202. *The Kinetics of Absorption of Gases from an Air Stream by Granular Reagents.*

By C. J. DANBY, J. G. DAVOUD, D. H. EVERETT, C. N. HINSHELWOOD, and R. M. LODGE.

A theoretical treatment is given of the kinetics of the removal of a gas from an air stream by passage through a column of granular solid with which it reacts or by which it is irreversibly adsorbed.

Various practically important relations are determined for typical systems and compared with those predicted theoretically. These relations include : (a) the escaping concentration as a function of time, column length, flow-rate and initial concentration, (b) the distribution of gas or reaction product in the column, and (c) the influence of granule size.

The independent parts played by capacity factors and rate factors are shown.

THE present paper is concerned with the uptake of a gas from a flowing air stream on passage through a bed of granular reagent or absorbent. Theoretical treatments of this problem have been made by several previous workers. Mecklenberg and Kubelka (*Z. Electrochem.*, 1925, **31**, 488) and Mecklenberg (*Kolloid-Z.*, 1930, **52**, 88) employed reasoning on somewhat similar lines to that of the present paper, but which applied only to the case of physical adsorption of the gas. Where comparison is possible the equations derived in the present work are generally similar in form to those of Mecklenberg and Kubelka, though the physical interpretation of the constants is different. Dubinin (*J. Russ. Phys. Chem. Soc.*, 1930, **62**, 683, 1947) introduced the properties of the adsorbent in a different way : his equations also have approximately the same form with respect to the thickness of the adsorbent layer and to the gas concentration.

Theoretical equations for the shape of the wave-front of unadsorbed gas in an adsorbent column were derived by Bohart and Adams (*J. Amer. Chem. Soc.*, 1920, **42**, 523). These workers, however, did not confirm their results quantitatively, or apply them to the treatment of the problem of " breakdown times." A rather different and more ambitious treatment, correlated with experimental data for the adsorption of carbon dioxide on charcoal, has been given more recently by Wicke (*Kolloid-Z.*, 1939, **86**, 167, 295) and by Weyde and Wicke (*ibid.*, 1940, **90**, 156).

The present paper seeks to obtain the relevant equations in the simplest possible form, and to relate them more directly than has hitherto been possible to experimental measurements. The inter-relation of the important variables has been studied in some detail for several different systems, so as to give a general understanding of the factors governing the behaviour of these systems.

In the theoretical treatment the uptake of the gas is assumed to be irreversible. This will be valid for a chemical reaction in which the gas is destroyed. It will also be a legitimate approximation for adsorption under those circumstances or in those parts of the system where the reverse reaction is negligible in comparison with the uptake.

Simple Approximate Treatment.

The following discussion is based upon assumptions which are not by any means exactly fulfilled in practice. It has the advantage, however, of introducing the important quantities and of yielding quickly and simply some of the most important relations between them.

Let a column of granular material of unit cross-section be traversed by a stream of air carrying gas which is to be removed by adsorption or by a chemical reaction.

Let c_0 be the concentration of this gas in the entering stream, l the distance from the point of entry to some given point in the column, c the concentration of the gas at the point l, and T the total time for which the column has been exposed to the stream. Initially, before any of the material has been used up, there will be a concentration gradient along the column, the concentration falling from c_0 at the point of entry at a rate depending on the speed at which the gas is removed. At a distance l along the column the gas will have been in contact for a time t, such that l/t is the linear rate of flow; t must be distinguished from T, the total time for which the stream has been passing. When a given element of the gas has been in contact for a time t, its concentration may be taken to have dropped to c, where

$$c = c_0 e^{-Kt} = c_0 e^{-Kl/L} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

L being the linear flow rate, and K a measure of the rate of adsorption or reaction. This assumes that the interaction follows the equation for a reaction of the first order. This supposition is likely to be rather closely

fulfilled, since the interaction rate will be governed either by diffusion, which will follow a first-order equation, or by the rate of a heterogeneous reaction, which will also do this, at least when the concentration of the reacting gas is small.

After time T, some of the material will have become saturated with adsorbed gas, or will have had some of its catalytic centres inactivated. The reaction time, t, will no longer be given by l/L, but by the time for which the element of gas reaching the point l has been in contact with *unexhausted* material. The exhaustion is gradual, and to obtain the complete relation between c, l, and T, the appropriate differential equation must be solved. Many of the essential results, however, may be obtained with the assumption that the region of saturation moves along the column with a constant speed.

With this simplification, the length of the unexhausted column up to the distance l is $l - bT$, where b is the rate of exhaustion.

Therefore

$$t = (l - bT)/L$$

and

$$c = c_0 e^{-K(l - bT)/L}$$

or

$$c = c_0 e^{-Kl/L} \cdot e^{KbT/L} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If λ is the total length of the column, then the concentration of the emerging gas is given by

$$c = c_0 e^{-K\lambda/L} \cdot e^{KbT/L} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

whence *log c increases in direct proportion to* T, the time of passage of the stream.

As will be shown, this relation is always roughly and sometimes rather closely fulfilled.

In practical applications it is customary to define a *service* or *breakdown time*, namely, the time from the beginning of flow at which a chosen concentration of gas (c') is reached in the effluent.

The breakdown time, τ, is then given by the equation

$$c'/c_0 = e^{-K\lambda/L} \cdot e^{Kb\tau/L} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and unless the column length is greater than a certain value, λ_c, given by

$$c'/c_0 = e^{-K\lambda_c/L} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

there would be an immediate " breakdown " (according to the arbitrary criterion).

Substitution of (5) in (4) gives

$$e^{Kb\tau/L} = e^{K(\lambda - \lambda_c)/L}$$

whence

$$\tau = (\lambda - \lambda_c)/b.$$

Now b is the rate of exhaustion of the active centres. Whether this represents the saturation of adsorptive regions, consumption of chemically active centres or progressive poisoning of catalytic points, it will be proportional to the total amount of gas passing (*i.e.*, to c_0L), and inversely proportional to the number of active centres originally available. With appropriately chosen units therefore

$$b = c_0 L/N_0$$

where N_0 is the initial number of active centres.

Therefore

$$\tau = N_0(\lambda - \lambda_c)/c_0 L \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The breakdown time should thus increase linearly with column length after a " critical length " has been passed. It should also be inversely proportional to the concentration of gas in the entering stream.

When the flow rate is varied, the column length being kept constant, a corresponding relation appears, there being a critical flow rate, L_c, for which breakdown is immediate. From (4) we have

$$\tau = \frac{\lambda}{b} + \frac{L}{Kb} \ln \frac{c'}{c_0}$$

$\tau = 0$ when $L = L_c$, whence

$$\frac{\lambda}{b} + \frac{L_c}{Kb} \ln \frac{c'}{c_0} = 0$$

Therefore

$$L_c = - \frac{K\lambda}{\ln c'/c_0}$$

so that we may write

$$\tau = \frac{\lambda}{b}[1 - L/L_c]$$

Since $b = c_0 L/N_0$ we have

$$\tau = \frac{\lambda N_0}{c_0} \left[\frac{1}{L} - \frac{1}{L_c} \right] \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The critical length diminishes and the critical flow-rate increases as the value of K increases. In the limiting case of instantaneous reaction the breakdown time increases linearly with column length and is inversely

proportional to the flow rate. With slower chemical reactions the divergence from simple direct or inverse proportionality becomes greater.

More Detailed Theory.

We consider a zone of the column between two parallel cross-sections of the column dl apart and distance l from the boundary of the column by which the gas enters. The gas entering this zone will be at a certain concentration $c_{l,T}$, where T is the time for which the gas stream has been flowing. Some of this gas is taken up and partially saturates or inactivates a portion of the material; the gas leaves the section at a lower concentration $c_{l+dl,T}$. If the concentration gradient is $(\partial c/\partial l)_T$, then

$$c_{l+dl,T} = c_{l,T} + \left(\frac{\partial c}{\partial l}\right)_T . dl$$

Now the active centres are being used up continuously and, it being assumed that the rate of removal of the gas depends upon the number of active centres available, this rate decreases with time. Consequently, the magnitude of the concentration gradient also decreases with time. It also follows that the concentration of gas at any point in the column increases steadily with time up to c_0, when the column up to that point is completely broken down and removes none of the gas. The concentration of gas in the stream is thus a function both of the distance along the column and of the time for which the stream has been passing.

The total amount of gas entering the section in the time dT is

$$V . c_{l,T} . dT$$

where V is the volume of gas flow per unit time.

In the same time the amount of gas leaving the section is

$$V . c_{l+dl,T} . dT = V[c_{l,T} + \left(\frac{\partial c}{\partial l}\right)_T . dl]dT$$

The excess of the amount of gas entering over that leaving is then

$$-V\left(\frac{\partial c}{\partial l}\right)_T dl . dT$$

Part of this excess has reacted or been adsorbed, while the rest has gone to increase the amount of free gas in the section. Thus

$$-V\left(\frac{\partial c}{\partial l}\right)_T dl . dT = \text{amount adsorbed or destroyed} + \text{increase in amount of free gas.}$$

If x is the amount of gas dealt with per c.c. of material, then the amount dealt with in the time dT in the zone we are considering is

$$A . dl \left(\frac{\partial x}{\partial T}\right)_l dT$$

A being the cross-sectional area of the column. The increase in the total amount of free gas in the section in the same time interval is

$$A . dl \left(\frac{\partial c}{\partial T}\right)_l . dT$$

Hence we have

$$-V\left(\frac{\partial c}{\partial l}\right)_T dl . dT = A . dl \left(\frac{\partial x}{\partial T}\right)_l dT + A . dl \left(\frac{\partial c}{\partial T}\right)_l . dT$$

i.e.,

$$-V\left(\frac{\partial c}{\partial l}\right)_T = A\left[\left(\frac{\partial x}{\partial T}\right)_l + \left(\frac{\partial c}{\partial T}\right)_l\right]$$

Or if $V/A = L$, the linear velocity of the gas, we obtain

$$-\frac{\partial c}{\partial l} = \frac{1}{L}\left[\frac{\partial x}{\partial T} + \frac{\partial c}{\partial T}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This is the fundamental equation for the removal of gas in the column and is independent of any assumptions as to the particular mechanism by which the removal is brought about, or of the kinetics of the removal.

To proceed further we must introduce an expression for the rate of removal of gas from the stream, and to obtain a reasonably simple mathematical treatment the following assumptions are made.

(1) The rate of removal of the gas is proportional both to the concentration of the gas in the stream and to the concentration of " active centres " remaining in the material at any given time. We thus have the relation

$$\partial x/\partial T = kcN$$

where k is a constant, c is the concentration of gas, and N is the number of active centres per c.c. of material.

(2) The active centres do not retain their activity indefinitely. If the gas is being adsorbed, the material becomes saturated with vapour and those parts of the surface which have been " active " become inactive, while if the gas is removed chemically the catalytically active centres become poisoned. We shall assume that, on an average, each active centre deals with n molecules of gas before becoming inactive. If the actual number of active centres per c.c. is N_0', then we may treat these as $nN_0' = N_0$ active centres of unit activity. The factor n is not in practice determinable.

(3) The heat of reaction, or of adsorption, is conducted away immediately.

(4) If local changes of water content of the column occur, they do not alter appreciably the rate of removal of the gas.

In practice the temperature of the adsorbing layer often increases, and breakdown times are dependent on the water content of the material, so that deviations from the theory are most likely to occur when the last two assumptions are unjustified.

Substitution of the above expression for $\partial x/\partial T$ in equation (8) gives

$$-\frac{\partial c}{\partial l} = \frac{1}{L}\left[kcN + \frac{\partial c}{\partial T}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Before proceeding to the general solution of this equation we may first consider conditions under which, contrary to assumption (2) above, the active centres retain their activity indefinitely. N is thus constant and (9) can be solved directly, giving

$$c = c_0\,e^{-kN_0l/L}$$

or
$$\ln c - \ln c_0 = -\,kN_0l/L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Thus the concentration of the gas falls off exponentially along the column, and the concentration at any point remains constant independent of the time. Hence, if at any given length the concentration is less than the critical concentration for breakdown, the breakdown time for a column of this length is infinity. In practice this ideal case is rarely observed. The solution just obtained, however, arises at zero time when none of the active centres has been used up; the relation (10) is thus the condition which the general solution of (8) must satisfy when T is zero.

The more general case is that in which the active centres are poisoned progressively and the column gradually breaks down. Since each hypothetical active centre, in the sense defined above, deals with one gas molecule and then becomes inactive, the rate of decrease in the number of active centres is equal to the rate of increase in the number of molecules removed from the stream.

Thus
$$-\frac{\partial N}{\partial T} = \frac{\partial x}{\partial T} = kcN \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

These simultaneous equations may now be taken with (8) and solved to obtain c as a function of both l and T.* This integration gives the general solution

$$c = \frac{f'(u)}{g(v) + k\,.\,f(u)}$$

where $u = T - l/L$, $v = -l/L$, and $f(u)$ and $g(v)$ are arbitrary functions of u and v respectively. The particular solution required is obtained by introducing the boundary conditions. These are, first, that when $l = 0$, *i.e.*, at the boundary of the column at which the gas enters, the concentration of gas is c_0, and second, that at zero time the concentration falls off exponentially as given by (10).

This leads finally to the relation

$$c = \frac{c_0}{e^{-kc_0T}\,(e^{kN_0l/L} - 1) + 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The concentration of gas escaping through a column of length λ is given by putting $l = \lambda$ in (12). On rearrangement this gives

$$\frac{c_0}{c} - 1 = (e^{kN_0\lambda/L} - 1)\,e^{-kc_0T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

so that
$$\ln\,(c_0/c - 1) = -\,kc_0T + \ln\,(e^{kN_0\lambda/L} - 1) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

In the early stages of breakdown, therefore, when c_0/c is large the graph of $\ln 1/c$ against T should be linear, the slope of the line giving the value of k for the removal of the gas. Later, when c_0/c is not large compared with unity, deviations from this relation are to be expected.

As before, we define the breakdown time, τ, as the time at which the concentration of gas escaping reaches some specified value c'. Putting $c = c'$ and $T = \tau$ in (14) and rearranging, this leads to

$$\tau = \frac{1}{kc_0}\,[\ln\,(e^{kN_0\lambda/L} - 1) - \ln\,(c_0/c' - 1)] \quad . \quad . \quad . \quad . \quad . \quad (15)$$

* We are indebted to Dr. J. H. C. Whitehead for the solution.

Effect of Column Length.—Equation (15) can be written in the form

$$\tau + \tau_0 = \frac{1}{kc_0} \ln \left(e^{kN_0\lambda/L} - 1 \right) \Bigg\}$$

where

$$\tau_0 = \frac{1}{kc_0} \ln \left(c_0/c' - 1 \right) \qquad \qquad \qquad (16)$$

From the values of k and N_0 given later it is seen that we may usually neglect unity in comparison with $e^{kN_0\lambda/L}$ so that we may write

$$\tau + \tau_0 = \frac{N_0}{c_0 L} \cdot \lambda \qquad \qquad \qquad (17)$$

In this form the equation is more readily interpreted while becoming only slightly less exact.

The graph of breakdown time against column length should be linear, the intercept on the τ axis being $-\tau_0$. Alternatively, on rearrangement,

$$\tau = \frac{N_0}{c_0 L} \left[\lambda - \lambda_c' \right] \qquad \qquad \qquad (18)$$

where λ_c' is the critical length below which the column breaks down immediately and is given by the relation

$$\lambda_c' = \frac{c_0 L}{N_0} \cdot \tau_0 = \frac{L}{kN_0} \ln \left(c_0/c' - 1 \right) \qquad \qquad (19)$$

However, from equation (10), when $T = 0$, the critical concentration is exceeded at all points along the column less than

$$\lambda_c = \frac{L}{N_0 k} \ln c_0/c' \qquad \qquad \qquad (20)$$

Thus the value of λ_c obtained by extrapolation of the linear portion of the column length–breakdown time curve differs from the true value by the factor

$$\ln \left(c_0/c' - 1 \right) / \ln c_0/c'.$$

When c_0/c' is large, the difference between the two values of λ_c is negligible, and it follows that the deviation from the linear relation predicted above is also negligible. Thus for most practical purposes we may use equation (17) or (18) in discussing breakdown phenomena.

Effect of Flow-rate.—(a) *If* k *is independent of flow-rate.* (18) and (19) may be rearranged in the form

$$\tau = \frac{N_0\lambda}{c_0} \left(\frac{1}{L} - \frac{1}{L_c} \right) \qquad \qquad \qquad (21)$$

where

$$L_c = \frac{N_0 k\lambda}{\ln \left(c_0/c' - 1 \right)} \qquad \qquad \qquad (22)$$

Thus a linear relation should exist between the reciprocal of the flow-rate and the breakdown time, and the breakdown time is zero at flow-rates greater than the critical flow-rate L_c.

The critical length and the critical flow-rate are closely related as we see by comparing equations (19) and (22). This may be further illustrated by putting $L = V/A$ in (17), whereupon

$$\tau + \tau_0 = \frac{N_0}{c_0 V} \cdot \lambda A$$

λA is, however, the volume of the column, W, so that

$$\tau + \tau_0 = \frac{N_0}{c_0 V} W \qquad \qquad \qquad (23)$$

Therefore since τ_0 is independent of L, the breakdown time of a column which has to deal with a volume V of gas per unit time is determined by the total volume of the adsorbent and is not dependent on the ratio of the cross-section of the column to its length. Corresponding to the critical length and the critical flow-rate there is of course a related critical volume.

(b) *If* k *depends on the flow-rate.* The removal of a vapour molecule from the air stream may be regarded formally as taking place in two stages. First, the molecule has to diffuse from the flowing air stream, through a layer of motionless air close to the surface, and secondly, the molecule is adsorbed or converted into products by an action taking place on the surface. The rate of removal will be determined by the slower of the two processes, and for different gases and different materials the rate-determining step is not necessarily the same.

If the rate-determining step is the surface reaction, then the formulæ derived above are valid. On the other hand, if the diffusion process determines the removal rate, then minor modifications have to be made in accordance with the following considerations.

The rate of a heterogeneous reaction governed by a diffusion process is usually given by an equation of the form introduced by Nernst :

$$\frac{dx}{dt} = \frac{DF}{\delta}(c - c^*) \qquad \ldots \ldots \ldots \ldots \qquad (24)$$

where D is the coefficient of diffusion of the reacting gas in air, F is the " effective area " of exposed surface, δ is the thickness of the immobile layer, c is the concentration in the air stream, and c^* is the vapour pressure of the gas over the adsorbed surface film. This is essentially the same as equation (11) when c^* is small and F is equated to N_0. The rate constant k is then given by

$$k = D/\delta \qquad \ldots \ldots \ldots \ldots \ldots \qquad (25)$$

Experimental evidence indicates that the hypothetical thickness δ depends on the rate of flow of the gas according to an expression of the form

$$\delta = \left(\frac{\delta_r}{L}\right)^n \qquad \ldots \ldots \ldots \ldots \ldots \qquad (26)$$

where δ_r and n are constants : n usually has a value of about $\frac{1}{2}$. Thus if the rate of diffusion governs the adsorption rate we shall expect k to vary with the flow-rate in the following way :

$$k = k_D \cdot L^{\frac{1}{2}} \qquad \ldots \ldots \ldots \ldots \ldots \qquad (27)$$

where k_D is proportional to the diffusion constant of the gas in air.

Consequently, we must substitute this expression for k in the equations derived above. This will alter the effect of the flow-rate upon quantities involving k.

Effect of Initial Concentration.—The variation of breakdown time with initial concentration of gas is less easy to express simply. We have, however, that

$$\tau = \frac{1}{kc_0}\left\{\frac{kN_0\lambda}{L} - \ln\frac{c_0}{c'}\right\} \qquad \ldots \ldots \ldots \ldots \qquad (28)$$

so that provided $kN_0\lambda/L \gg \ln c_0/c'$ (*i.e.*, when c_0 is sufficiently small), the breakdown time is inversely proportional to c_0. As c_0 increases, however, the relation deviates steadily from linearity.

Effect of Granule Size.—The above theory applies equally to a column consisting of a single piece of porous material or of a large number of granules. The experiments refer to columns consisting of closely packed granules, and we require to know how the properties of the column depend upon the size of the granules.

The behaviour of each solid–gas system is determined by the two quantities k and N_0. Since k measures the rate of removal of the gas from the air stream, we do not expect it to depend on the size of the granules. Consequently, any changes in the properties of the column with granule size will be due to the effect of granule size on the value of N_0. Now N_0, the " number of active centres " per c.c. of adsorbent, is proportional to the " effective area of exposed surface " in one c.c. of the column, and this in turn depends on the actual surface area of the granules. For a large number of closely packed spheres of equal size, the volume occupied by a given mass is independent of the radius of the spheres provided that the radius remains small compared with the dimensions of the container; the apparent density is independent of the degree of subdivision. The number of particles present in a given volume is, however, inversely proportional to the cube of the radius, while the surface area of each granule is directly proportional to the square of the radius. Consequently, the total surface area of the particles in a given volume will vary inversely with the first power of the radius. If active centres in the core of the particles do not contribute to the adsorptive capacity, then

$$N_0 = Q/d \qquad \ldots \ldots \ldots \ldots \ldots \qquad (29)$$

where Q is a constant and d is the diameter of the particles.

However, the essential property of an adsorbent is porosity, and the " number of active centres per c.c." is proportional to the *accessible* area. Subdivision results in an increase in the accessible surface which is much less than in proportion to the increase in the area of the formal geometrical boundary of the granule. Further, the accessible area of a given amount of porous material approaches a finite limit as the granule size is reduced and all the pores become accessible from the surface of the granule.

Thus a more rational relation between N_0 and d is of the form

$$N_0 = S \cdot f(d)$$

where $f(d) \longrightarrow 1$ as $d \longrightarrow 0$ and decreases as d increases; S is the limiting value of N_0 when d is very small.

The exact form of the function is not readily obtained theoretically : we write therefore

$$f(d) = 1 - \alpha d + \beta d^2 \qquad \ldots \ldots \ldots \ldots \qquad (30)$$

and determine experimentally the relative importance of successive coefficients. As will be shown, only the first two terms are important, so that

$$N_0 = S(1 - \alpha d) \qquad \ldots \ldots \ldots \ldots \qquad (31a)$$

The complete breakdown time equation now becomes

$$\tau = \frac{\lambda}{c_0 L} S(1 - \alpha d) - \frac{1}{k c_0} \ln c_0/c' \qquad \dotfill \qquad (31b)$$

and the critical length is given by

$$\lambda_c = \frac{L}{k S(1 - \alpha d)} (\ln c_0/c' - 1) \qquad \dotfill \qquad (31c)$$

Thus decrease in the granule size decreases the critical length and increases the breakdown time. Furthermore, the slope of the column length–breakdown time graph is a linear function of the granule diameter. The value of $-\tau_0$, the intercept of the column length–breakdown time graph on the τ axis is, however, independent of the granule size, so that for a series of similar materials of different granule sizes the column length–breakdown time curves should consist of a pencil of straight lines intersecting on the τ axis at $-\tau_0$.

Distribution of Gas in the Column.—The refinements introduced in the more exact treatment, although giving them a sounder foundation, do not result in any important modifications in the breakdown formulæ; the limitations of the approximate treatment become apparent, however, when we consider the distribution of the vapour both in the gaseous phase and on the solid in the column.

(a) *In the gas phase.* The distribution in the gas phase at various distances along the column is given at time T by equation (12) which may be written in the form

$$\ln (c_0/c - 1) = \ln (e^{k N_0 l/L} - 1) - k c_0 T \qquad \dotfill \qquad (32)$$

When l is large and c is small then

$$\ln c_0/c = \frac{k N_0 l}{L} - k c_0 T \qquad \dotfill \qquad (33)$$

The graph of $\ln c$ against l should then be a straight line of slope $k N_0/L$. At smaller distances along the column, deviations from this simple form [which also follows directly from equation (4) of the approximate treatment] become large.

(b) *On the solid.* The way in which we have defined an " active centre " is such that the amount of gas which has been adsorbed on or removed by a given element of material is equal to the number of active centres which have been exhausted. The concentration of active centres left at time T, at a distance l along the column is given by

$$N_{l,T} = N_0 - x_{l,T} \qquad \dotfill \qquad (34)$$

where $x_{l,T}$ is the concentration of adsorbed gas or reaction product per c.c. of material at this point. Taking this equation with (11) and (12), we have

$$\frac{dx}{dT} = \frac{k c_0 (N_0 - x)}{[e^{-k c_0 T} (e^{k N_0 l/L} - 1) + 1]}$$

Thus

$$\int_0^x \frac{dx}{N_0 - x} = \int_0^T \frac{k c_0 \, dT}{[e^{-k c_0 T} (e^{k N_0 l/L} - 1) + 1]}$$

Integration of this gives

$$\ln \frac{N_0}{N_0 - x} = \ln [e^{-k N_0 l/L} (e^{k c_0 T} - 1) + 1]$$

This can be rearranged to give

$$\left. \begin{aligned} \ln \frac{x}{N_0 - x} &= -\frac{k N_0 l}{L} + \ln (e^{k c_0 T} - 1) \\[2mm] \ln \frac{x}{N_0 - x} &= -\frac{k N_0 l}{L} + k c_0 T \end{aligned} \right\} \qquad \dotfill \qquad (35)$$

or approximately, when T is large,

Thus at a given time, $\ln x/(N_0 - x)$ should fall off linearly with l, while at a given distance along the column, it should increase approximately linearly with the time. Alternatively, we can rearrange (35) to give

$$\frac{x}{N_0} = \frac{c}{c_0} (1 - e^{-k c_0 T}) \qquad \dotfill \qquad (36)$$

which shows that at a given time the concentration of gas or product which has accumulated is proportional to the concentration of gas in the gas phase at the same distance along the column.

Total Amount of Gas Penetrating the Column.—The breakdown time of a column has been defined as the time at which the concentration of escaping gas exceeds an arbitrarily chosen value c'. Experimentally, however, it is often more convenient to determine the time at which the *total amount* of gas which has penetrated the column reaches a certain value γ'. The equations obtained above correspond to the first definition. It is

of interest, therefore, to consider the equations obtained when the breakdown time is defined by the latter criterion.

The total amount of gas escaping through the column in a time T is given by

$$\gamma = L \int_0^T c \, . \, \mathrm{d}T \text{ per unit cross section.}$$

Substituting for c from (12), we obtain

$$\tau_{\gamma'} = \frac{1}{kc_0} \ln \left[e^{kN_0\lambda/L} \left(e^{k\gamma'/L} - 1 \right) + 1 \right] \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (37)$$

It may be noticed that, whereas the condition for the approximation made in passing from (16) to (17) is

$$e^{kN_0\lambda/L} \gg 1 \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (i)$$

yet in the present case the corresponding one would be

$$e^{kN_0\lambda/L} \left(e^{k\gamma'/L} - 1 \right) \gg 1 \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (ii)$$

It is easily shown that corresponding to the usual breakdown criteria $e^{k\gamma'/L} - 1 < 1$, so that condition (ii) holds less exactly than (i) at a given column length. Consequently, on decreasing λ or increasing L, deviations from the simple linear relations should appear sooner if we take the γ' criterion instead of the c' criterion of breakdown.

Comparing (15) with (37), we see that the form of the breakdown equation is not altered by changing the criterion of breakdown. The slope of the column length–breakdown time curve is the same but the intercept on the τ axis is now given by

$$(\tau_0)_{\gamma'} = \frac{1}{kc_0} \ln \left(e^{k\gamma'/L} - 1 \right)^{-1} \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (38)$$

instead of by

$$(\tau_0)_{c'} = \frac{1}{kc_0} \ln \left(c_0/c' - 1 \right) \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (16)$$

Similarly, in the other formulæ $(e^{k\gamma'/L} - 1)^{-1}$ occurs in place of $c_0/c' - 1$. The two criteria of breakdown thus become identical if we choose γ' and c' so that

$$(c_0/c' - 1)(e^{k\gamma'/L} - 1) = 1$$

i.e.,

$$c'/c_0 = 1 - e^{-k\gamma'/L} \quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (39)$$

Thus if we determine the value of c' which corresponds to a chosen breakdown criterion γ' for a given material at a certain flow-rate, then γ' will correspond to a different value of c' if we change the flow-rate or use another material for which the value of k is different.

The effect of changing L on the value of $(\tau_0)_{\gamma'}$, as compared with $(\tau_0)_{c'}$ is seen by the following rough calculation.

If under given conditions γ' corresponds to $c'/c_0 = 0.01$, then $e^{k\gamma'/L} - 1$ has the value of 0.01 also, and $\ln (e^{k\gamma'/L} - 1)^{-1} = 4.6$. If the value of L is doubled, this value changes by 0.7 approximately, *i.e.,* by about 15%; $(\tau_0)_{c'}$ is unchanged by the change in L (if k is independent of L). A change of 15% in the value of τ_0 corresponds to a change of not usually more than 10% of the breakdown time for a 6-cm. column. Similar considerations apply to the effect of change in k, and it is seen that no very serious differences will be likely to occur in practice if we find it more convenient to use the γ' criterion rather than the c' criterion.

Survey of Experimental Results.

In this section are collected together a representative series of experimental results to illustrate the formulæ above. The material used was granular active charcoal, and the uptake of various gases by this was studied. No attempt has been made to present all the available data, but only sufficient to demonstrate the general validity of the relationships.

The charcoals used were either standard commercial active carbons or charcoals of increased catalytic activity prepared from them by chemical impregnation in the laboratory. Similarly named charcoals are not necessarily identical; separate batches of the small-scale laboratory preparations vary somewhat among themselves. There is, however, no reason to believe that any important difference in behaviour is shown by different charcoals of a given type.

Details of the charcoals used are as follows :

A.1 Steam activated coconut-shell charcoal of low adsorptive capacity.

A.2 ditto, medium adsorptive capacity.

A.3 ditto, high adsorptive capacity.

B   Steam-activated, briquetted coal, medium adsorptive capacity.

C   Charcoal A.2 impregnated with silver nitrate.

D   Charcoal B, containing copper.

E   Charcoal B, containing CuO and MnO_2.

F   Charcoal B, impregnated with iodic acid.

G   Charcoal B, impregnated with ammonium vanadate.

H   Charcoal A.2 containing copper.

J   Charcoal A.2 impregnated with iodic acid.

Fig. 1.
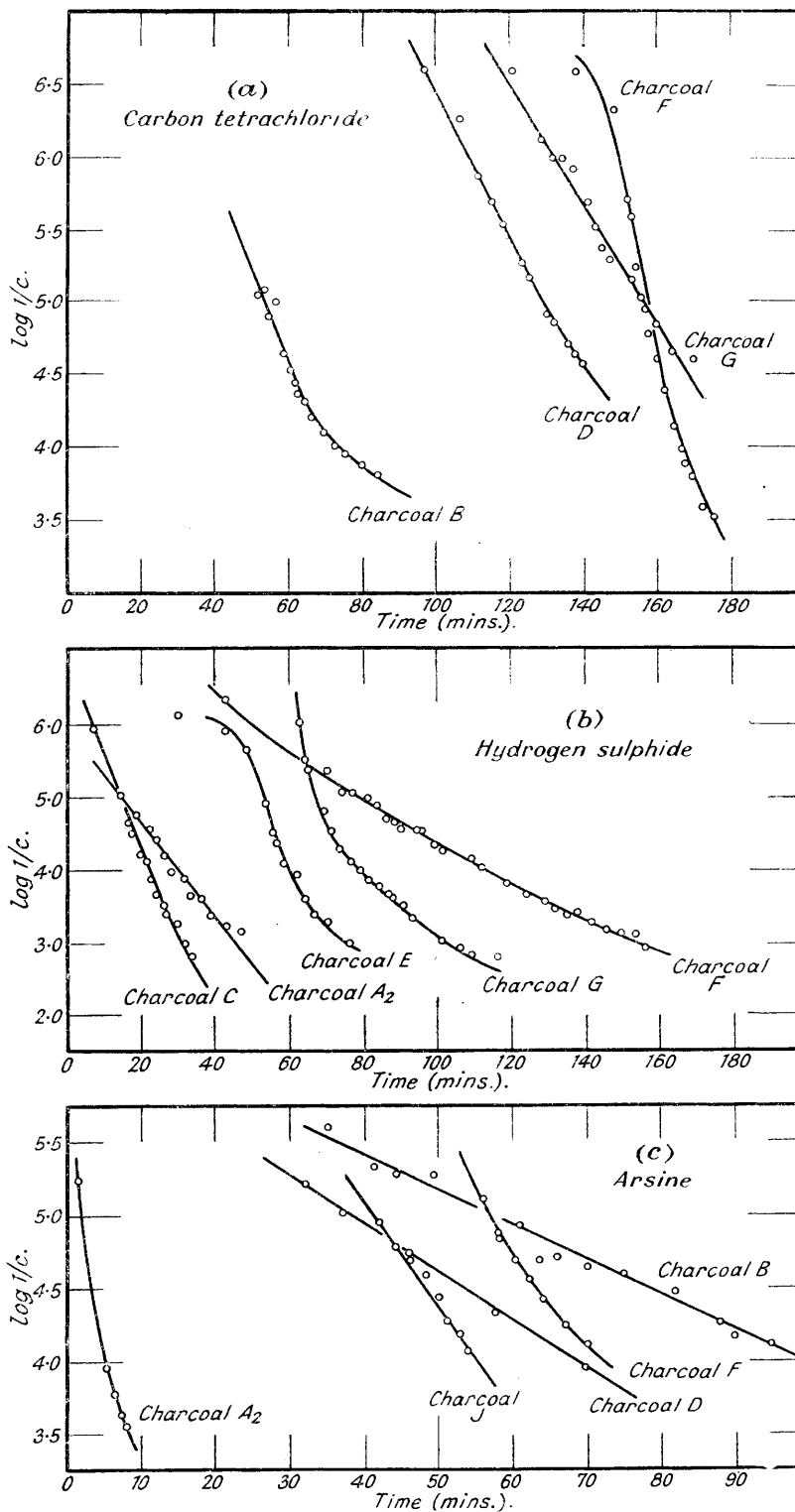
Variation of $\log \left(\dfrac{1}{escaping\ concentration} \right)$ with time for various charcoals :
(a) carbon tetrachloride, (b) hydrogen sulphide, (c) arsine.

All the charcoals were tested when containing 16% of moisture. Except where otherwise stated they were in the form of granules graded between 8 and 18 B.S.S. sieve sizes.

In all experiments columns of charcoal 1 cm. in diameter were used. The column length was 6 cm., and the flow-rate of the air stream 200 c.c./min., except where the effect of variation in these quantities was being investigated.

Many gases were used but the results given below refer mainly to arsine, hydrogen sulphide, and carbon tetrachloride. Of these the first two satisfy the condition of being irreversibly destroyed on active charcoal (by oxidation).

Relation between Escaping Concentration and Time.—Equation (14) predicts that on plotting the logarithm of the concentration of gas escaping from the column against the time a straight line should be obtained. Results are shown graphically in Figs. 1(a), 1(b) and 1(c).

In general, the linear relationship is followed over an appreciable range of concentration. At higher concentrations we expect deviations from linearity, while at low concentrations experimental difficulties

FIG. 2.
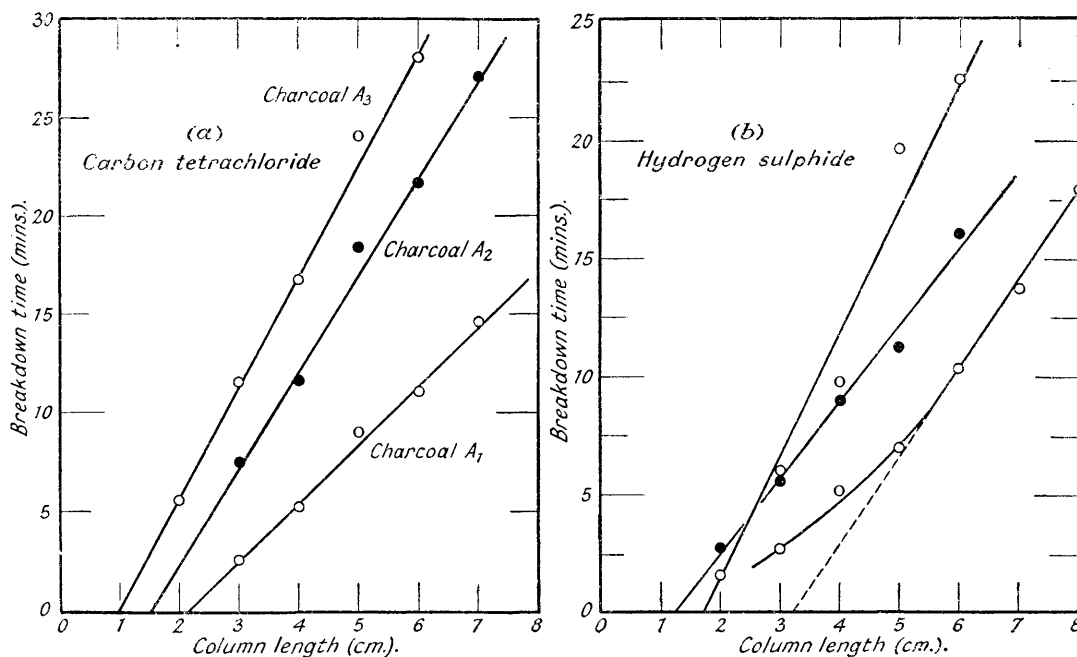
Effect of column length on breakdown time : (a) *carbon tetrachloride,* (b) *hydrogen sulphide.*

make the exact determination of the curves difficult. The slope of each of these lines gives the value of kc_0 and hence k for each gas–charcoal combination.

Effect of Column Length.—In Figs 2(a) and 2(b) are plotted results for the effect of column length on the breakdown of several charcoals towards two typical gases. In general, the linear relation predicted between the breakdown time and the column length is well obeyed. The values of the critical column length under which breakdown, under the conditions used, is instantaneous are seen to vary from about 1 cm. to 3 cm. N_0, the concentration of active centres, may be calculated from the slope of the column length–breakdown time curves.

Effect of Flow-rate.—According to equation (21) a linear relation should exist between the breakdown time and the reciprocal of the flow-rate, the intercept on the $1/L$ axis giving the value of the critical flow-rate above which the column of charcoal breaks down instantaneously. The flow-rate and the column length effects are closely related, and change in flow-rate alters the critical length and the slope of the column length–breakdown time curves.

Table I contains the results of experiments in which both column length and flow-rates were varied.

The breakdown of the charcoal was followed over a range of escaping concentrations and the rate constant k evaluated (Table II, col. 2). It is seen that this constant depends on the flow-rate, and in col. 6 the approximate constancy of $k/L^{\frac{1}{2}}$ suggests that we are dealing with a process governed by the rate of diffusion of the vapour.

In Fig. 3(a) are plotted the column length–breakdown time curves at different flow-rates. The intercepts λ_c and τ_0 depend on the flow-rates. λ_c is proportional, and τ_0 inversely proportional, to $L^{\frac{1}{2}}$ as shown in cols. 7 and 8 of the table. The slope of the lines ($d\tau/d\lambda$) is inversely proportional to L (col. 9).

The relation between τ and $1/L$ is shown in Fig. 3(b). The critical flow-rate appears to vary with column length as indicated by equation (22). The results are not sufficiently accurate, however, to provide more than a qualitative verification of the relation.
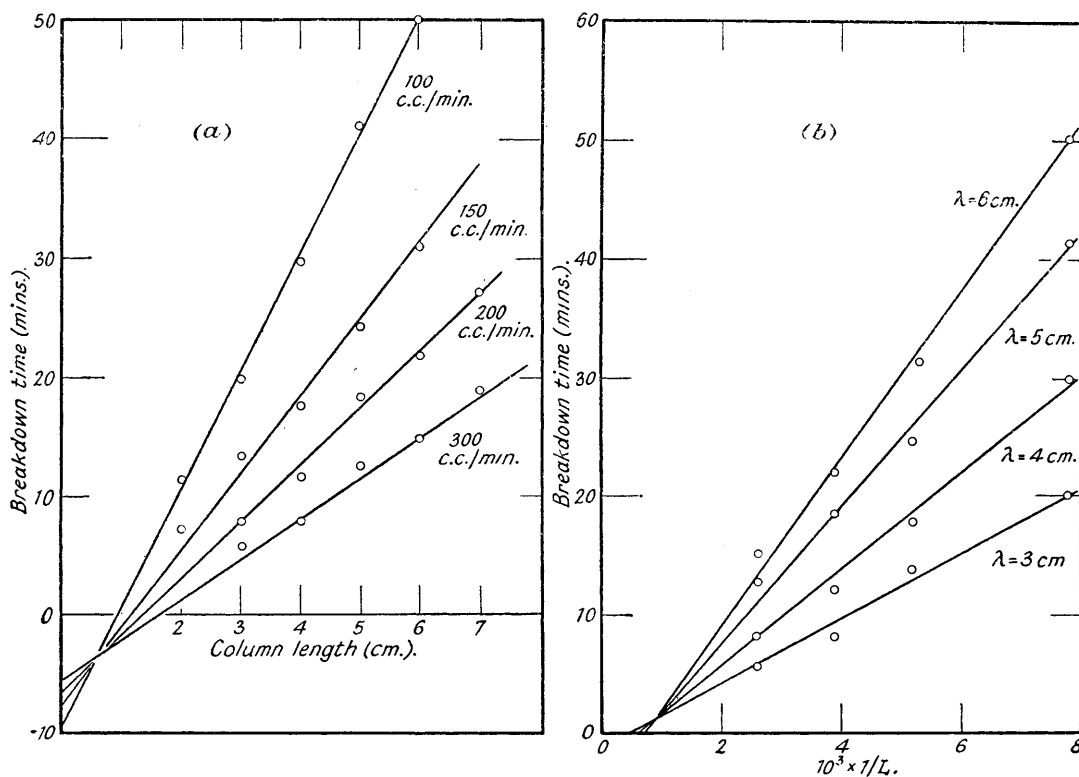
TABLE I.

Charcoal A.2, graded 10—12 B.S.S.

Carbon tetrachloride, $c_0 = 2\cdot16\%$.

	$L = 128$ cm./min.			$L = 192$ cm./min.			$L = 256$ cm./min.			$L = 384$ cm./min.	
λ.	τ.	$\dfrac{kc_0}{2\cdot3}$.	λ.	τ.	$\dfrac{kc_0}{2\cdot3}$.	λ.	τ.	$\dfrac{kc_0}{2\cdot3}$.	λ.	τ.	$\dfrac{kc_0}{2\cdot3}$.
2·0	11′ 28″	0·30	2·0	7′ 10″	0·24	3·0	7′ 40″	—	3·1	5′ 45″	0·41
3·0	19 47	0·24	3·0	13 30	0·31	4·0	11 35	—	4·0	7 47	0·39
4·0	29 41	0·24	4·0	17 29	0·35	5·0	18 20	—	5·0	12 28	0·34
5·0	42 12	0·22	5·0	24 13	0·32	6·0	21 40	0·34	6·0	14 47	0·37
6·0	51 25	0·25	6·0	30 56	0·37	7·0	27 00	—	7·0	18 50	0·38
	Mean 0·25			Mean 0·32			Mean 0·34			Mean 0·38	

FIG. 3.

Effect of column length and flow-rate on breakdown time for carbon tetrachloride : Charcoal A.2.

The relationship between the breakdown time and the total volume of charcoal, as expressed by (23), may also be illustrated. Table III gives the values of λ required to obtain a predetermined breakdown time at different flow-rates. The ratio of the column length to the flow-rate is given, and in the last column are the volumes of charcoal required to give the stated breakdown times.

It is seen that for arsine and hydrogen sulphide the volumes required are independent of the flow-rate. For carbon tetrachloride and ammonia there is a slight increase in the requisite volume for low flow-rates,

TABLE II.

L.	k.	λ_c.	τ_0.	$d\tau/d\lambda$.	$k/L^{\frac{1}{2}}$.	$\lambda_c/L^{\frac{1}{2}}$.	$\tau_0 L^{\frac{1}{2}}$.	$L(d\tau/d\lambda)$.
128	600	0·95	9·5	10·0	53	8·4	108	1280
192	760	1·15	7·5	6·3	56	8·4	103	1220
256	810	1·30	6·3	4·7	51	8·2	101	1200
384	910	1·60	5·5	3·4	47	8·2	108	1300

corresponding to a short, wide column. This effect may be accounted for by the dependence of k on the flow-rate for these two gases.

TABLE III.

Total flow, 16 litres/min.

		W, c.c.					W, c.c.		
L, c.c./sq. cm. per min.	A, sq. cm.	Charcoal A.2, 10—12 B.S.S.	Charcoal A.3, 10—12 B.S.S.	Charcoal B, 10—12 B.S.S.	L, c.c./sq. cm. per min.	A, sq. cm.	Charcoal B, 14—16 B.S.S.	Charcoal F, 10—12 B.S.S.	Charcoal D, 10—12 B.S.S.
Carbon tetrachloride, $c_0 = 2 \cdot 16\%$. Required breakdown time, 26 mins.					Arsine, $c_0 = 0 \cdot 50\%$. Required breakdown time, 75 mins.				
128	125	450	—	—	192	83·5	440	465	455
192	83·5	435	335	490	255	62·5	450	430	455
255	62·5	430	315	445	320	50·0	455	500	430
320	50·0	—	300	410					
384	41·5	390	—	—					

		Ammonia, $c_0 = 1\cdot00\%$. Required breakdown time, 40 mins.					Hydrogen sulphide, $c_0 = 2\cdot56\%$. Required breakdown time, 23 mins.	
		Charcoal A.3, 10—12 B.S.S.	Charcoal A.3, 16—18 B.S.S.	Charcoal C, 7—18 B.S.S.			Charcoal B, 12—14 B.S.S.	Charcoal D, 10—12 B.S.S.
192	83·5	960	810	775	192	83·5	415	375
255	62·5	940	750	640	255	62·5	415	375
320	50·0	925	700	630	320	50·0	420	350

Effect of Initial Concentration.—The results of a series of experiments on the effect of initial concentration on breakdown times are given in Fig. 4(*a*), where τ is plotted against $1/c_0$ for a series of gases and charcoals. The existence of a critical initial concentration given by

$$(c_0)_c = c' \, e^{k N_0 \lambda / L}$$

above which the breakdown of a 6-cm. column is instantaneous is illustrated by the results for arsine on charcoal C and hydrogen sulphide on charcoal A.2. In the other cases shown the critical initial concentrations are very large so that the lines pass practically through the origin. In all cases these critical values are greater than 5%. Fig. 4(*b*) contains the same results, but here $1/\tau$ is plotted against c_0. It is seen that a pencil of lines through the origin is obtained, and that as c_0 increases deviations from linearity occur, the charcoal becoming relatively *less* efficient at higher concentrations.

The deviations from linearity are in the direction to be expected theoretically. The behaviour may, however, be complicated by temperature changes in the charcoal column. With high concentrations the temperature and the efficiency of the column will be considerably higher than with low, and this effect will tend

TABLE IV.

	Carbon tetrachloride. Charcoal A.2.		
	$c_0 = 1\cdot08\%$.	2·16%.	3·34%.
λ.	τ.	τ.	τ.
2·0	8′ 47″	—	—
3·0	17 47	7′ 40″	—
4·0	—	11 35	8′ 35″
4·5	29 08	—	—
5·0	—	18 20	11 36
6·0	40 50	21 40	15 44
7·0	—	27 00	19 05
8·0	—	—	24 14
$d\tau/d\lambda$, mins./cm.	8·5	4·8	3·4
λ_c, cm.	0·9	1·4	1·6
τ_0, mins.	8·0	4·7	3·4
$c_0 \, (d\tau/d\lambda)$	9·2	10·4	10·9

to operate in the opposite sense. Thus we may expect to find in different cases deviations from linearity in both senses. For practical purposes, however, we may regard $1/\tau$ as directly proportional to c_0 for small initial concentrations.

Effect of Initial Concentration on the Critical Length and the Critical Flow-rate.—The influence of the initial concentration on the variation of breakdown time with column length has been investigated for the adsorption of carbon tetrachloride by charcoal A.2. The results are given in Table IV. The critical length decreases with the initial concentration and, over the rather small range studied, equation (19), which predicts a linear relation between λ_c and log c_0, appears to hold. The inverse proportionality between $d\tau/d\lambda$ and c_0 is also confirmed within the experimental error.

Fig. 4.

Effect of initial concentration on breakdown time for various gases.
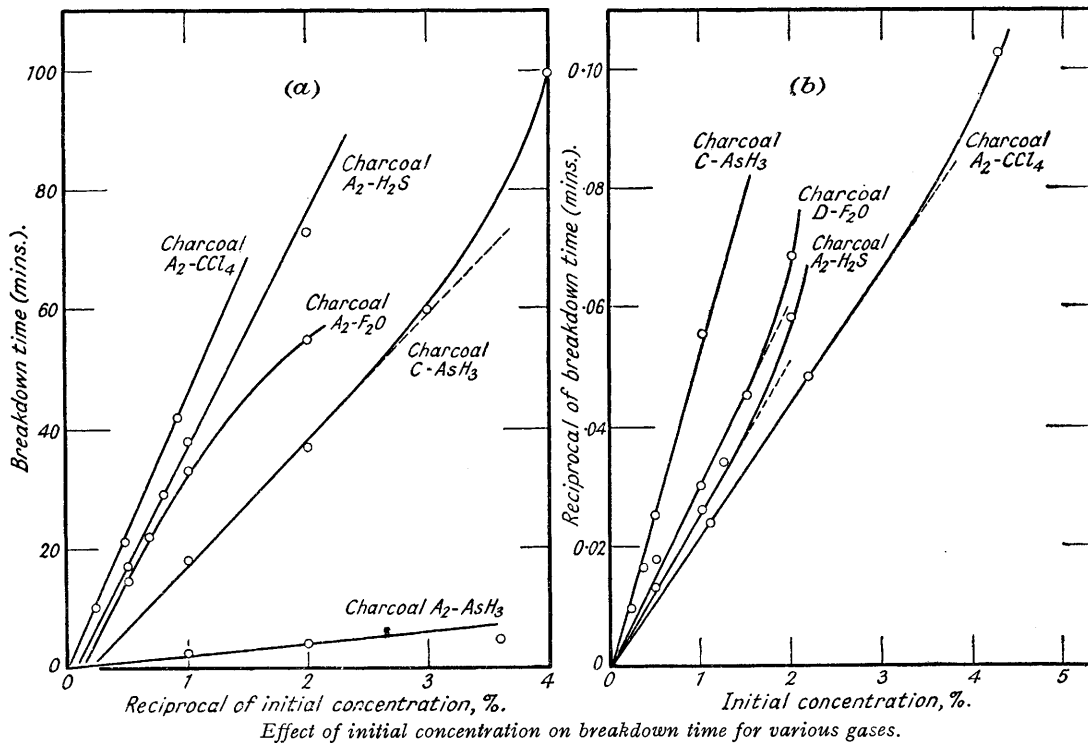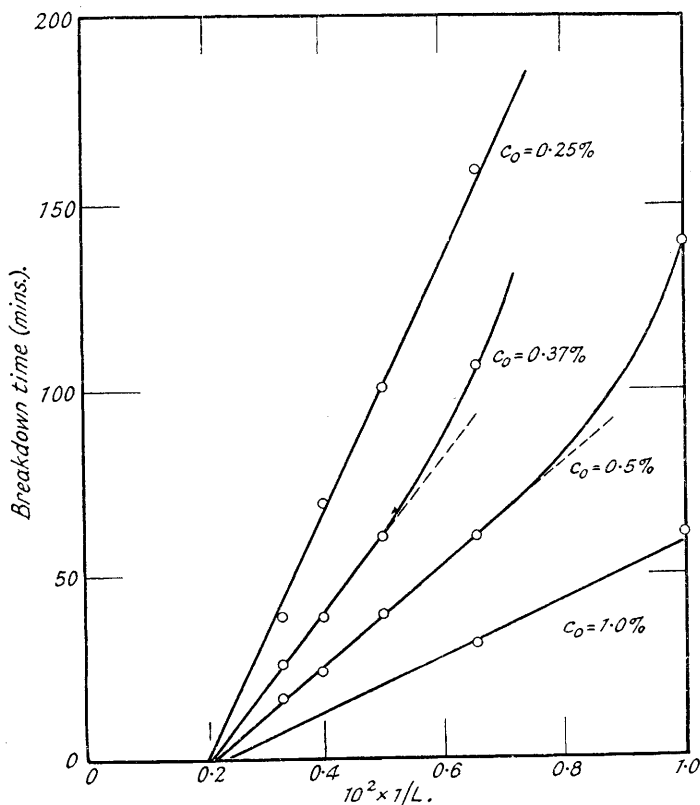
Fig. 5.

Effect of initial concentration and flow-rate on breakdown time for arsine : Charcoal C.

The variation of breakdown time with flow-rate has been studied at several different initial concentrations in the removal of arsine by charcoal C. The results are shown in Fig. 5, where the breakdown times are plotted against the reciprocal of the flow-rate : $1/L_c$ is found to vary linearly with log c_0 (equation 22) ; a 10-fold change in c_0 (from 1% to 0·1%) only increases the critical flow-rate from 600 to 850 cm./min. The slopes of the lines in Fig. 5 are proportional to $1/c_0$.

Effect of Granule Size.—If k is independent of granule size, equation (17) predicts that the column length–breakdown time curves for charcoals differing only in their granule sizes should consist of a pencil of lines intersecting on the τ axis at $-\tau_0$. Furthermore, the variation of the slopes of these lines with granule diameter will give the relation between N_0 and granule size.

Typical results are plotted in Fig. 6(a). The intercept on the τ axis of the graphs of τ against λ is nearly

FIG. 6.
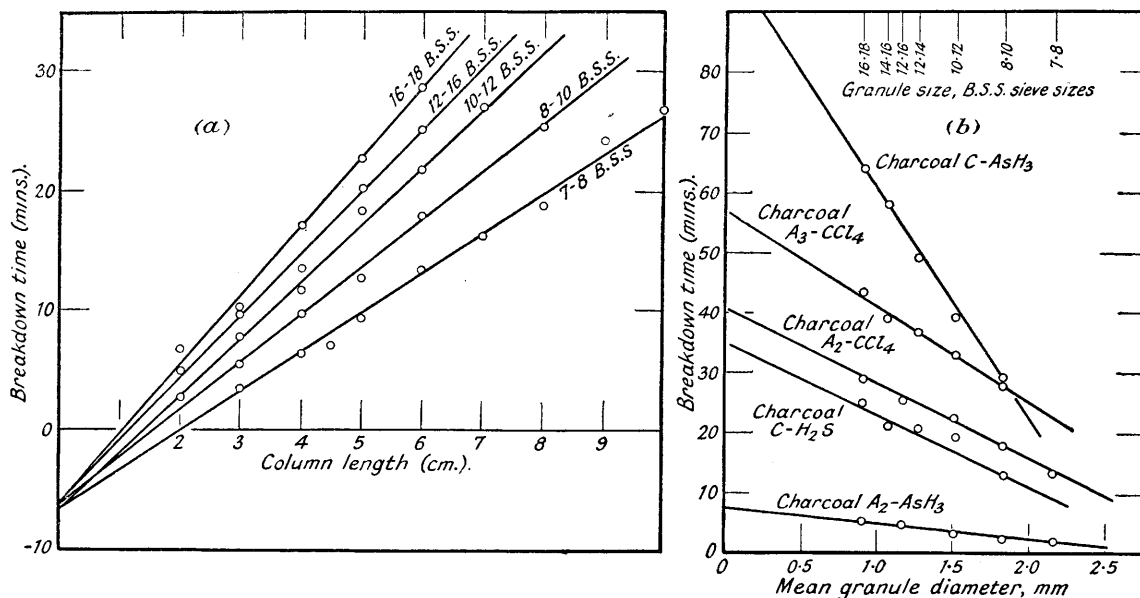
Effect of granule size on breakdown time : (a) *Column length–breakdown time relation for various granule sizes : carbon tetrachloride–charcoal A.2.* (b) *Relation between granule size and breakdown time for various gas–charcoal systems at constant column length (6 cm.).*

constant, thus confirming that k is independent of the granule size. On plotting the values of $d\tau/d\lambda$ against the mean granule size, linear graphs are obtained, showing that N_0 is of the form

$$N_0 = S(1 - \alpha d) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31a)$$

Equation (29) is thus shown to be invalid, and the coefficient of d^2 in equation (30) is negligible. In Fig. 6(b), τ is plotted against mean granule size for a series of gas–charcoal systems; these results confirm equation 31(b).

The above equation has been found to represent the effect of granule size for a large number of gas–charcoal pairs, the value of α for all these being $0·26 \pm 0·04$ when d is expressed in mm.

Distribution of Gas in the Column.—The simple treatment of the theory of breakdown gives no indication of the amount of gas dealt with by successive layers of charcoal as the deactivating wave proceeds along the column. The more complete treatment leads to equations giving the form of the distribution curves of gas held on the charcoal and of gas remaining in the air stream (equations 32 and 35). These equations should hold for systems in which the gas is removed irreversibly (*e.g.*, by chemical reaction), but they will be in error if appreciable desorption of the gas takes place. The amount of gas held by the charcoal at any point will then be less than that predicted by equation (35), the discrepancy increasing with the amount held.

The experiments described below illustrate the behaviour of two typical gases, *viz.*, arsine, which is irreversibly destroyed, and hydrogen cyanide, for which the desorption is considerable.

The distribution of arsine on the charcoal at various points in the column was investigated by direct analysis of small sections, preliminary experiments having shown that arsine is oxidised to a mixture of arsenate and arsenite on the charcoal surface.

Five sections of charcoal C, each weighing 0·7 g., were packed into the testing tube, the sections being separated by small cotton-wool pads. The arsine–air stream was passed for a given time, and the arsenic in each section was determined by extraction with hot alkali, reduction of the acidified extract with sulphur

dioxide, removal of excess sulphur dioxide, and titration of the neutralised sample with standard iodine. The results are contained in Table V.

TABLE V.

Time of passage of stream.	30'.	63'. (Breakdown.)	120'.
	Number of c.c. of AsH_3 dealt with by each section.		
1st Section	19·9	33·2	43·0
2nd ,,	10·7	24·4	37·8
3rd ,,	1·9	13·9	26·8
4th ,,	0·3	3·0	21·0
5th ,,	0·1	0·4	8·0

In Fig. 8(a), log $x/(N_0 - x)$ is plotted against the column length at three different times; approximately linear graphs are obtained of approximately the same slope. In this example equation (35) seems to be followed closely.

FIG. 7.
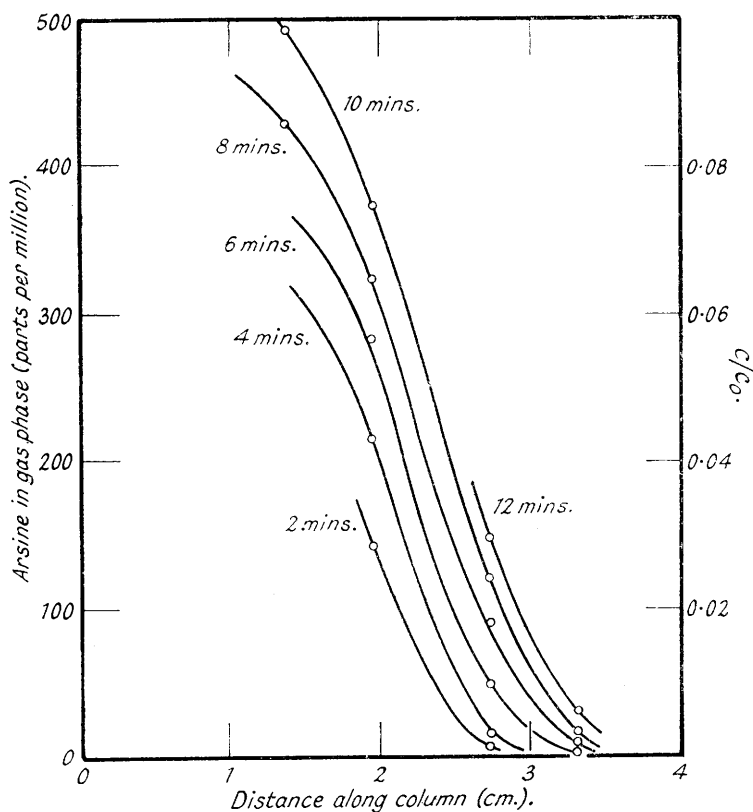
*Distribution of arsine in gas phase along column during breakdown (Charcoal C).*

To investigate the concentration of arsine in the gas phase at various points in the column during the initial stages, concentration–time curves for various column lengths of charcoal C were obtained. From these curves the concentrations leaking through at various times at different column lengths were read off. These concentrations were then plotted against the respective column lengths, giving the concentration gradients at various times (Fig. 7). The curves give a fair idea of how the concentration gradient moves along the column.

Similar experiments were made with hydrogen cyanide by a method to be described in detail in a later paper. The relation between log $x/(N_0 - x)$ and l for this system [Fig. 8(b)] is seen to depart from linearity as the amount of gas on the charcoal increases; the deviation is in the direction expected. The theory developed in this paper is, in fact, inadequate to predict the distribution curves for gases reversibly adsorbed on charcoal. A treatment of this problem is attempted in a later paper.

Discussion of k *and* N_0.—Table VI gives the experimentally determined values of k, N_0, and S for various gas–charcoal combinations. k has been determined either directly from the slope of the curves of log $1/c$ against time or from the intercept on the τ axis of the curves of column length against breakdown time : the

units are (g.-mol./l.)$^{-1}$(min.)$^{-1}$. Where direct comparison between values of k evaluated by the two methods is available, there is moderate agreement except for some results with arsine; the figures given are mean values. N_0 has been calculated from the slope of the column length–breakdown time graphs and is expressed in terms of the number of "active centres" of unit activity per c.c. of packed granular charcoal and refers to a standard

FIG. 8.
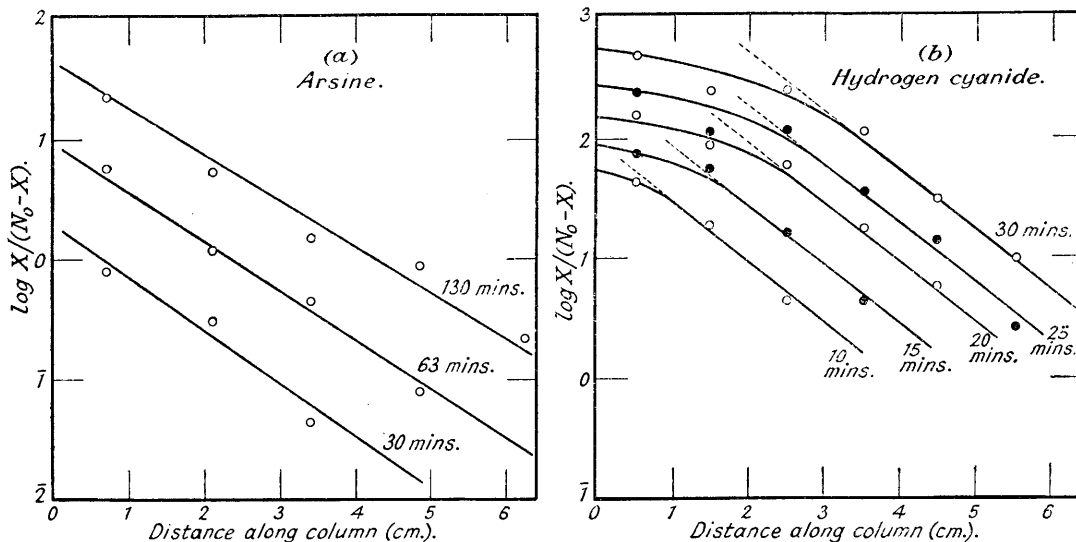
Distribution of adsorbed gas along column during breakdown : (a) *arsine,* (b) *hydrogen cyanide.*

TABLE VI.

Values of k, N$_0$, S, *and* α.

Charcoal.	k.	$N_0 \times 10^{20}$.	$S \times 10^{20}$.	a.	Mean k.	$k\sqrt{VD}$.
Carbon tetrachloride.
A.1	760	4·5	—	—		
A.2	755	7·2	11·3	−0·26		
A.3	870	8·7	16·5	−0·26	700	6100
B	660	—	—	—		
D	600	—	—	—		
Ammonia.
A.3	2240	2·0	3·2	−0·23		
C	1800	2·5	4·4	−0·28	2020	5760
Hydrogen cyanide.
A.3	1600	3·5	6·3	−0·29		
C	1600	4·2	8·1	−0·29	1600	5900
Chloropicrin.
A.2	615	—	—	—		
A.3	589	11·0	18·5	−0·24	620	5600
B	670	—	—	—		
Arsine.
A.2	4000	0·7	—	—		
B	240	—	—	—		
C	500	4·6	7·0	−0·28		
D	430	7·2	11·5	−0·28		
E	780	6·0	—	—	—	—
F	600	5·7	—	—		
H	550	6·4	—	—		
J	820	—	—	—		
Hydrogen sulphide.
A.2	475	7·0	—	—		
C	510	8·8	12·0	−0·24		
D	—	9·4	14·0	−0·21		
E	450	5·6	—	—	—	—
F	183	9·0	—	—		
J	146	—	—	—		

spectrum of granule sizes in the range 8—18 B.S.S. sieve sizes; S is the limiting value of N_0 when the granule size is indefinitely small.

It is immediately apparent that k and N_0 (or S) are quite independent properties of a gas–charcoal system, high values of N_0 being accompanied by both small and large values of k.

The Rate Constant, k.—The rate of removal of the gas may be determined either by the rate of diffusion to the surface, or by the rate of the process which occurs at the surface, whichever is the slower.

If diffusion determines the overall rate, then a dependence of k on the flow-rate is predicted. The experimental results in Table II show that for the adsorption of carbon tetrachloride k is proportional to the square-root of the flow-rate; similar, though less extensive, results are also available for ammonia, hydrogen cyanide, and chloropicrin. Further evidence that diffusion is the rate-determining step in these cases is provided by the figures in Table VI. For the above-mentioned gases k is the same for the various charcoals, and is determined only by the nature of the gas. The observed values of k should be proportional to the diffusion coefficients of the gases in air, which we may suppose to be roughly inversely proportional to the square-roots of the gas densities. The last column of Table VI shows that for carbon tetrachloride, ammonia, hydrogen cyanide, and chloropicrin, the product $k\sqrt{VD}$ is in fact constant within the experimental error.

For the oxidation of arsine and hydrogen sulphide on charcoal the values of k are practically independent of flow-rate but vary from one charcoal to another. This suggests that the chemical reaction on the surface determines the value of k. This view is strengthened by a consideration of the magnitude of k to be expected for these gases if diffusion were rate-determining. Taking the mean value of $k\sqrt{VD}$ for the adsorbable gases, we calculate $k = 1000$ for arsine and $k = 1530$ for hydrogen sulphide. These are both much greater than the observed values.

The Number of Active Centres, N$_0$.—As originally defined, N_0 is the total number of accessible active points, each of unit activity, per c.c. of charcoal. For gases removed by chemical reaction this quantity is directly proportional to the actual number of catalytically active centres. If the gas is removed by adsorption, however, the present treatment only applies strictly to " breakdown " phenomena and cannot account accurately for the behaviour of the system when the partial pressure of gas over the charcoal is high. We shall thus not expect to correlate N_0 with the saturation capacity of the gas under static conditions. N_0 will be rather the number of *possible* sites on which the gas could be adsorbed; at equilibrium only a fraction of these need be occupied. In this way N_0 will determine the rate of adsorption when the reverse process is negligible.

The absolute magnitude of N_0 for all the gases is of the order 10^{21}. The total number of carbon atoms in one c.c. of granulated charcoal is roughly 3×10^{22}, so that a high degree of availability of the carbon atoms in a granule is indicated.

The variation of N_0 with granule size, for nine gas–charcoal systems examined, follows with fair accuracy the relation $N_0 = S(1 - 0.26d)$. The coefficient 0.26 measures the way in which additional pores of the charcoal structure become available as the granule size is reduced. No simple geometrical interpretation of the expression has, however, been found.

For a given charcoal, the value of S varies with the gas. For adsorbed gases S increases with the molecular weight, the magnitude of the effect being itself dependent upon the charcoal.