

THE ADSORPTION WAVE¹

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CONTENTS

I. Introduction.....	241
II. Theories predicting effluent concentration as a function of time.....	243
A. Theories in which one step is rate-controlling.....	244
1. The general differential equation.....	244
2. Diffusion as the rate-controlling step.....	246
3. Adsorption or reaction on the surface as the rate-controlling step.....	247
B. Theories in which more than one step contributes to rate of removal.....	249
1. Diffusion in air and deposition on surface contributing.....	249
2. Diffusion in air and processes within the granule contributing.....	249
C. Comparison of theories with experiment.....	249
III. Semiempirical treatments.....	251
A. Factors affecting break-time.....	251
1. Nature of gas flow in charcoal.....	251
2. The effect of bed depth.....	253
(a) General character of life-thickness curves.....	253
(b) The Mecklenburg equation.....	254
(c) Curvature due to cumulative method of test.....	255
(d) Curvature in systems using instantaneous tests.....	255
3. The effects of velocity of flow, concentration, and particle size.....	256
(a) General equation for critical bed depth.....	256
(b) Mechanism of removal of some gases.....	260
4. Dependence of critical bed depth on adsorbent.....	262
(a) Effect of nature of adsorbent.....	262
(b) Effect of capacity of adsorbent.....	262
B. Equations for canister life.....	263
1. Cases in which diffusion in air is the rate-controlling step.....	263
2. Cases in which more than one step contributes to the rate.....	264
IV. Conclusions.....	265
V. References.....	266
VI. Appendix: meaning of symbols.....	267

I. INTRODUCTION

The general object in the study of the adsorption wave (8, 12, 24, 25, 28, 31, 37) has been to obtain an understanding of the various factors which determine the variation in concentration of a gas effluent from a bed of adsorbent. The study of the adsorption wave consists in the consideration, from an experimental and theoretical point of view, of the distribution of gas throughout a bed, both on the adsorbent and in the air above the adsorbent. A typical distribution curve showing the concentration of gas in the air above various points in the bed of adsorbent is shown in figure 1(A). The curve for the concentrations

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which would be in equilibrium with the adsorbed gas at various points in the bed would be similar in shape but displaced slightly to the left. The term "adsorption wave" is generally applied to the movement of these distribution curves, to the right in figure 1(A), during the continuous passage of gas-laden air through the bed of adsorbent. A complete mathematical description of the wave would effect a number of important consequences. It would be possible to predict the performance of a particular bed of adsorbent, e.g., a gas-mask canister, from a minimum of experimental data and without exhaustive tests on the bed itself. It would also be possible to devise the best test procedures on small-scale beds from which to obtain the information necessary for the prediction and evaluation of the behavior of large reactors. A complete understanding of the adsorption wave would lead also to the design for the most efficient type of reactor.

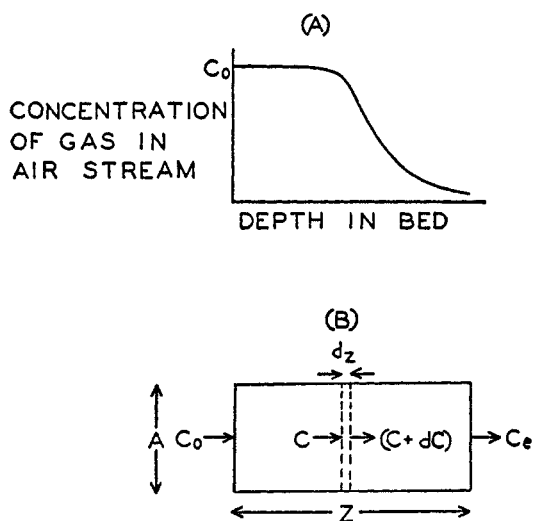


FIG. 1. Flow of gas through an adsorbent

Equal in importance to these consequences would be the elucidation of the mechanism of the adsorption process for various gases on different types of adsorbent, for such an understanding would suggest additional treatments for the improvement of the adsorbent and would also indicate when the natural limit to such improvement had been attained.

The problem of the adsorption wave has not been solved in its most general form, primarily because of the prodigious mathematical difficulties entailed (7, 8, 32, 34). In connection with this problem of correlating the performance of small-scale and large-scale reactors in chemical-engineering processes (1, 9, 11, 12, 33), the opinion has been expressed (5) that the correlation is impossible of attainment in a truly rigorous manner. Nevertheless, a number of simplified special cases of the adsorption wave have been considered and with these results as guides it has been possible to develop several semiempirical approaches to the problems of performance and mechanism of reaction.

It is generally recognized (8, 17, 20) that the removal of a gas from air by a porous adsorbent may involve one or more of the following steps: (1) diffusion (mass transfer) of the gas from the air to the gross surface of the granule; (2) diffusion of the molecules of gas into (or along the surface of) the large pores of the adsorbing particle; (3) adsorption of the molecules on the interior surface of the granule; (4) chemical reaction between the adsorbed gas and the adsorbent or adsorbed oxygen, water, or impregnant.

The relative importance of each of these four steps may vary widely with the particular conditions under which the removal is taking place. Mass transfer is influenced strongly by the flow rate of the gas stream, by the diffusion coefficient of the gas, and by the particle size of the adsorbent, but is relatively unaffected by temperature. The importance of diffusion in the pores is determined by such factors as the particle size, the structural characteristics of the pores, certain diffusional properties of the system, and the rate of reaction at the internal surface. The speed of adsorption at the interface depends on the nature and extent of the surface as well as on the activation energy for the adsorption of the particular gas under consideration. Chemical reaction is also determined by the properties of the surface, but much more specific effects will be obtained than in adsorption. Since large activation energies may be expected in steps (3) and (4), these processes will be highly sensitive to temperature.

In the general case, all four steps in the removal process may proceed with rates of approximately the same magnitude, and hence a problem of extreme mathematical difficulty is presented. On the other hand, in many situations one particular step may be much slower than the others, and hence may be considered the rate-controlling process. For a single rate-controlling process, a number of mathematical approaches have been developed. A few attempts have also been made to treat situations with more than one rate-controlling step, and for certain special circumstances, partial success has been attained.

II. THEORIES PREDICTING EFFLUENT CONCENTRATION AS A FUNCTION OF TIME

The ultimate aim of a mathematical analysis of the adsorption wave is an expression for the dependence of the effluent concentration on time. Even without such an expression, however, some qualitative description of the shape of an effluent-time curve can be given. Figure 2 illustrates a number of interesting cases. If the reaction on the adsorbent were instantaneous and if the adsorbent were infinitely fine-grained, none of the adsorbable gas would penetrate until some time t , at which time the adsorbent would be saturated, and then the gas would penetrate at full influent concentration. Such an adsorbent would exhibit a transmission curve such as A in figure 2. On the other hand, if the reaction is not instantaneous, a curve such as B would be exhibited. This curve would be symmetrical only for certain simple rates of adsorption. In addition to these two examples, one may encounter cases (e.g., in the removal of carbon monoxide) where the adsorbent, or its impregnant, acts as a catalyst for a reaction involving the toxic gas. As a result, the effluent-concentration curve, C, may rise very slowly; and if the catalyst remains at least partially unpoisoned,

the transmission of gas may never reach the full influent value. It is also conceivable, although no such case has yet been encountered, that the rate of catalysis may be very high compared to the rate of supply of gas, and in such circumstances the transmission curve would be the time axis, that is, none of the gas would penetrate.

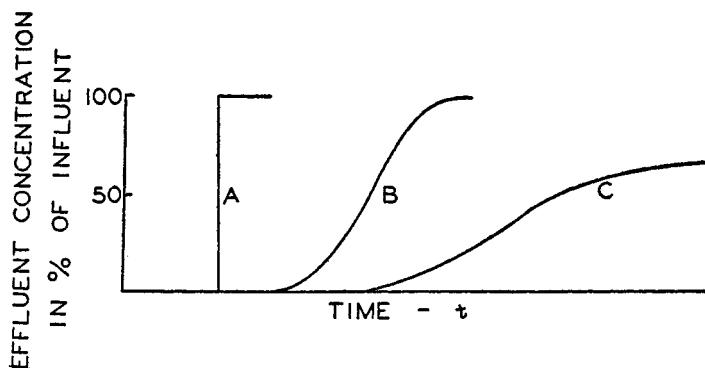


FIG. 2. Transmission of a gas by an adsorbent

A. THEORIES IN WHICH ONE STEP IS RATE-CONTROLLING

1. *The general differential equation*

Consider a stream of gas and air flowing through a bed of adsorbent, as is indicated in figure 1(B). Each layer of the adsorbent removes a portion of the gas from the air; hence the concentration of gas drops from an influent value of c_0 to an effluent value of c_e . A cross-section of infinitesimal thickness, dz , will reduce the concentration from c to $c + dc$ (dc is, of course, negative). From the principle of conservation of mass it follows that

$$\begin{aligned} \text{Quantity of gas entering} \\ = \text{quantity of gas picked up by adsorbent} + \text{quantity of gas leaving} \end{aligned} \quad (1)$$

The quantity of gas entering the infinitesimal section of bed will be equal to the concentration, c , times the volume rate of flow, L , times the interval of flow, dt .

$$\text{Quantity of gas entering} = cLdt \quad (2)$$

The amount of gas picked up by the charcoal will be given by the rate of pickup per unit volume, $\partial n/\partial t$, times the volume of the infinitesimal section of the bed (area \times depth), multiplied by the interval of exposure.

$$\text{Quantity picked up by the charcoal} = \frac{\partial n}{\partial t} (Adz)dt \quad (3)$$

The quantity of gas leaving the section dz will obviously be given by:

$$\text{Quantity leaving} = (c + dc)Ldt \quad (4)$$

Setting up the equality demanded by the conservation principle, one obtains

$$cLdt = \frac{\partial n}{\partial t} (Adz)dt + (c + dc)Ldt \quad (5)$$

which can be rearranged to give

$$-dc = \frac{A}{L} \frac{\partial n}{\partial t} dz \quad (6)$$

Since c is a function of the variables z and t , the total differential is (38):

$$dc = \left(\frac{\partial c}{\partial z}\right)_t dz + \left(\frac{\partial c}{\partial t}\right)_z dt \quad (7)$$

And since

$$\partial z / \partial t = V \quad (8)$$

and

$$L = VA\alpha \quad (9)$$

where V is the linear velocity through the interstices between the particles of the adsorbent and α is the porosity (i.e., the fraction of voids per unit gross volume of bed), one obtains

$$-\left[\frac{\partial c}{\partial z} dz + \frac{\partial c}{\partial t} dt\right] = \frac{1}{\alpha V} \frac{\partial n}{\partial t} dz \quad (10)$$

which can be rearranged to give

$$-\frac{1}{\alpha} \frac{\partial n}{\partial t} = \frac{\partial c}{\partial t} + V \frac{\partial c}{\partial z} \quad (11)$$

It is implicitly assumed in the derivation of this equation that the concentration of gas is small and that diffusion in the direction of flow is negligible.

The solution to equation 11 depends on the mathematical relation one assumes for $\partial n / \partial t$, the local rate of removal of the gas by the granules, and the particular mathematical form to be chosen depends on the mechanism of the removal process. No matter what mechanism is visualized, the local rate of removal would be dependent in general on the following variables:

- (1) The nature of the adsorbent
- (2) The nature of the gas to be removed
- (3) The geometrical state of the adsorbent
- (4) The temperature
- (5) The local concentration of the toxic gas, as well as of other gases in the air
- (6) The relative amount of the toxic and other gases already adsorbed by the granules
- (7) The velocity of the gas-air stream

In all cases which have been considered, it has been assumed that the first four variables are maintained constant, but that $\partial n/\partial t$ may depend on one or more of the remaining three.

2. Diffusion as the rate-controlling step

Case a: In some cases one may encounter a gas which has no back-pressure on the adsorbent, but which nevertheless ceases to be removed by the granules when the moles of gas on the granules, n , approaches N_0 , the saturation capacity of a unit gross volume of adsorbent for the gas. Under these conditions the local rate of removal would be given by the relation:

$$\frac{1}{\alpha} \frac{\partial n}{\partial t} = \frac{F a c}{\alpha \rho} \quad (12)$$

where F is the mass-transfer coefficient, a is the superficial surface per unit volume of granules, and ρ is the density of the air-gas mixture. The solution (10) of the differential equation may be resolved into two cases. For all times up to t_0 when $n = N_0$ at the entrance face, the concentration at a given point in the bed is given by the equation:

$$\frac{c}{c_0} = \text{Exp} \left[-\frac{F a z}{\alpha \rho V} \right] \quad (13)$$

For times greater than t_0 , the following relation holds:

$$\frac{c}{c_0} = \text{Exp} \left[-\frac{F a}{\alpha \rho} \left(\frac{z}{V} - \frac{c_0 t}{N_0} \right) - 1 \right] \quad (14)$$

Case b: If a gas is adsorbed reversibly, the equation obtained for c/c_0 depends on the character of the adsorption isotherm. One of the simplest cases that has been considered is that of the linear isotherm, for which

$$c^* = b n \quad (15)$$

where c^* is the concentration of the gas in the air stream at a given point in the bed in equilibrium with the adsorbent at that point, and b is a constant. With a linear isotherm governing the back-pressure of the gas, the equation for the local rate of removal becomes (10):

$$\frac{1}{\alpha} \frac{\partial n}{\partial t} = \frac{F a}{\alpha \rho} (c - c^*) \quad (16)$$

The solutions of the differential equations, for the boundary conditions encountered in charcoal, are well known because completely analogous equations have been encountered in the problem of heat exchange in granular beds. Analytical expressions, in terms of Bessel functions, for the solutions are cumbersome to handle, and hence the results are given best in the form of reference curves of c/c_0 as a function of the important variables. The curves worked out by Furnas (2, 13), however, are very incomplete in regions of low concentrations, the regions of great interest in work on toxic gas transmission, and consequently a

semilogarithmic plot taken from a report by Hougen and Dodge (16) is given in figure 3. For values of c/c_0 below 0.01, reference should be made to the report of Drew, Spooner, and Douglas (10).

Case c: Most gases do not exhibit a linear isotherm on charcoal. A better approximation is the Langmuir isotherm, which may be expanded (10) in a power series of the form

$$c^* = \frac{Kn}{N_0} + \frac{Kn^2}{N_0^2} + \dots \quad (17)$$

where K is a constant. Using the first two terms in equation 17 as a parabolic approximation to the isotherm, one may substitute for c^* in equation 16. The solutions of the resultant equations in terms of standard graphical procedures have been worked out and are described by Drew, Spooner, and Douglas (10).

3. Adsorption or reaction on the surface as the rate-controlling step

Case a: The earliest analysis of the adsorption wave was made by Bohart and Adams (3) on the assumption that the gas is adsorbed irreversibly and at a local rate of removal governed by the equation:

$$\frac{1}{\alpha} \frac{\partial n}{\partial t} = k_1 c(N_0 - n) \quad (18)$$

where k_1 is a constant. A similar treatment has been carried out more recently by Hinshelwood *et al.* (6). Both groups of investigators have derived the following expression for the variation of the concentration of gas in the air stream:

$$c_0/c = 1 + (\text{Exp} [-k_1 c_0 t]) \left(\text{Exp} \left[\frac{k_1 N_0 z}{V} \right] - 1 \right) \quad (19)$$

This equation in its various forms has been used very widely to interpret and to interpolate data on the performance of various charcoals against toxic gases. Unfortunately, present indications are that there are few cases where the rate of removal of a toxic gas by charcoal as presently impregnated is governed primarily by adsorption or reaction at the surface. Diffusion, or mass transfer, seems to make some contribution to the slowness of removal of almost all gases by charcoal; hence equation 19 is not strictly applicable.

Case b: An attempt has been made by Lister (23) to consider the relations to be obtained when adsorption on the surface is the rate-controlling step but for the case where the adsorption is reversible and the adsorbed gas exerts a back-pressure. For such conditions, the equation for the local rate of adsorption becomes

$$\frac{1}{\alpha} \frac{\partial n}{\partial t} = k_1 c(N_0 - n) - k_2 n \quad (20)$$

where k_1 and k_2 are constants.

No complete solution of the resultant differential equations has been given. Approximations have been given for the conditions obtained with fresh charcoal, but the general validity of these has been questioned (9).

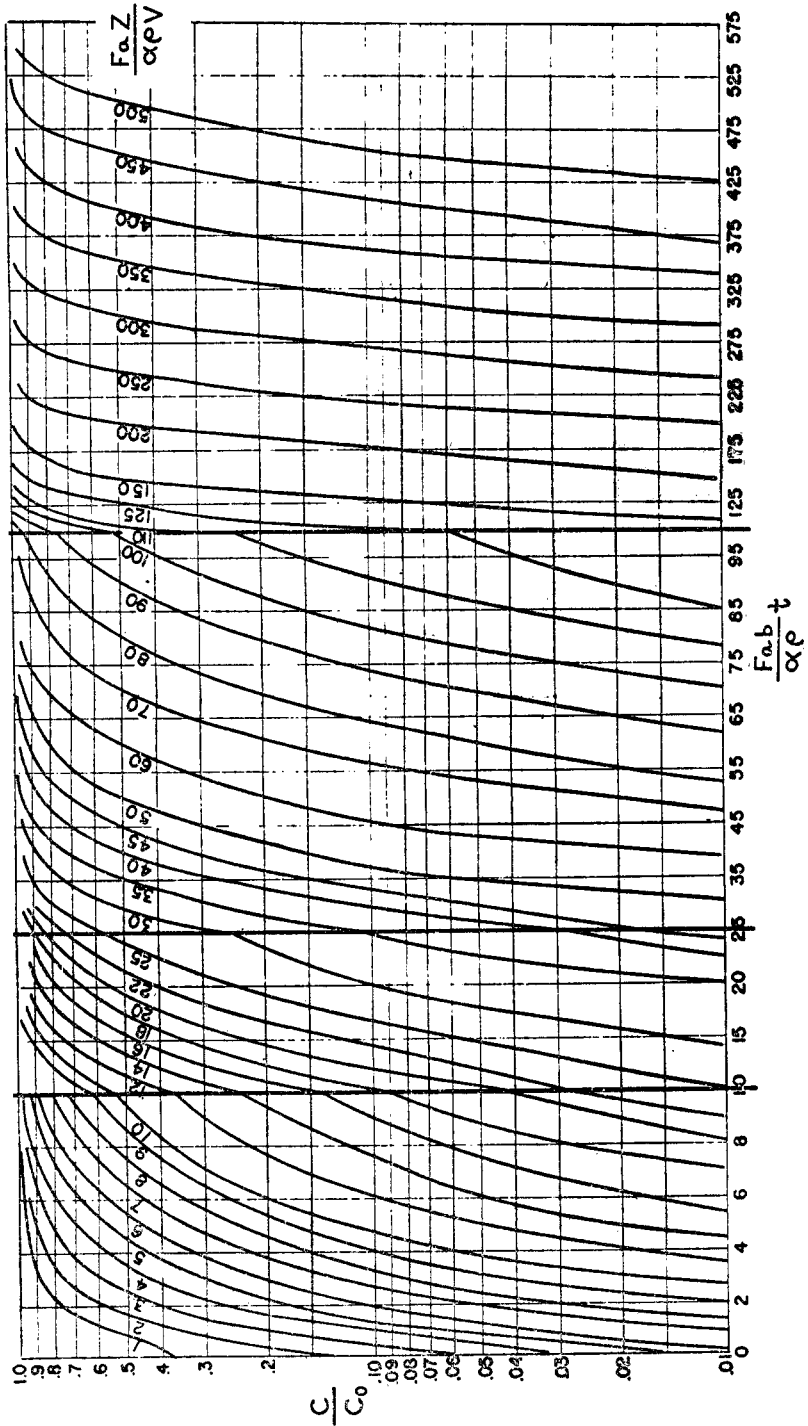


FIG. 3. Fraction of gas unremoved as a function of time and position in bed

B. THEORIES IN WHICH MORE THAN ONE STEP CONTRIBUTES TO RATE OF REMOVAL

1. Diffusion in air and deposition on surface contributing

It has been possible to construct (10) a differential equation for the local rate of removal, on the assumption that the diffusion of the toxic molecule from the air to the charcoal and the subsequent deposition process, whether chemical or adsorptive in nature, both contribute to the slowness of removal. The general equation for this process has not been solved. Nevertheless, certain special cases have been considered, but each of them reduces to one of the single-step processes discussed above and hence does not warrant further elaboration.

2. Diffusion in air and processes within the granule contributing

A very detailed consideration of the nature of the processes involved in the removal of gases by adsorbents has been made by Wicke (35). Emphasis has been given particularly to diffusion within the pores and to the various factors which influence the cross-sectional and longitudinal mixing in the intergranular spaces. Where the equilibrium adsorption of a gas follows a linear isotherm, the differential equations have been solved and have been shown to be applicable to the experimental data on the removal of carbon dioxide at 100°C. For gases with curved isotherms, however, the general solution to the differential equation has not been obtained, though certain special cases have been considered.

C. COMPARISON OF THEORIES WITH EXPERIMENT

None of the theoretical approaches gives a satisfactory correlation of the experimental data on the removal of a toxic gas by charcoal. Even with gases such as chloropicrin, where, as is shown later, mass transfer seems to be the rate-controlling step, the observed dependence of effluent concentration on time does not agree, over any appreciable range, with the curves given in figure 3. The primary cause of the deviation, for other gases as well as for chloropicrin, is the curvature of the adsorption isotherm, a condition which so far has not been incorporated, except in an approximate, empirical manner (27), into the wave equations. In addition to the curvature of the isotherm, a further difficulty that arises with most other toxic gases of interest is the combination of mass transfer and one or more of the succeeding steps in controlling the rate of removal of the gas by the adsorbent. Minor discrepancies may also arise from thermal factors. Temperature changes in the removal process, which in some cases are many tens of degrees, may raise the back-pressure of the adsorbed gas or may affect the rate of mass transfer in the carrier stream.

There exist sufficiently fundamental differences in the differential equations for the local rate of removal in the mass-transfer and surface-adsorption mechanisms so that one can determine the presence or absence of a slow diffusional step. In equation 18, based on surface adsorption as the rate-controlling step, the velocity, V , does not appear; hence in the integrated equation for c/c_0 , V will enter only as z/V , as can be verified by glancing at equation 19. Similarly,

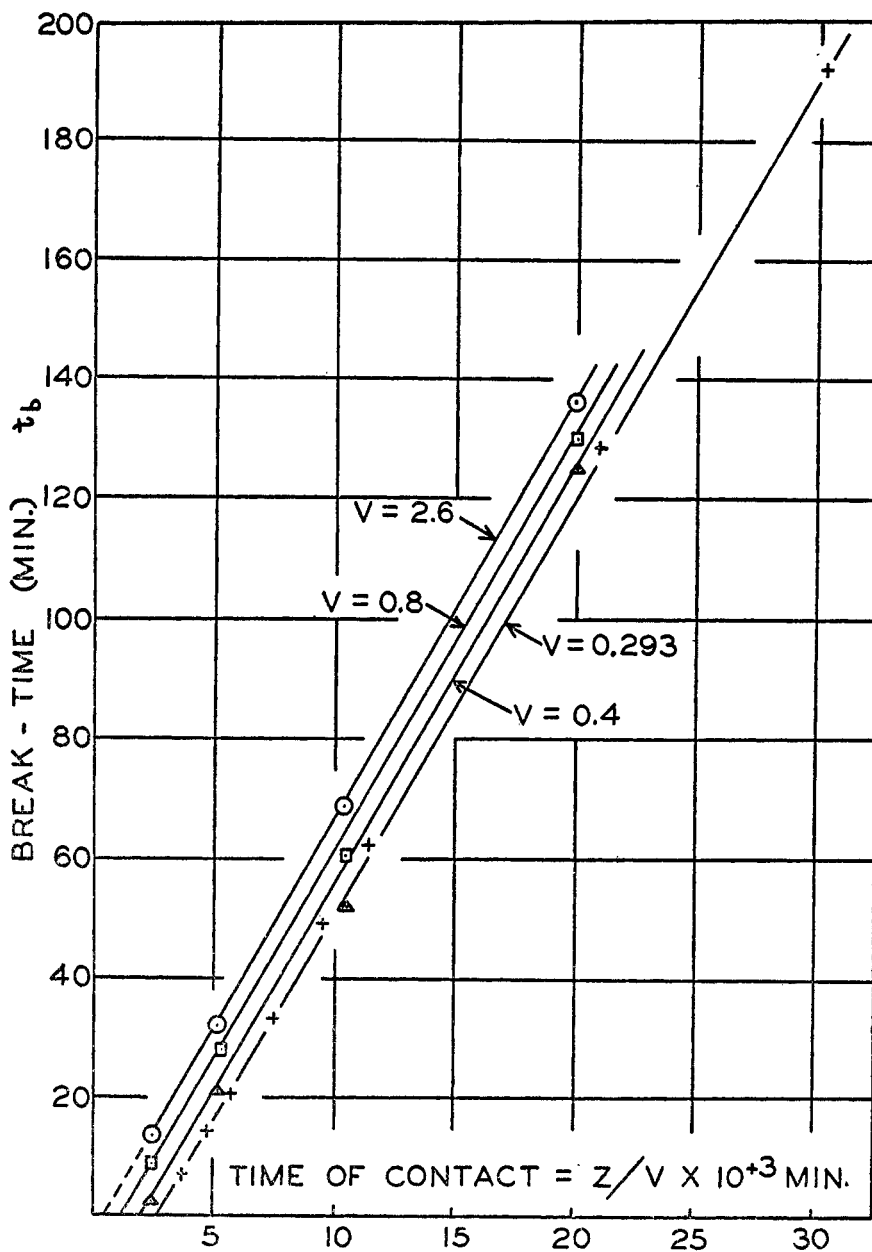


FIG. 4. Test of effect of rate of flow on local rate of removal of chloropicrin

on expanding and rearranging equation 19 to obtain an equation for t_b , the instantaneous break-time,² one obtains an expression in which V enters only as z/V . In contrast, when mass transfer (diffusion) is the controlling step, the

² For definition see the appendix.

velocity of flow enters the equation for the local rate of removal, inasmuch as F , the mass-transfer coefficient, depends on the rate of flow. In consequence, the instantaneous break-time depends on V as well as on z/V , and a plot of t_b versus z/V will give different curves for different rates of flow. (It should be emphasized that the cumulative break-time, i.e., the time in which a total quantity of gas sufficient to produce a change in some indicator has escaped from the bed, depends on V and z/V whether or not V enters the expression for the local rate of removal. Therefore, the cumulative break-time cannot be used to distinguish between mechanisms of removal.) Thus, a criterion has been established (9) for detecting the presence of a slow diffusional step. In figure 4, this criterion is applied to some data on chloropicrin (36). It is obvious from the graph that t_b depends on V as well as on z/V , and in consequence that diffusion contributes to the slowness of removal of chloropicrin by charcoal. Consequently, it is unlikely that the theories based on surface adsorption or surface reaction as the rate-controlling process will be applicable to any charcoal which has sufficient activity to make it useful in protection against toxic gases.

Unfortunately, these relationships were not realized in much of the early work and many extrapolations were made on the basis of the Bohart-Adams-Hinshelwood equation (3, 6), which is based on a surface-deposition, rate-controlling mechanism. The particularly misleading fact was the observation that in many circumstances a plot of $\log [(c_0/c) - 1]$ was linear with time, a necessary condition derivable from equation 19. Unfortunately, such linearity is not a reliable test of the applicability of equation 19, for all the other mechanisms will also lead to such linear equations over wide ranges if suitable values are chosen for the constants. When constants for equation 19 are determined from plots of $\log [(c_0/c) - 1]$ versus time, one finds that both k_1 and N_0 vary with the rate of flow of the air stream. Such behavior is completely at variance with the postulates of the mechanism and illustrates the inapplicability of the equation to the removal of gases by the usual charcoal adsorbents.

III. SEMIEMPIRICAL TREATMENTS

In the absence of a satisfactory comprehensive theory of the adsorption wave, investigators have been forced to develop semiempirical methods of treating data. Primary emphasis in work with toxic gases and charcoal has been given to equations which relate break-time to the common variables such as bed depth, rate of flow, particle size, and concentration of influent gas. With the accumulation of results from different modes of approach, it has also been possible to correlate certain relations with particular mechanisms of removal.

A. FACTORS AFFECTING BREAK-TIME

1. Nature of gas flow in charcoal

The flow of fluids through beds of granular solids is very complicated in nature for, as is quite obvious, the channels are very tortuous and non-uniform. It is impossible to fix the dimensions or number of channels, for quite frequently

two streams may merge or a single stream may redistribute itself into several new paths of flow. Since sudden contractions or enlargements in intergranular spaces may exist, it is quite possible to have both streamlined and turbulent flow occurring simultaneously in different portions of a granular bed. In consequence, there is a much slower transition from conditions of laminar flow

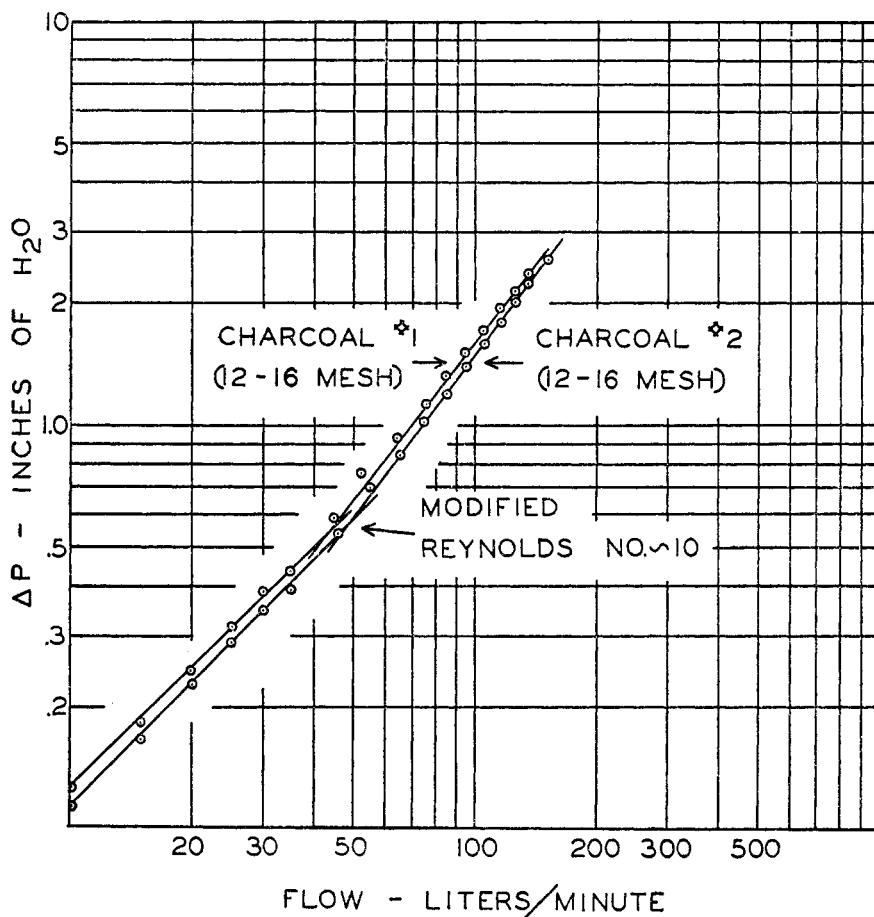


FIG. 5. Pressure-drop data

to those of turbulent flow in the passage of gas through an adsorbent bed than in the flow of fluid through pipes.

The nature of the flow of fluids is studied usually by measuring the pressure drop in the bed or pipe. Correlations are then made with the dimensionless parameter known as the Reynolds number, $D_p V \rho / \mu$. When a graph of a function of the pressure drop known as the friction factor (see 14 or 15) is plotted against the Reynolds number, two linear portions are observed, and they intersect at the so-called critical Reynolds number, a value corresponding to conditions under which laminar flow is transformed into turbulent flow.

Studies have been made of the flow of fluids through porous carbon (15), and a critical Reynolds number of about 4 has been found. Extensive work has also been carried out on the flow of gases through beds of charcoal (22). Two representative curves are shown in figure 5. From these curves and other data it has been concluded that in the charcoals investigated the critical Reynolds number is about 10. The Chemical Warfare Service laboratories (30) and English workers (19) have found a transition in the same region. Nevertheless, one cannot be certain that the same critical value will be observed with all charcoals of any possible shape. It is quite conceivable that curious shape factors may occasionally be encountered, in view of the rather arbitrary use of particle diameter, D_p , in place of pore size in the Reynolds number. In all of the work described here, however, it has been assumed that the critical region is in the neighborhood of a Reynolds number of 10.

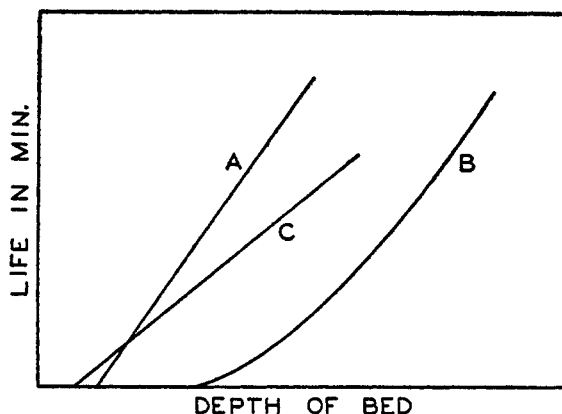


FIG. 6. Life-thickness curves

2. The effect of bed depth

The dependence of canister or tube life on the depth of charcoal has been investigated more widely than has the dependence on any other variable. The reason for such emphasis is perhaps obvious, for the amount of adsorbent necessary determines very largely the bulk of the canister. Life-thickness curves have become, therefore, the most common method of representing the performance of a charcoal. In consequence, the interpretation of performance in terms of the mechanisms of removal has revolved around the elucidation of life-thickness curves.

(a) General character of life-thickness curves

A survey of performance data shows that two types of life-thickness curves are encountered. The simplest case is a linear relation such as is shown in curve A of figure 6. Most organic gases when tested in a dry condition against dry charcoal exhibit linear life-thickness curves. In principle, a break-time test using a cumulative indicator should not show a linear relation with bed depth,

at least not at small depths (27), but this lack of linearity is frequently overlooked because few tests are carried out at very small depths. Curve B exhibits a very common observation of curvature at low lives with a tendency to linearity at high break-time. Such behavior should always be encountered in cumulative tests of the break-time. It is also usually observed when tests are carried out with humidified gases and charcoal, and in some cases occurs in tests under dry conditions.

Whether or not curvature occurs, the life-thickness curve intersects the bed-depth axis at a finite value. It follows then that there exists a critical bed depth, I , below which the life is zero. This critical length will vary with the conditions of flow, concentration, mesh size, and nature of the charcoal, and it is this manifold dependence which has engaged much attention. Numerous attempts have been made to correlate these variables in some convenient analytic expression, for in small beds, as are encountered in canisters, it is the critical bed depth which primarily determines the degree of protection.

(b) The Mecklenburg equation

A very convenient expression for the linear life-thickness curve has been derived by Mecklenburg (26) from elementary considerations of conservation of mass. At the break-time a negligible portion of the toxic gas has penetrated the bed; hence one can assume that

$$\text{Weight of gas supplied} = \text{weight of gas picked up by adsorbent} \quad (21)$$

The weight of gas supplied by the air stream will be equal to the time of flow (the break-time in minutes) times the rate of flow (in liters per minute) times the concentration (in grams per liter). In turn, the pickup by the charcoal may be *arbitrarily* considered as occurring in a certain portion of the bed instantaneously and up to the saturation value, while the remainder of the bed, defined by Mecklenburg as the "dead layer," remains completely free of gas. As was emphasized by Mecklenburg, the "dead layer" is a purely fictional concept devised merely to facilitate the derivation of the following equation and to obviate the necessity of considering in detail the distribution of gas in the bed of adsorbent. With this arbitrary division it follows that the amount picked up by the charcoal will be equal to the saturation value per unit volume times the area times the difference between the bed depth and the depth of the "dead layer," h . In algebraic terms the equality in equation 21 may be expressed as follows:

$$t_b L c_0 = N_0 A (z - h) \quad (22)$$

This equation may be rearranged readily to give an expression for the break-time:

$$t_b = \frac{N_0 A}{L c_0} (z - h) \quad (23)$$

From this equation it is obvious that the slope of the life-thickness curve (i.e., a plot of t_b versus z), for a fixed rate of flow, input concentration, and bed cross-

section, is a measure of the capacity (N_0) of the charcoal. For a system which obeys this equation throughout the complete life-thickness curve, the "dead layer," h , and critical bed depth, I , must be equal, so that

$$t_b = \frac{N_0 A}{Lc_0} (z - I) \quad (24)$$

The great deficiency of equation 24 is that it cannot be used to extrapolate information from one set of flow or concentration conditions to another without further information on the dependence of the critical bed depth on these variables. The wave theories discussed above set certain requirements for the variation of critical bed depth, and where these theories are applicable they may be used to extend equation 24. Further details are considered in a subsequent section.

(c) Curvature due to cumulative method of test

If the break-time is defined in terms of the period necessary for a total cumulative amount of gas to penetrate the bed, it can be shown (27) that the life-thickness curve even in the simplest mechanism of removal would obey an expression of the form

$$t_c = \frac{N_0 A}{Lc_0} k_3 V^{k_4} \ln \left[\frac{k_5 \text{Exp} \left(\frac{z}{k_3 V^{k_4}} \right)}{N_0 A k_3 V^{k_4}} + 1 \right] \quad (25)$$

In general, equation 25 would not be linear; however, for large bed depths, the first term inside the brackets becomes large in comparison to the second term, 1, and the equation as a whole approaches the linear relation:

$$t_c = \frac{N_0 A z}{Lc_0} + k_5 \quad (26)$$

These predictions are in agreement with the behavior observed in cumulative tests.

(d) Curvature in systems using instantaneous tests

In the testing of metal-ion-impregnated charcoals with certain inorganic gases it has always been observed that the life-thickness curves for humidified gas streams and humidified charcoal show pronounced curvature at small bed depths but approach linearity with deep beds. Curve B of figure 6 is a typical example. The increasing slope of this curve with increase in bed depth implies an increasing capacity per unit volume of adsorbent for the toxic gas. This expectation has been verified by an examination of the distribution of gas adsorbed on the bed at various time intervals. For a substance such as chloropicrin, which exhibits a linear life-thickness curve on dry charcoal, the amount of gas taken up by a unit volume of charcoal reaches a maximum which is not surpassed by increasing the time of exposure of the bed to the toxic gas. As a result, the distribution curves behave as shown in figure 7(A). In contrast, a humidified impregnated charcoal shows a continuously increasing capacity

per unit volume for certain inorganic gases and in consequence exhibits a set of distribution curves such as is shown in figure 7(B). The capacity of the influent end of the bed approaches, but never quite reaches, a true saturation value, probably because a second slow reaction follows an initial rapid one. Consequently, the distribution curve is displaced upward as well as to the right toward the inside of the bed.

In a number of cases, tests carried out with dry gases on dry base charcoal have also shown curvature in their life-thickness curves. A typical example would be methyl alcohol or ethyl chloride. The curvature in all such cases, however, is less than that observed with the inorganic gases mentioned above.

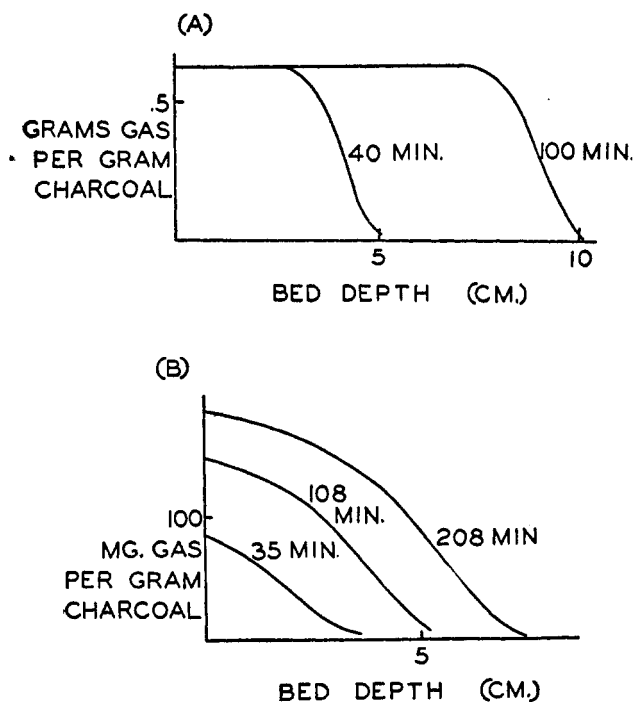


FIG. 7. Distribution of gas on adsorbent: (A) chloropicrin; (B) inorganic gas

Although no distribution curves were obtained for these dry gases, it seems likely that in these cases also some slow secondary reaction occurs in addition to the initial rapid one. For methyl alcohol it is possible that an oxidation process is being catalyzed by the charcoal. With other inert gases, and perhaps also with methyl alcohol, it seems likely that the slow reaction is a diffusion process within the pores of the granule.

3. The effects of velocity of flow, concentration, and particle size

(a) General equation for critical bed depth

It can be shown (21) from considerations similar to those discussed by Hurt (18) for the design of catalytic reactors, that if more than one step contributes to

the rate of removal of a gas from the carrier stream, the critical bed depth, I , will be the sum of two terms, I_t and I_r . I_t represents the portion of the critical bed depth due to the slowness of diffusion of gas from the air stream to the surface of the charcoal, whereas I_r represents the fraction due to processes occurring within a charcoal granule. Since the critical bed depth can be thought of as the distance which the gas may penetrate the bed before its concentration is reduced to the break value, it seems reasonable to expect a certain minimum value of I , for a fixed set of conditions, which would represent the smallest penetrable depth possible even if every process in the granule were instantaneous and the rate were determined entirely by the speed with which the gas diffuses to the particle. This limiting value of I for a fixed set of conditions would be I_t . Any critical bed depth above I_t must be the contribution of the processes within the granule. That this contribution should be an additive term, rather than a multiplicative factor, has been shown in principle by Hurt (18).

The critical bed depth due to diffusion, I_t , can be expressed (20, 21) in terms of a number of familiar parameters, independent of the nature of the charcoal, but dependent on the properties of the air-gas mixture and on the granular characteristics of the bed. Considerations of dimensional analysis lead to the conclusion that, at a fixed ratio of influent to effluent concentration, I_t should be a function of the particle size of the granules and of two dimensionless parameters $D_p G/\mu$ and $\mu/\rho D_v$, the Reynolds number and Schmidt number, respectively. The specific function which has been adopted is essentially that of Gamson, Thodos, and Hougen (14)³:

$$I_t = \frac{2.303}{a} \left(\frac{D_p G}{\mu} \right)^{0.41} \left(\frac{\mu}{\rho D_v} \right)^{0.67} \log \left(\frac{c_0}{c_b} \right) \quad (27)$$

In the derivation of this equation it is assumed that c_0/c_b is very large. Strictly speaking, this equation should be applicable only in cases of turbulent flow, but it has been found that in the region of laminar flow in charcoal, I_t is approximated satisfactorily by equation 27. For a fixed ratio of influent to effluent concentration, the equation expresses the variation of the critical bed depth with particle size, D_p , rate of flow G , and diffusion coefficient of the gas, D_v . The factor a , the superficial surface of the granule (ignoring pore structure), depends on the particle size and on the percentage of voids in the bed. Values of a have been calculated and are tabulated by Gamson, Thodos, and Hougen (14). Where the absolute value of I_t is not desired but only the form of the equation is necessary, one can substitute the following approximate equation:

$$a = \text{constant} \times D_p^s \quad (28)$$

The power s takes into account the variation of percentage voids with particle size and generally has a value slightly less than 1.

For convenience in comparing data on critical bed depths with analogous

³ Slight changes have been suggested recently by C. R. Wilke and O. A. Hougen (Trans. Am. Inst. Chem. Engrs. **41**, 445 (1945)).

performance data in chemical-engineering processes the following transformation is useful:

$$H_t = \frac{I_t}{2.303 \log (c_0/c_b)} = \frac{1}{a} \left(\frac{D_p G}{\mu} \right)^{0.41} \left(\frac{\mu}{\rho D_v} \right)^{0.67} \quad (29)$$

H_t is called the "height of a transfer unit."

In contrast to I_t , I_r would be a complex function of the structure and nature of the charcoal and would be specific for the particular gas being removed. While it would be independent of the Reynolds number, it should (judging from consequences of equation 19) vary directly with the rate of flow of the gas-air stream, and it may be quite sensitive to temperature. Since many of these variables cannot be estimated in any general way, it is only possible to suggest the following relation for I_r (on the assumption that c_0/c_b is large and that the reaction is first order):

$$I_r = k_8 V \ln c_0/c_b \quad (30)$$

The total critical bed depth therefore should be given by the expression

$$I = I_t + I_r = \frac{1}{a} \left(\frac{D_p V \rho}{\mu} \right)^{0.41} \left(\frac{\mu}{\rho D_v} \right)^{0.67} \ln \left(\frac{c_0}{c_b} \right) + k_8 V \ln \left(\frac{c_0}{c_b} \right) \quad (31)$$

To determine the relative contributions of I_t and I_r , one may proceed in at least two ways. One approach would be to calculate I_t from equation 27 and obtain I_r by difference from the total critical bed depth. To facilitate these calculations a series of graphs has been prepared in which I_t is plotted as a function of the common variables (20). A second approach is to obtain data on I as a function of the linear velocity, V , and then to plot the data against $V^{-0.59}$. It is obvious from equation 31 that for all conditions, except flow rate, fixed, I/V may be expressed as

$$I/V = k_9 V^{-0.59} + k_{10} \quad (32)$$

where k_9 and k_{10} are constants. The intercept of the line obtained is a relative measure of I_r , and the value of the first term in equation 32 at any particular linear velocity is a relative measure of I_t .

The variation of the critical bed depth with particle size will depend on the relative importance of the two terms in equation 31, that is, on the mechanism of the removal process. I_r will be independent of particle size, whereas I_t will vary as some power of D_p , usually near 1.4. If diffusion in air and surface reaction contribute about equally, a plot of I against D_p will approach a finite limiting value as D_p approaches zero. This is illustrated by curve A in figure 8. If mass transfer alone is rate-controlling, one obtains a similar curve (B in figure 8) but with an intercept at the origin. In contrast, if the surface reaction were rate-controlling, I would be independent of granule size, as is illustrated in curve C of figure 8.

Where both terms contribute appreciably to the critical bed depth, one obtains an interesting graph in a plot of break-time *versus* particle size. For large sizes,

the life is less than that for small particles, but as the granule size decreases the life rises and approaches a limiting value, corresponding to conditions where the

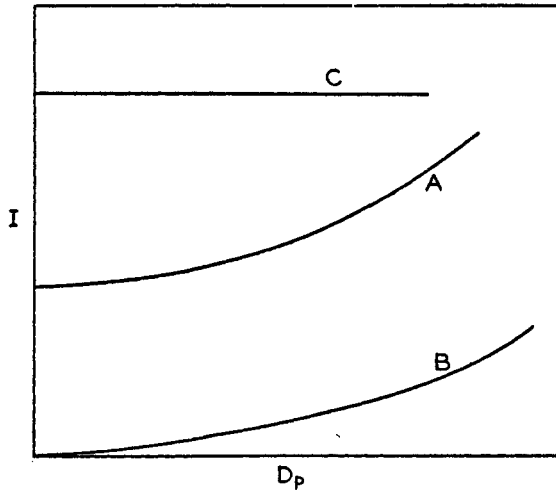


FIG. 8. Dependence of critical bed depth on particle size with different mechanisms of removal.

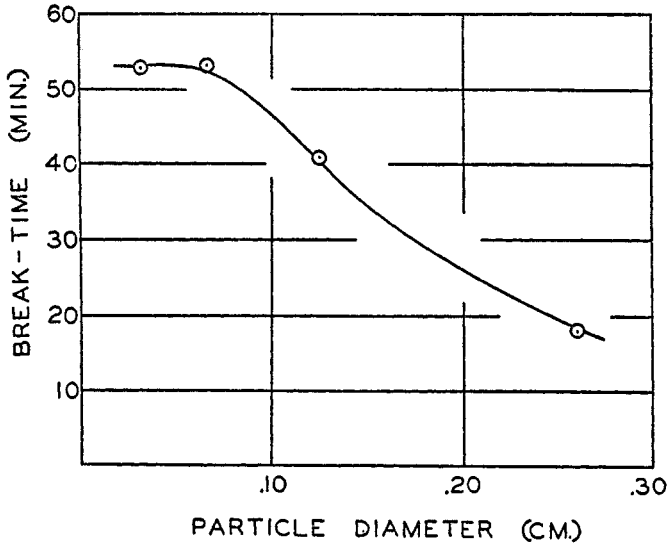


FIG. 9. Dependence of break-time on particle size; phosgene as the penetrating gas surface reaction becomes the important factor and mass transfer has been effectively eliminated. A typical curve (29) is shown in figure 9.

The variation of the critical bed depth with velocity of flow also depends on the relative importance of the two terms in equation 31. If the slow step is a reaction in the granule, I will vary directly with the velocity. In contrast, if

mass transfer is rate-controlling, I will vary with the 0.4 power of the velocity. Where the two processes contribute, I can usually be expressed in terms of some power of the velocity between 0.4 and 1.0, although it must be realized that such a function would be merely an approximation to the fundamental one of equation 31.

The available evidence indicates that the critical bed depth is a logarithmic function of c_0/c_b . According to equation 31, the logarithmic relation should hold for any mechanism of removal. Sufficient data on effluent concentration as a function of time are available only for a few gases, so that the predicted

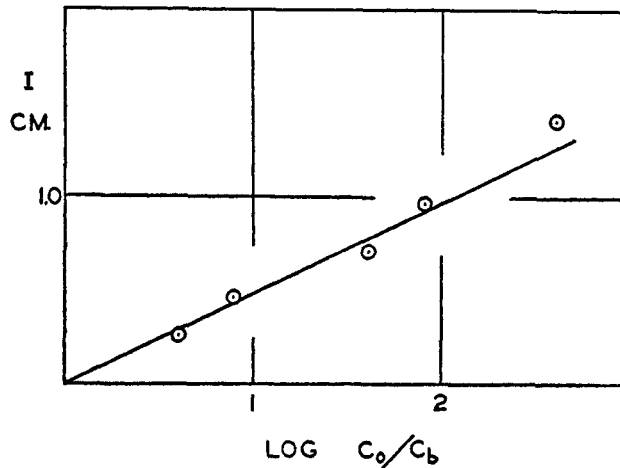


FIG. 10. Dependence of critical bed depth on ratio of influent to effluent concentration

relation has not been tested adequately. That it does hold for chloropicrin (20) is shown in figure 10.

(b) Mechanism of removal of some gases

The criteria described for estimating the relative contributions of diffusion in air and physical or chemical reactions in the charcoal to the critical bed depth have been applied to a number of gases, with the aim of elucidating the mechanism of their removal (21).

Chloropicrin is an example of a gas whose rate of removal is governed primarily by the rate of diffusion to the particle surface. In figure 11 the observed values of the critical bed depth (8, 36) are plotted as a function of the linear velocity, and for comparison the curve calculated for I_t is also shown. The observed values do not deviate significantly from the calculated curve. Such behavior indicates no appreciable contribution of any factors other than mass transfer (diffusion in air) to the removal of chloropicrin, at least not in the initial stages of the process.

In direct contrast to chloropicrin stands water, whose rate of removal seems to be governed primarily by some slow surface process. Experimental data on

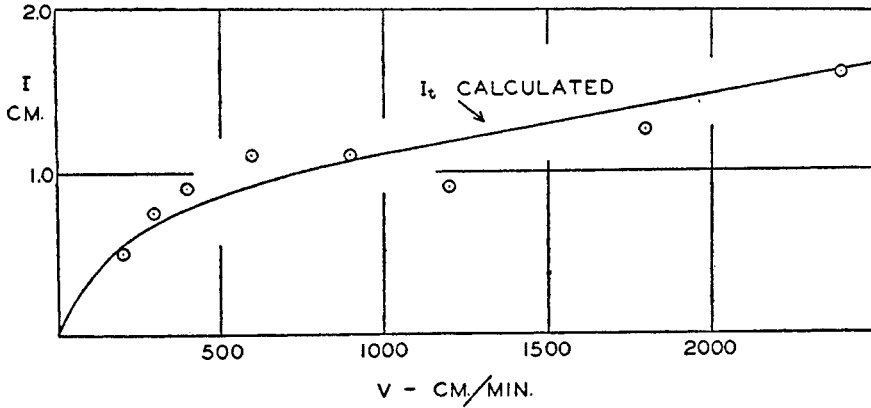


FIG. 11. Critical bed depths for chloropicrin

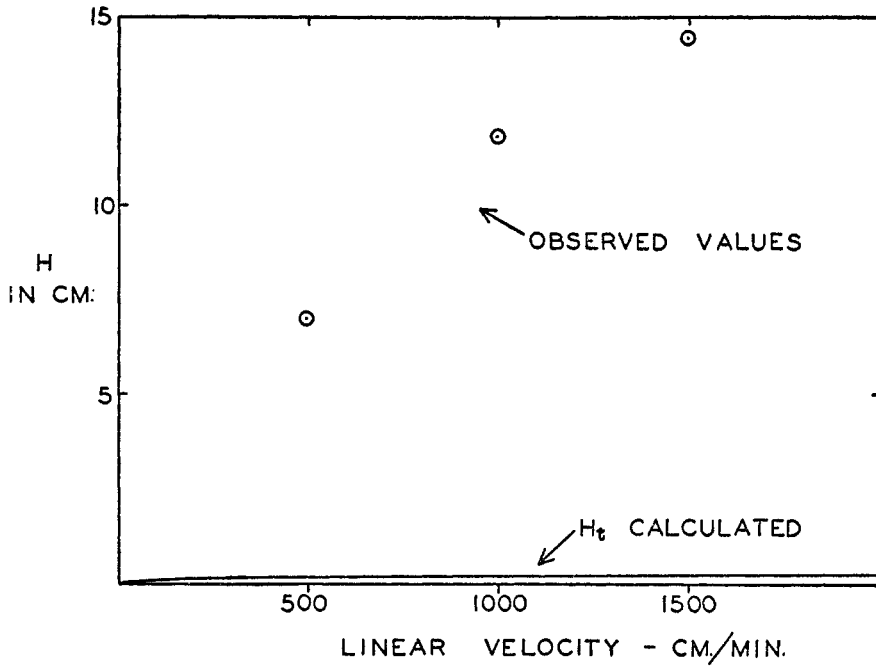


FIG. 12. Removal of water by charcoal (12-16 mesh)

the rate of removal of water (4) have been expressed in terms of a quantity which we may call H and which may be defined by the equation:

$$H = \frac{I}{\ln (c_0/c_b)} \tag{33}$$

Values of H on a sample charcoal are shown in figure 12. In comparison to the values to be expected if diffusion in air were the controlling process, the observed

values are very high and indicate the large contribution that is made by factors which appear within or on the granule.

Other gases are intermediate in behavior between water and chloropicrin, in that diffusion in air and surface factors contribute more nearly equally to the rate of removal of the gas.

4. Dependence of critical bed depth on adsorbent

(a) Effect of nature of adsorbent

It must be realized, of course, that the relative contribution of various steps to the rate of removal will be very sensitive to the nature of the adsorbent. This dependence is illustrated well in the case of water where different base charcoals, having different pore structures and surface complexes, can react with water

TABLE 1
Dependence of H on adsorbent

ADSORBENT	H (4)
	<i>cm.</i>
Charcoal, wood base.....	38-64
Charcoal, coal base.....	20-30
Charcoal, wood base, impregnated.....	7-15
Silica gel.....	0.5-2.5

with different speeds and hence influence strikingly the critical bed depth or the value of H . Similarly, charcoals treated with impregnants usually react more rapidly with water, apparently because of their ability to form hydrates; hence the magnitude of H is reduced considerably. In adsorbents such as silica gel, where the combination with water vapor at low pressures is probably due to hydrogen bonding rather than primarily to van der Waals forces, the removal reaction is extremely rapid and H approaches the limiting value due to diffusion in air alone. These factors are illustrated by the values of H listed in table 1.

The measurement of critical bed depths for charcoals which have been subjected to various treatments is a useful method of analyzing the results obtained. For gases such as chloropicrin, at least some of the available charcoals can react so rapidly that the limiting factor in the removal of gas—the rate of diffusion to the granule—has been reached, and it is futile to attempt to improve the adsorbent any further toward these particular toxic materials. On the other hand, toward most possible toxic agents there is still sufficient room for additional treatments or impregnations which may speed up processes which occur within the granule.

(b) Effect of capacity of adsorbent

A clear statement of what is meant by "capacity" of a charcoal is not as readily available in a flow type of experiment as it is in the static case. In the latter situation, capacity refers to the amount of gas picked up by a unit weight of

charcoal after sufficient time has elapsed for equilibrium to have been attained. The inapplicability of such a definition is particularly evident for a gas such as the inorganic one illustrated in figure 7(B), where the influent end of a bed has still not reached a static state even after 200 min.

The primary value of a measure of capacity is in the prediction of the dependence of life on bed depth. Consequently, it is customary to define N_0 in terms of the slope of a life-thickness curve (see equation 23). In this manner, two samples which show linear life-thickness curves can be compared reliably in their performance under a set of conditions requiring a slight extrapolation from the measured ones. It is realized of course that such a "capacity" may be far different from the final equilibrium value, even for gases removed by adsorption alone. Nevertheless, it is more useful than a definition based on a static experiment.

For small bed depths, the break-time will be determined primarily by the critical bed depth of the adsorbent, inasmuch as the critical bed depth will be a large fraction of the total bed. On the other hand, as the bed is made deeper, the critical bed depth becomes less important, whereas the capacity becomes increasingly significant and in large depths is the determining factor. These relations became evident in a comparison of the lines A and C in figure 6.

The capacity is also a useful function for estimating the maximum possible life one can obtain from a sample. By assuming a critical bed depth of zero, one can calculate the total amount of gas that could be picked up by the bed and, from the flow conditions, the maximum limit for the break-time.

B. EQUATIONS FOR CANISTER LIFE

To predict the performance of gas-mask canisters under any set of conditions other than those used in routine tests, it is necessary to have convenient analytic relations for life as a function of the common variables. This problem has not been solved satisfactorily except in a few special cases. Where the life-thickness relations show distinct curvature, no suitable analytical method has been evolved for extrapolating data. Since many tests are carried out under humid conditions, in which curvature is generally observed, this large field of testing still remains to be considered. However, in testing under dry conditions, where linear life-thickness curves are obtained, useful equations for the break-time have been developed.

1. Cases in which diffusion in air is the rate-controlling step

Under these conditions it is a simple matter to combine the Mecklenburg relation for t_b and equation 27 for I_t . The result is the expression:

$$t_b = \frac{N_0 A}{L c_0} \left[z - \frac{1}{a} \left(\frac{D_p G}{\mu} \right)^{0.41} \left(\frac{\mu}{\rho D_s} \right)^{0.67} \ln \left(\frac{c_0}{c_b} \right) \right] \quad (34)$$

It allows the prediction of the complete break-time history for any gas whose removal is controlled by mass transfer, after the determination of one constant, N_0 , the capacity of the charcoal for the particular toxic material. The diffusion

coefficient, D_v , of the gas can be estimated readily from relations available in the literature, or in most cases to a sufficiently good approximation from the molecular-weight curve illustrated in figure 13. Tables of a , the superficial area, for various particle sizes and percentage of void spaces are listed by Gamson, Thodos, and Hougen (14). All other constants may be evaluated from the conditions of flow and from the dimensions of the adsorbent bed.

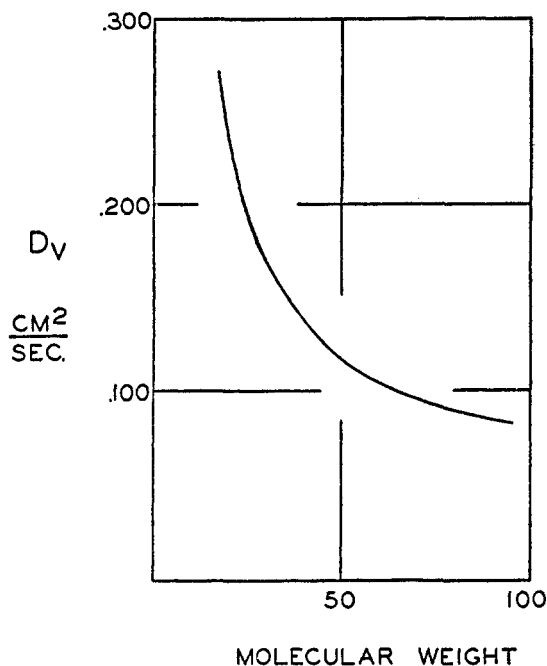


FIG. 13. Relation between diffusion coefficient and molecular weight

2. Cases in which more than one step contributes to the rate

It has been shown above that under these conditions the critical bed depth may be expressed as a sum of two terms, each of which contains the linear velocity, V , to a different power. Equation 31 for I could be inserted into the Mecklenburg relation, but the resultant expression is not as convenient for manipulation as an alternative developed by Short and Pearce (30).

It has been observed in most experiments that a plot of the critical bed depth *versus* the logarithm of the rate of flow can be approximated sufficiently well by a straight line. Because of the large errors inherent in the determination of the critical bed depth, the relation

$$I = \text{Constant} \times V^d \quad (35)$$

where d is a constant, can be used in place of the two-term expression of equation 31. The insertion of this simple relation into the Mecklenburg equation gives:

$$t_b = \frac{N_0 A}{Lc_0} \left[z - g \left(\frac{L_e}{A_b} \right)^d \log \left(\frac{c_0}{c_b} \right) \right] \quad (36)$$

in which g is a constant which depends on the mesh size of the charcoal and the particular gas being removed, d is a constant determined by the test gas, A_0 is the open area at the baffle at the effluent end of the canister, and L_0 is the steady flow rate equivalent to the pulsating rate of flow actually used. Canister tests are made with a "breather" apparatus, designed to simulate respiratory conditions, in which the flow may vary from a high peak rate down to zero. The equivalent steady flow may be determined by measuring critical bed depths for a series of different constant flow rates and plotting I versus V . Then in a subsequent experiment with pulsating flow, the value of I is determined and from the reference graph a corresponding equivalent steady flow is read off. The reference curve may vary with the test gas as well as with large changes in the shape factor of the charcoal.

The use of equation 36 requires the evaluation of three constants, N_0 , g , and d . The other parameters would be fixed by the conditions of flow and the geometric properties of the bed.

The equation has been applied (30) to a number of test gases (including chloropicrin and phosgene) and to a number of different charcoals and has been found to be reliable within the precision of the experimental data. Thus it affords a very convenient interpolation formula for the prediction of the performance of axial canisters.

The principles used in the derivation of equation 36 have been applied to the radial-flow canister also. The result depends, of course, on the geometrical configuration of the canister. For details reference should be made to the report of Short and Pearce (30).

IV. CONCLUSIONS

In examining the whole of the theoretical and experimental results of the work on the adsorption wave, one observes that progress has been attained in the following respects: The nature of the steps involved in the removal of a toxic gas from air by a granular adsorbent has been clearly stated. Where the rate-controlling process is a single one of these steps, it has been possible, within recognized restrictions, to develop a complete analytical expression for the adsorption wave. Where two steps contribute to the rate of removal, a complete theory is still lacking, but it has been possible to develop criteria for the evaluation of the relative importance of diffusion in air and reactions in the granule in the removal process. These criteria have been applied to a number of different gases and the mechanism of their removal by charcoal has been elucidated. From the general nature of the various equations for the adsorption wave it has been possible to develop semiempirical relations for the prediction of gas-mask canister lives under dry conditions and to predict qualitatively the effects of mesh size, flow rate, and concentration under dry or wet conditions.

The great gap in the present work is a suitable analytical treatment of results obtained under humid conditions or in other cases where non-linear life-thickness relations are obtained. Related to this is the absence of a complete treatment of the adsorption wave where many steps contribute to the rate of removal.

These failures, however, are bound very closely to the general obscurity of the structural characteristics of granular adsorbents and of the nature of catalytic reactions. As fundamental relations in these latter fields are gradually evolved, one may anticipate further progress in the treatment of the adsorption wave.

The author wishes to express his appreciation to Professor W. C. Pierce, Professor W. L. McCabe, and Captain F. G. Pearce for their advice and suggestions in the preparation of the original report from which this paper is taken. Special thanks are due to Dr. Duncan MacRae of the Chemical Warfare Service, who contributed so much to the development and clarification of the newer concepts described in this manuscript.

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VI. APPENDIX: MEANING OF SYMBOLS

- a = superficial surface of the granule (ignoring pore structure) per unit volume of bed,
 A = cross-section of adsorbent bed,
 A_b = open area of the baffle at the effluent end of the gas-mask canister,
 b = constant in equation for linear adsorption isotherm,
 c = concentration of toxic gas in air stream at any point in bed of adsorbent,
 c^* = concentration of toxic gas in air stream at any point in the bed in equilibrium with the charcoal at that point,
 c_b = concentration of toxic gas in air stream chosen as the "break" value,
 c_e = concentration of toxic gas in air stream at exit face of bed,
 c_0 = concentration of toxic gas in air stream at entrance face of bed,
 d = constant in equation for critical bed depth,
 D_p = diameter of granule,
 D_v = diffusion coefficient of the (toxic) gas (units of area per unit time),
 Exp = notation for the exponential e ; i.e., $\text{Exp}(x) = e^x$,
 F = mass-transfer coefficient,
 g = constant in equation for gas-mask canister life,
 G = mass velocity, i.e., weight per unit time per unit cross-section of bed,
 h = depth of the "dead layer,"
 H = height of a removal unit = $I/(\ln c_0/c_b)$,
 H_t = height of a transfer unit = $I_t/(\ln c_0/c_b)$,
 I = critical bed depth, i.e., the actual intercept of a life-thickness curve on the thickness axis,
 I_r = fraction of critical bed depth due to slowness of processes occurring within a charcoal granule,
 I_t = fraction of critical bed depth due to slowness of diffusion of gas from air stream to the surface of the charcoal,
 k_1 = constant in rate equation,
 k_2 = constant in rate equation,
 k_3 = constant in equation for t_c ,
 k_4 = constant in equation for t_c ,
 k_5 = constant in equation for t_c ,
 k_6 = constant in equation for t_c ,
 k_7 = constant in equation for critical bed depth,
 k_8 = constant in equation for critical bed depth,
 K = constant in the expanded form of the Langmuir isotherm,

L = rate of flow in liters per minute,

L_e = rate of steady flow equivalent to rate of pulsating flow,

n = moles of toxic gas on or in the granules contained in a unit volume of bed,

N_0 = saturation capacity of a unit gross volume of adsorbent for the (toxic) gas,

s = constant in equation for superficial area,

t = time,

t_b = "instantaneous" break-time, i.e., the time at which the effluent concentration reaches a value specified as the break concentration,

t_c = "cumulative" break-time, i.e., the time necessary for a given total amount of gas to penetrate the adsorbent,

V = linear velocity through the interstices between the particles of the adsorbent = $G/\alpha\rho$,

z = distance from the entrance face of the bed,

α = porosity, i.e., the volume of intergranular voids per unit gross volume of bed,

μ = viscosity of gas-air stream,

ρ = density of gas-air stream.