of column length. The relationship between breakdown time and column length of equation (2) holds very precisely for the range investigated, *i.e.*, 1–8 cm. (see Fig. 2). In this and the following

FIG. 2.

Effect of column length on breakdown time.

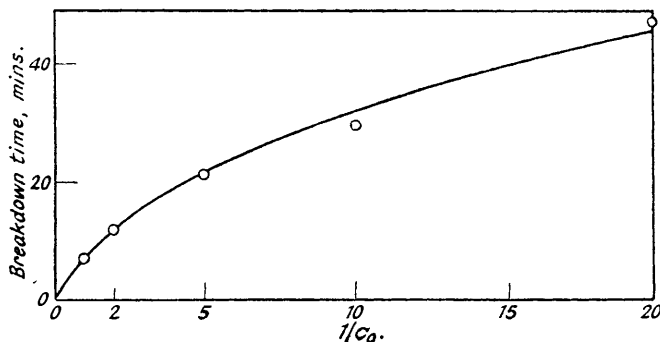


investigations it was found necessary to make slight corrections when the flow rate varied slightly from 2 c.c./min. The correction was made to the breakdown volume on the basis of the curves in Fig. 1, and the breakdown time deduced from the corrected breakdown volume.

Effect of initial concentration of solution. The breakdown times of 4-cm. columns to acetic acid solutions varying in concentration from N to $N/20$ were determined at a flow rate of 2 c.c./min. The

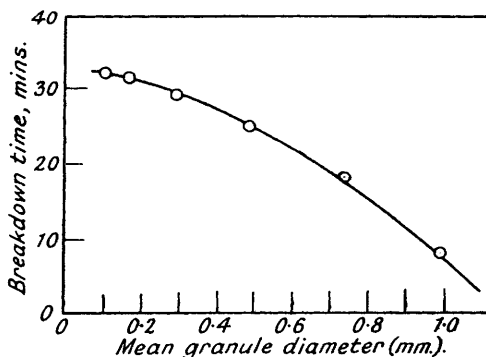
results are given in Fig. 3, where the breakdown time is plotted against $1/c_0$. The results are in accord with equation (1).

FIG. 3.
Effect of concentration of acetic acid on breakdown time.



Effect of granule size of charcoal. The breakdown times of 4-cm. columns of charcoal to N/10-acetic acid flowing at 2 c.c./min. were determined for a series of different gradings. According to the equation given in the original theory, the breakdown time should vary linearly with $1/d$, where d is the mean diameter of the granules at a given grading. This relationship is not obeyed. Fig. 4, however, shows

FIG. 4.
Effect of granule size on breakdown time.



that the results follow a linear relationship between breakdown time and mean granule diameter (as required by Equation 6), though there is some falling off from linearity at fine gradings.

Discussion.—The results given above show that the general theory (*J.*, 1946, 918) is largely applicable to the adsorption by charcoal of acetic acid from aqueous solution. One important exception has been found in the effect of grading on breakdown time. In the discussion on gases it was stated that the behaviour of any gas-charcoal pair is determined by the two quantities k and N_0 . It was assumed for that case that k is independent of granule size and that therefore any effect of grading on breakdown time must be due to changes in N_0 . This seems unlikely in the present case, since the area of adsorbing surface per g. suffers no appreciable change with granule size. It seems more probable that it is k , rather than N_0 , which changes with grading, on account of alteration in the accessibility of the adsorbing surface.

The possibility of the general application of the theory to all solutes cannot be assessed until further data are available. The present results suggest: (a) That under similar conditions, all charcoals are likely to behave qualitatively in the same way as that used in this work; there will, however, be considerable quantitative differences in rates of adsorption, diffusion and so on, according to the degree of activation of the charcoal and the limitations imposed by the nature of the raw material. (b) That a change in the solute is also likely to cause quantitative changes in the rates; if these changes are great, they may result in what appears to be a qualitative change—thus the breakdown time of charcoal columns to methylene-blue is not directly proportional to the square root of the flow rate (C. J. Danby, private communication). The linear relationship given

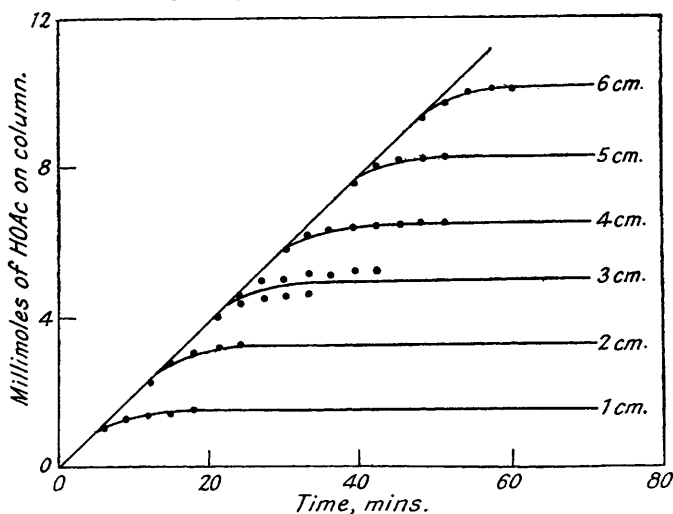
by acetic acid indicates that diffusion is the rate-determining step in the adsorption process. This is not so for methylene-blue, for which it is probable that several other factors such as actual rate of adsorption on the surface are involved, combining to give a complex relation between breakdown time and flow rate. These may depend upon the size and shape of the molecule of adsorbate.

Distribution Phenomena.

We have so far considered mainly the changes occurring in the streams carrying the adsorbate; we shall now consider the complementary problem of the way in which the adsorbate is distributed along the column: first, the development of the distribution during adsorption and then the corresponding changes taking place in subsequent desorption when a stream of pure solvent flows into the column. We shall use the second approximation (see above), which depends on the assumption that equilibrium between the adsorbate in the stream and on the charcoal is attained rapidly relative to the rate of flow of the stream. With this assumption, the only experimental datum required for calculating the distribution of any adsorbate at a given flow rate is its adsorption isotherm.

A rigid mathematical treatment would use the continuous process of the calculus. The approximate method follows this as closely as possible by considering the events taking place in a

FIG. 5.
Adsorption of acetic acid on charcoal columns.



succession of small elements of the column in successive small time intervals. The method of calculation is described in detail by Barrow, Danby, Davoud, Hinshelwood, and Staveley (*loc. cit.*). We shall consider the following cases: (a) the adsorption of acetic acid on a charcoal column, (b) desorption of acetic acid from an initially completely saturated column, (c) desorption of acetic acid from a column of which the first section only (*viz.*, one-third of the column) is initially saturated.

In adsorption the advance of the wave-front proceeds at a fairly uniform rate throughout and a standard time interval can therefore be used for the whole of the calculation. Desorption, however, although initially fast, becomes much slower as the process continues. The time intervals must therefore be small at the beginning of the calculation, but may become much longer towards the end.

Experimental.—A steam-activated nutshell charcoal, graded 80–100 B.S.S. mesh, was used in a column 6 cm. long and of 16 mm. diameter. A standard flow rate of 2 c.c./min. was used throughout. In the adsorption experiments, $N/10$ -acetic acid was passed through the column.

For the desorption experiments, a supply of the charcoal was shaken with N -acetic acid (1 g. of charcoal with 25 c.c. of solution) until equilibrium was established. The supply was used for making up the columns for experiment (b) and for the first 2 cm. of the columns for experiment (c), the remainder of which were formed from untreated charcoal. Desorption was carried out with distilled water.

The experimental determination of the distribution is based on the principle that, if a solution is passed for a given time through a column 1 cm. long, then the amount of acetic acid adsorbed on this

column is identical with the amount adsorbed on the first cm. of any longer column under the same conditions. Thus, for a 2-cm. column, the difference between this amount and the total amount adsorbed by the 2-cm. column is the amount on the second cm. length. Repetition of this process for columns 1, 2, 3, 4, 5, and 6 cm. long gives the distribution for the whole column.

FIG. 6.
Distribution of acetic acid on a charcoal column during adsorption.

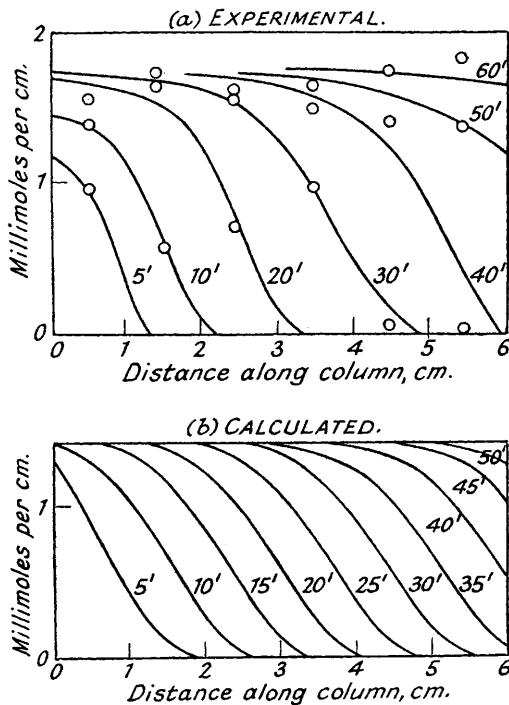


FIG. 7.
Desorption of acetic acid from charcoal columns.

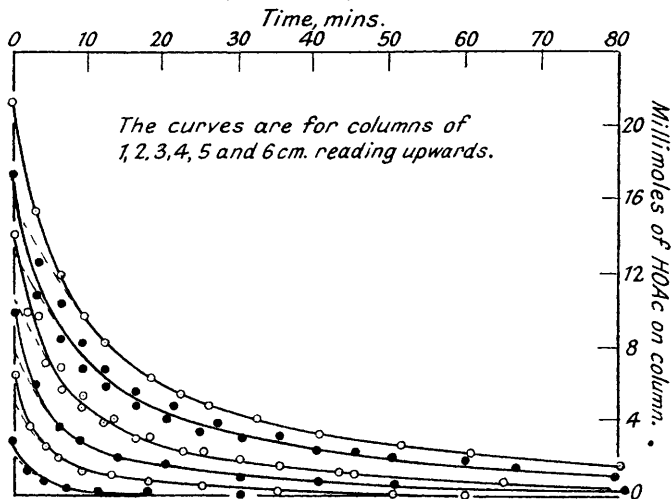


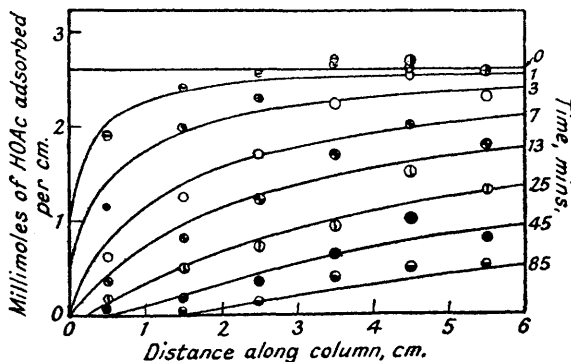
Fig. 5 shows the curves of total adsorption against time for the six columns. At any instant the vertical heights between the adjacent curves give the amounts of acetic acid adsorbed on the corresponding sections of the standard column. In the distribution curves (Fig. 6a), the points have been plotted, as a first approximation, at the centre of the respective cm. lengths.

The curves in Fig. 5 were obtained by titrating the acid in the effluent from the columns after successive small time intervals. The difference between the amounts appearing in the effluent and the amount entering the column is the amount adsorbed on the column during the interval.

In desorption, the same technique applies. Titration of the effluent gives the amount desorbed in any given time interval. From the amount initially present on the charcoal, the amount remaining can be deduced. This gives the curves of Figs. 7 and 9, from which the distributions are obtained.

FIG. 8.

Distribution of acetic acid during desorption: initial distribution uniform.

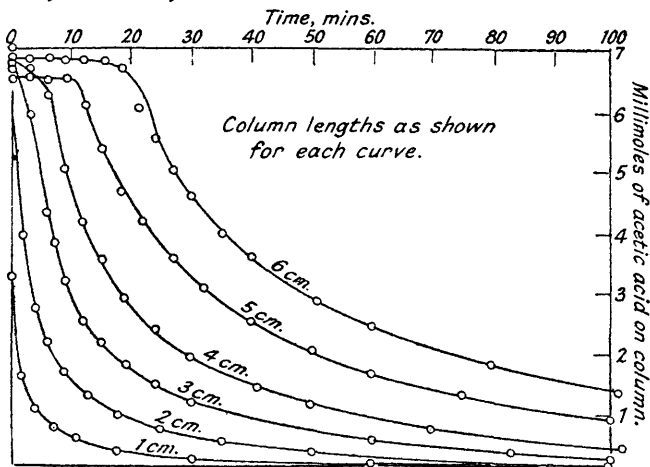


*The points represent "corrected" experimental determinations.
The curves are calculated distributions.*

In the case of desorption, a correction must be applied to the experimentally determined distributions before they can be compared quantitatively with the calculated distributions. It arises because, after adsorption has taken place, the column contains, in addition to the acetic acid adsorbed on the surface, an extra amount present in the carrier stream which is retained in the pore spaces of the charcoal granules. The problem does not arise in the case of gases, since the usual concentrations are so small that the amount held in the carrier stream is negligible. For acetic acid, however, a much higher molecular concentration

FIG. 9.

Desorption of acetic acid from charcoal columns. Initial distribution non-uniform.



has been used and the amount retained in the pores (but not adsorbed) is an appreciable fraction of the amount adsorbed on the surface. The isotherm from which the calculations have been made refers only to surface adsorption. Hence there is a discrepancy between the calculated and the observed results. During adsorption the effect of retention of adsorbate in the pores is only to heighten the experimentally determined wave front; the shape is otherwise unaffected. During desorption, however, the effect is more marked. It is difficult to allow for the desorption of solutions from the pores in the calculations, but an empirical correction has been applied to the experimental results of Fig. 7. The dotted curves are produced back to a value at zero time corresponding to surface adsorption only. These curves give the experimental distributions of surface-adsorbed acetic acid, which are in very close agreement with the calculated distributions (Fig. 8). A similar correction would be more difficult to apply in the case of

non-uniform initial distribution, but the effective agreement between the calculated and uncorrected experimental distributions is sufficiently clear from Fig. 10.

FIG. 10.

Distribution of acetic acid during desorption. Initial distribution non-uniform.

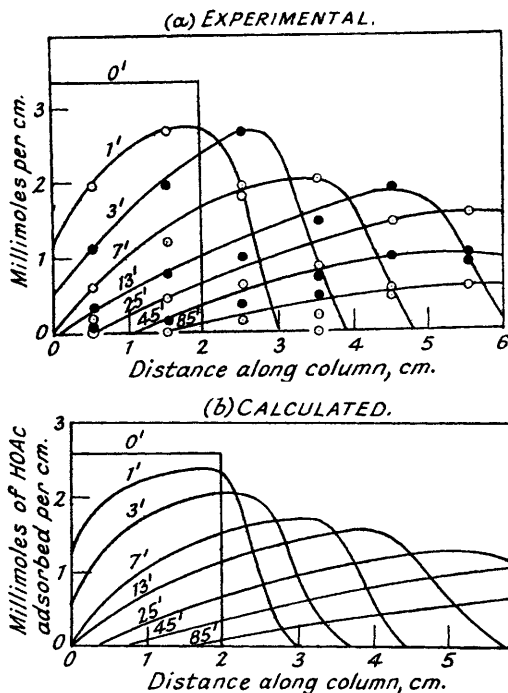
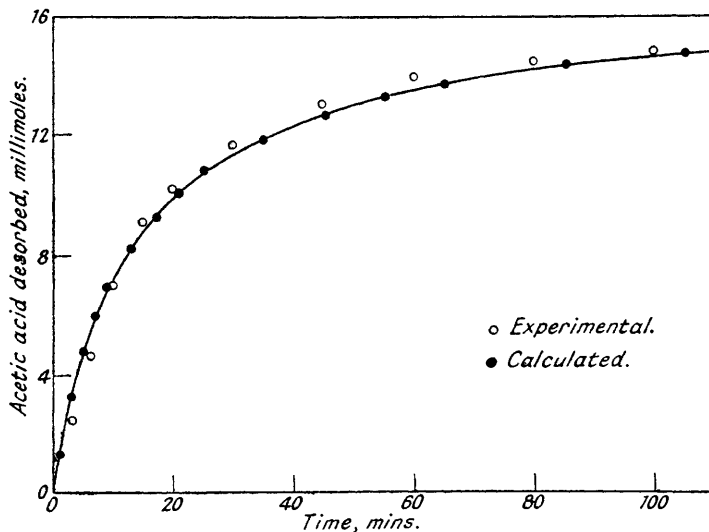


FIG. 11.

Desorption of acetic acid from a charcoal column : total acetic acid in effluent.



The calculations also give the total amount of acetic acid appearing in the effluent as a function of time. The calculated values are compared with the corrected experimental results in Fig. 11.

The experimentally determined isotherm for the charcoal used in this work can be represented approximately by the Langmuir equation

$$x/m = 2c/(1 + 11.6c)$$

1496 *The Behaviour of Charcoal Columns in the Adsorption, etc.*

where x/m is the adsorption of acetic acid in g. of acid per g. of charcoal, and c is the normality of the solution.

Discussion.—The agreement between the experimental and the calculated results is very close, not only for simple adsorption and desorption, but also for the more complex case of the adsorption-desorption cycle which occurs in desorption from a non-uniform initial distribution of adsorbate. We can conclude that both adsorption and desorption are very fast processes. Taken in conjunction with the conclusion of the first part of this paper that diffusion is probably the rate-determining step in these processes, the evidence suggests that adsorption and desorption take place as fast as the molecules can be brought to or removed from the charcoal surface. In gaseous adsorption, where the flow rate which has been used is so fast (the linear flow rate is 250 cm./min.) that contact time of the molecules with the surface is very small, the establishment of equilibrium at the surface must be almost instantaneous. With solutions, a much slower linear flow-rate of about 1 cm./min. has been used. There is consequently no direct evidence of the rate of the surface reactions. It seems probable, however, that these may still be fast and that the rate of removal of solute from solutions is governed by rate of diffusion to the surface.

Of the combined processes of diffusion to the surface and reaction there, during adsorption, and of the corresponding processes for desorption, it can certainly be said that the flow rates used in this work have allowed sufficient time for equilibrium to be almost completely established throughout.

In these circumstances the shape of the isotherm completely determines the distributions of the adsorbate along the column. The most important feature of the isotherm is that a high degree of adsorption is obtained at low concentrations of acetic acid. Hence the wave-front in adsorption is very sharp and nearly vertical, *i.e.*, the column becomes nearly saturated before any adsorbate appears in the effluent. When breakdown occurs, however, the effluent concentration rises very rapidly to that of the ingoing stream. It is a direct consequence of the shape of the isotherm in the region near the origin, which has the practical result that the charcoal is very efficient in removing small traces of acetic acid from aqueous solution and remains so until it is nearly saturated.

In desorption the wave-front is initially very steep, but rapidly becomes much flatter. This again is because large amounts of adsorbate can remain on the surface and yet give rise to only a small concentration in the stream. Consequently, the whole column *tends* towards a common level of adsorption at which the rate of desorption is very slow, *i.e.*, the wave-front tends to become very flat.

We conclude that the theories of adsorption developed for the general case apply very well to adsorption of acetic acid from aqueous solution. There is a strong similarity between the adsorption characteristics of acetic acid and of carbon tetrachloride vapour (which is typical of gases which undergo simple physical adsorption only). This similarity is possible because, of the molecular and ionic species present in acetic acid solutions, only the undissociated molecules are adsorbed, *i.e.*, the same phenomenon of physical molecular adsorption is shown by both substances. The isotherms are of very similar shape. The fundamental processes appear to be the same in both media.

For both substances, the conditions controlling the breakdown time indicate that the rate-determining step in this process is diffusion of the adsorbate to the internal surface of the granule. The reaction at the surface seems to be very rapid. Provided that the flow rate be slow compared with the rate of diffusion, the conditions of adsorption are effectively those of equilibrium. Consequently, the distribution of the adsorbate on the column depends on the shape of the adsorption isotherm only.

The results outlined above apply to aqueous solutions of acetic acid and would be expected to apply to other solutes in which diffusion to or from the charcoal surface is the rate-determining step in the process. It is unlikely, however, that they will apply to all solutes, since rates of adsorption and desorption for larger molecules are sometimes very slow.

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