82. *The Redistribution and Desorption of Adsorbed Gases.*

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The distribution of adsorbed gases in columns of adsorbent and their redistribution and eventual desorption on passage of a stream of air are relevant to several problems of general importance. The present paper gives experimental results on the distribution of various gases on charcoal columns during progressive saturation, and for the changes in the distribution of adsorbed gas caused by diffusion or by the passage of an air stream. In the latter case the variations with time in the concentration of gas in the effluent stream are also considered.

It is shown that the behaviour of these systems can be calculated with considerable accuracy from a knowledge of the adsorption isotherm by a process of successive approximation. The calculations involve the assumption—not predictable theoretically, but fully justified by the agreement with experiment—that adsorption equilibrium between gas and solid is maintained throughout.

The removal of gases and vapours from air streams by solid adsorbents sometimes takes the form of a definite chemical reaction, as, for example, when active charcoal destroys, by oxidation, hydrogen sulphide and certain other gases. Such processes are irreversible and have been considered in a previous paper (*J.*, 1946, 918). On the other hand, if the gas is held on the solid by simple adsorption, the process is reversible and gas may be desorbed into the air stream. Some of the phenomena which arise under these conditions are discussed in the present paper.

The processes of redistribution and desorption are of interest in connexion with several practical problems. One is that of solvent recovery. Another is that of the safe use of respirators which have had a short exposure to toxic gases and are subsequently breathed through, either immediately, or after an interval in which diffusion may occur. The results given in this paper show that the actual rates of redistribution and desorption may vary by factors of several hundred from one gas to another. Nevertheless the behaviour can be quantitatively predicted from a knowledge of the adsorption isotherm of the gas. The calculations depend upon an auxiliary assumption, not predictable but fully justified by

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* The results given in this paper are taken from a very much greater volume of experimental material—much of it obtained in connexion with specific practical problems and contained in reports to the Ministry of Supply, with the following additional co-authors : G. T. Kennedy, J. J. Kipling, J. A. E. Moy, and J. H. Nicholls.

experiment, namely, that throughout adsorption and desorption—within the range of experimental conditions employed—adsorption equilibrium between gas phase and solid is maintained.

The system whose physical chemistry is considered is essentially a column of granular adsorbent into which a certain amount of adsorbable gas is first carried by a stream of air. The gas stream is passed for only a fraction of the time required to saturate the column, pure air being then passed through so that redistribution and desorption of the gas occur. The initial treatment of the column with the gas–air stream may be followed by a period of rest during which redistribution can occur by diffusion, before the resumption of the air stream. The methods of calculation employed are, however, applicable to a wider range of problems than these.

The complete equations for the rate of change of concentration of the gas as a function of time and position in the column can be written down, but they are, in general, quite insoluble. In the special case where the adsorption isotherm of the gas on the solid is a straight line a cumbrous solution in series may be obtained (Wicke, *Kolloid-Z.*, 1940, **93**, 129). Adsorption isotherms are, however, usually not linear, and in fact can rarely be represented by any simple equation. Since the phenomena of desorption are found to depend to a remarkable extent on the *precise shape* of the isotherm, the treatment of the problem by direct solution of the differential equation is not practicable.

The theoretical treatment is based on the following principles : (1) The column is divided into a series of small finite elements of length which are treated as though differential methods could be accurately applied to them. In the same way a series of small time intervals are treated as differentials. By suitable choice of the magnitude of these column elements and time intervals a compromise may be achieved between loss of accuracy on the one hand and excessive laboriousness of calculation on the other. (2) Equilibrium between each element of the column and the gas stream is assumed to be attained very rapidly. The justification of this assumption will appear later, where it will be seen that equilibria, rather than rates of attainment of equilibria, govern the observed effects. (3) The equilibrium assumed is that represented by the *actual experimentally determined* isotherm.

In discussing desorption we must consider the following phases :

(*a*) The adsorption phase : in which the gas is carried into the column by the air stream and adsorbed—to the greatest extent—in the initial layers. The distribution of gas in the column at the end of this phase is the initial distribution for (*b*).

(*b*) The redistribution phase : in which the passage of pure air leads to desorption from the initial layers and progressive transference of the gas along the column.

(*c*) The desorption phase : in which this transferred gas reaches the final layer of the column and is desorbed into the effluent stream.

After considering experimental methods, we shall discuss these stages in turn. In each section, experimental results relating to columns of active charcoal and the gases hydrogen cyanide, carbon tetrachloride, cyanogen chloride, and water will be compared with the behaviour calculated from the above principles.

Experimental Methods.

The experiments fall into four groups : (i) Investigation of the distribution of gases along charcoal columns during adsorption and desorption. (ii) Measurement of the changes in effluent concentration with time during the passage of air through columns previously exposed to gas streams. (iii) Investigation of the redistribution of adsorbed gas under the influence of diffusion alone. (iv) Determination of the adsorption isotherms of the different gases on charcoal.

(i) *Distribution of Adsorbed Gases along Charcoal Columns during Adsorption and Desorption.*—All experiments were made at approximately 20° with an unimpregnated commercial charcoal produced from briquetted coal. The charcoal was graded 7—18 mesh B.S.S. sieve sizes, and was dried before use. Gas compositions are stated in volume per cent.

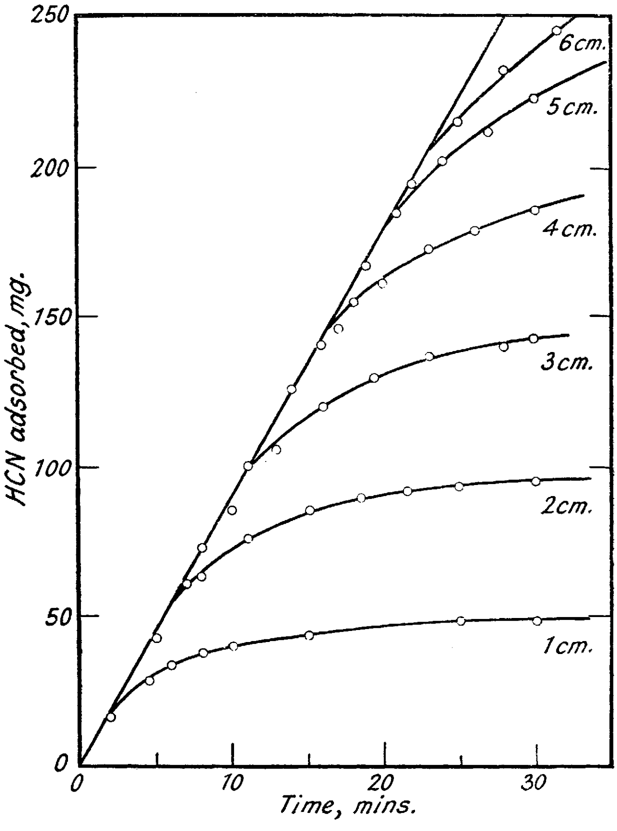
(a) *Hydrogen cyanide.* The adsorption of hydrogen cyanide was followed by direct weighing. Its distribution was determined by the application of the following principle. If an air stream containing an adsorbable gas is passed through a layer of adsorbent 1 cm. in length, then the gain in weight of this layer will be identical with the adsorption which would have taken place in the first cm. length of a long column under the same conditions. Similarly, the difference between the uptake of columns 2 cm. and 1 cm. in length gives the adsorption in the second 1 cm. section of a long column. By successive measurements on columns of increasing length the complete distribution of gas at any stage may be obtained. The curves in Fig. 1 show the gain in weight of columns of charcoal from 1 cm. to 6 cm. in length during the passage of 1·0% hydrogen cyanide (800 c.c./min. through a 2 cm. diameter column). The vertical distance between two curves at any given time gives the amount of gas adsorbed on the corresponding 1 cm. length of the column. We can thus obtain complete information about the changes in distribution of the gas in the column as adsorption proceeds.

In plotting distribution curves (such as those shown in Fig. 4), the amount of adsorbed gas has been averaged over each successive cm. length of the column at a series of successive times. The centre of gravity of the gas adsorbed on any section has been assumed to be at the mid-point. This will only be strictly true when the section has become saturated : until then the centre of gravity of the adsorbed material will be nearer the end at which the gas enters. The error introduced by plotting the gas concentrations at the mid-point of each section is small and has been neglected.

In experiments on desorption, a relatively small amount of gas is admitted to the column, and the changes in its distribution on passage of a stream of pure air are followed. This can be done in exactly the same way by carrying out measurements on columns of different length.

(b) *Carbon tetrachloride.* The distribution of carbon tetrachloride was investigated by the use of a column of adsorbent which could be separated into sections. By weighing each section of the column individually at intervals during adsorption and desorption the amount of carbon tetrachloride on it at any instant could be determined.

FIG. 1.



The adsorption of hydrogen cyanide from a 1% *stream by charcoal columns of different lengths.*

(c) *Cyanogen chloride.* For this gas, instead of determining the increase in weight of the adsorbent, the amount of gas escaping from the end of the column was estimated by chemical analysis. Subtraction from the known input of gas gave the amount retained at any instant.

(d) *Water.* A similar method was used with water vapour, which was estimated by passing the effluent stream through a calcium chloride tube weighed at intervals. The values obtained in this way for the water adsorbed were checked by direct weighing of the column itself.

(ii) *Determinations of Effluent Concentrations.*—After appropriate treatment of the column with the gas under investigation, a stream of pure air was passed through at a standard rate (200 c.c./min. for a column 1 cm. in diameter). The concentration of the gas in the effluent was then determined at successive times by a suitable analytical method. Water and carbon tetrachloride were estimated gravimetrically; hydrogen cyanide by adsorption in sodium hydroxide solution, buffering to a controlled pH, and titration with standard iodine; cyanogen chloride by conversion into ferric thiocyanate which was determined colorimetrically. The experimental arrangements were very similar to those described in a previous paper (*J.*, 1946, 918).

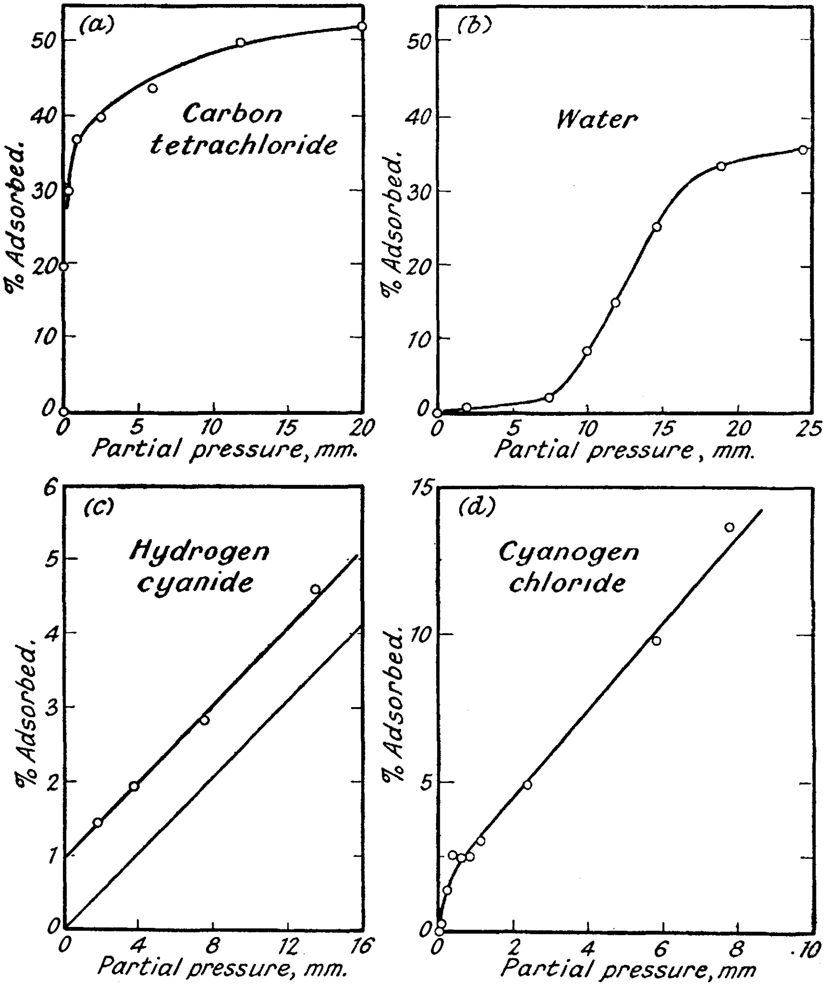
(iii) *The Redistribution of Gases by Diffusion.*—The experimental methods were similar to those described under (i).

(iv) *The Determination of Adsorption Isotherms.*—The isotherms of carbon tetrachloride and cyanogen chloride were determined by use of a quartz-spring adsorption balance. The measurements were made either directly, or by the method of Allmand and Burrage (*J. Soc. Chem. Ind.*, 1928, **47**, 369).

Water isotherms were measured by a static method. Small amounts of charcoal in wire-gauze containers were allowed to come to equilibrium with the water vapour over a series of saturated salt solutions at 25°. The amount of water taken up was determined by weighing. The vapour pressures of the solutions were taken from Obermiller (*Z. physikal. Chem.*, 1924, **109**, 145).

The hydrogen cyanide isotherm called for special treatment. For lower pressures it was determined by passing HCN–air streams of various concentrations through charcoal till saturation was reached, and measuring the increase in weight. For higher pressures the quartz adsorption balance was employed.

Fig. 2.



Adsorption isotherms for carbon tetrachloride, water, hydrogen cyanide, and cyanogen chloride on active charcoal.

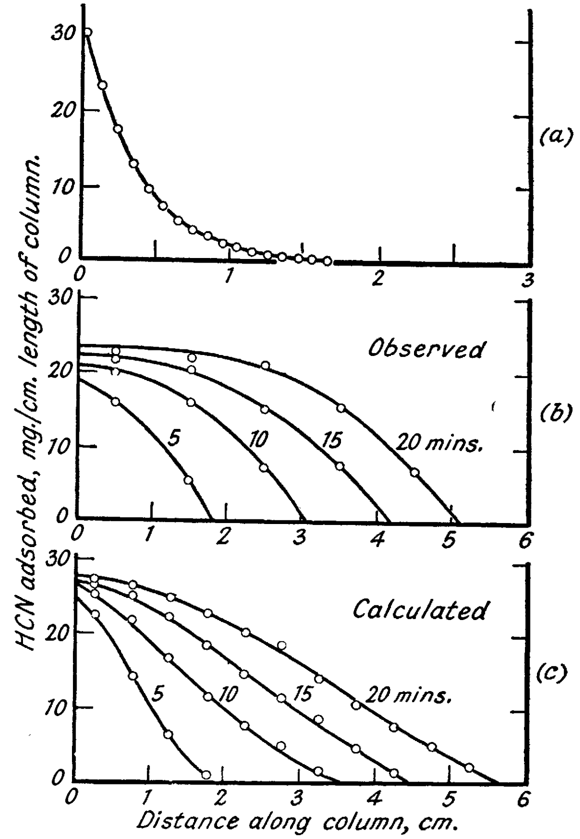
The experimentally determined isotherm shows an apparent intercept on the weight axis. This is illusory and is due to slow reaction of the adsorbed hydrogen cyanide; the intercept represents the amount of the gas which has reacted in the time taken for the experiment. The precise form of curve obtained is thus to some extent a function of the time for which the gas has been in contact with the charcoal, and is not really that of a true isotherm. In subsequent calculations, where the phenomenon under consideration involves prolonged contact of gas and charcoal, this experimental curve showing the intercept has been used. It makes allowance, even if a somewhat arbitrary one, for loss of gas in chemical reaction. For the calculation of the initial penetration of gas into the column, where the gas and charcoal have been in contact for only a very short period of time, a better approximation to the true isotherm was taken to be a line drawn parallel to the experimental curve, but passing through the origin.

The experimental isotherms for the four gases used in the present series of experiments on the charcoal employed are given in Fig. 2.

The Distribution of Adsorbed Gas in Charcoal Columns during Adsorption.

The phenomena which arise during the desorption of gas from a partially saturated column on passage of air are dependent on the initial distribution of the adsorbed gas in the column. We must first, therefore, consider the distribution of adsorbed gases which have been taken up from air streams under various conditions.

FIG. 3.

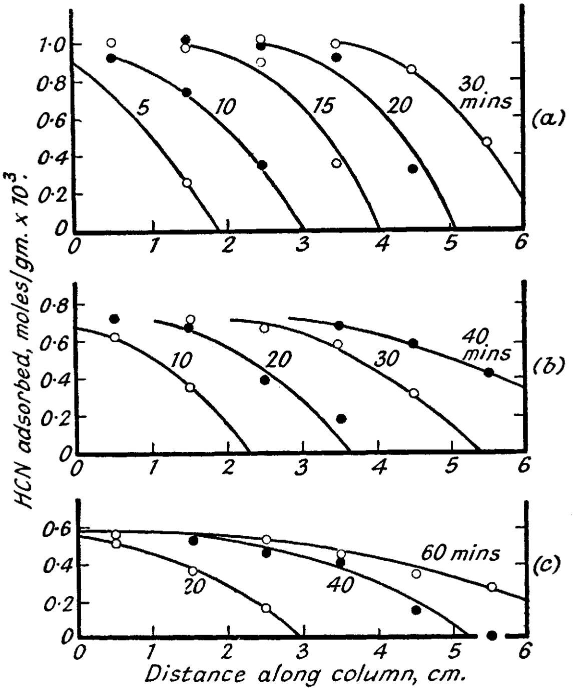


(a) *Calculated initial penetration of hydrogen cyanide into a charcoal column.* (b) *Experimental curves showing the distribution of* HCN *in a charcoal column during the progressive saturation of the column.* (c) *Calculated distributions of* HCN *for comparison with* (b).

(i) *The Attainment of Equilibrium between Charcoal and Gas.*—The whole treatment adopted in this paper depends on the assumption that equilibrium is maintained, and the agreement with experiment is a vindication of that assumption. One direct way of illustrating the extent to which adsorption equilibrium is attained during the passage of a gas through a charcoal column may be derived from curves such as those in Fig. 1. The slope at any point gives the rate of adsorption of gas. The difference between this value and the rate at which gas is being admitted is the rate at which gas is escaping from the end of the column. The rate at which gas is entering the nth unit-length section of a column is the rate at which it would have been escaping from the end of a column ($n - 1$) units long after the same time. We can therefore obtain the rates at which gas is entering and leaving each section of the column, and hence the mean concentration in each section at any instant. The total amount of gas adsorbed in each section at any moment is also known. We can therefore plot the amount of gas adsorbed against the mean partial pressure. If the charcoal were in equilibrium with the gas this curve would be identical with the adsorption isotherm. Fig. 6 is an example of the type of result obtained in this way and shows how nearly equilibrium between charcoal and gas is maintained throughout adsorption and desorption—at least under the conditions of flow-rate and concentration employed here.

(ii) *The Method of Calculation of the Adsorption of Gases in Charcoal Columns.*—From a knowledge of the adsorption isotherm the changes in the distribution of a gas during progressive saturation of the column may be calculated. The column is considered as a number of finite elements of length. The first volume-element of the gas stream is assumed to reach instantaneous equilibrium with the first element of the column. Gas is adsorbed, so that the concentration of gas leaving the element will be less than the initial concentration. Hence the second element of the column will adsorb less than the first. Each successive element adsorbs less than the one preceding it. Theoretically, the column would have to be of infinite length to reduce the concentration to zero, but in practice the concentration falls to a negligible value in a definite distance. This immediate penetration of gas may be calculated by the following process of successive approximation :

FIG. 4.



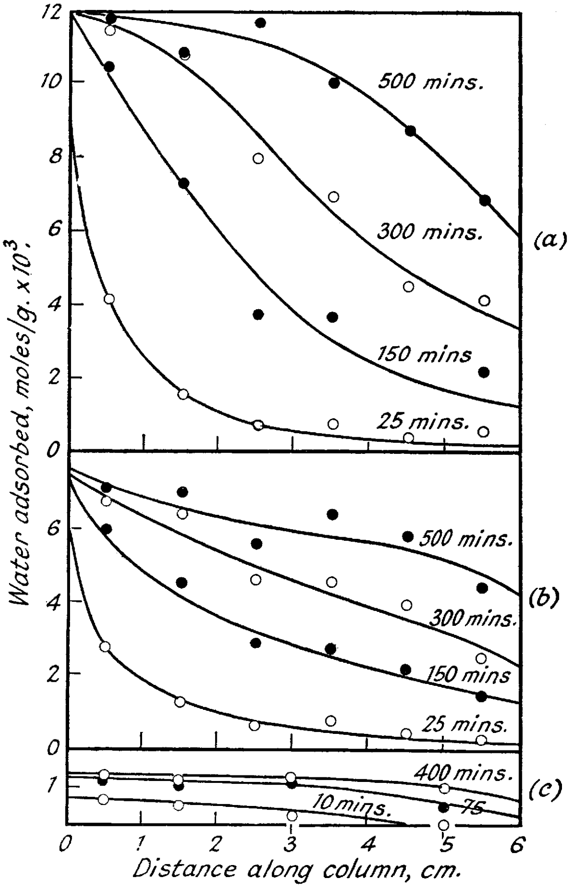
Distribution changes accompanying the progressive saturation of a charcoal column by HCN *at* (a) 1·0%, (b) 0·5% *and* (c) 0·25%.

A volume of the gas stream of known initial concentration (for example, that passing in the first minute of flow into the column) is assumed to come to adsorption equilibrium with the first unit section of the column. We require to find a value for the amount of gas adsorbed such that it will be in equilibrium at the partial pressure of the gas remaining in the stream. If the gas concentration were unchanged by the adsorption, the isotherm would give directly a value for this amount. This will be an *upper limit* for the adsorption. Subtraction of this from the total initial amount in the volume-element gives a *lower limit* for the final gas concentration, which, from the isotherm, will give a *lower limit* for the adsorption. The value required will lie between these extreme values : to a first approximation it will be given by their mean. The use of this to subtract from the initial amount of gas gives a better value for the amount left in the stream, and the amount adsorbed which would be in equilibrium with this partial pressure is read off from the isotherm. The mean of this value and the previous approximation is then taken, and the process repeated. Eventually a pair of values for the adsorbed and unadsorbed gas are found which correspond to equilibrium according to the experimental isotherm.

The equilibrium partial pressure for the first element of the column is the initial concentration for the second. The above calculations are repeated for each succeeding section until the residual partial pressure reaches a negligible value. This gives the distribution of the gas in the column at the end of the first minute of flow of the gas stream. Taking this distribution as a new initial state we can consider the passage of the stream for a further minute. By repeating this process for a whole series of successive time intervals we can calculate the distribution changes during the gradual approach of the column to saturation.

(iii) *A Comparison of Experimental and Calculated Results.*—(a) *Hydrogen cyanide.* Fig. 3(*a*) shows the amounts of hydrogen cyanide adsorbed by each successive cm. length of a charcoal column 2 cm. in diameter after the first minute of passage of 1·0% hydrogen cyanide, calculated from the isotherm [Fig. 2(*c*)] by the method described. Fig. 3(*c*) gives the calculated distribution of the gas at five-minute intervals during the saturation of the column. Experimental results for comparison with Fig. 3(*c*) are given in Fig. 3(*b*). The agreement is satisfactory as regards the time scale for the desorption.

FIG. 5.



Distribution changes accompanying the progressive saturation of a charcoal column by water vapour at (a) 1·9%, (b) 1·6% *and* (c) 0·9%. (*The immediate penetration through the column is to be noted.*)

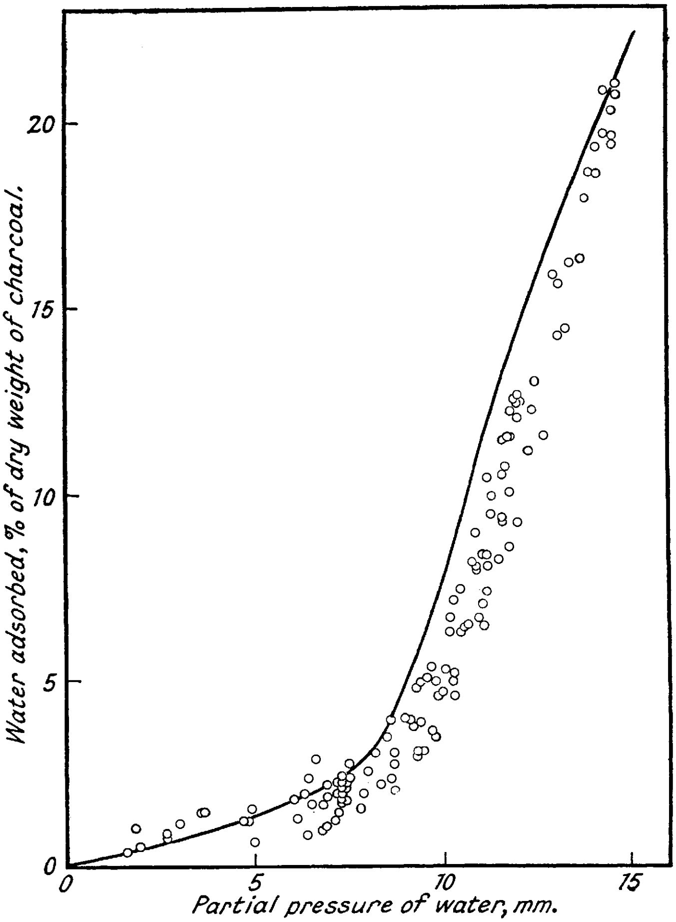
Fig. 4 gives the experimental results for the changes in distribution during the saturation of charcoal columns by 0·25%, 0·5% and 1·0% hydrogen cyanide. The lower the initial concentration at which a given amount of hydrogen cyanide is passed into the column, the greater the depth to which it penetrates.

(b) *Carbon tetrachloride.* Experiments were made to determine the initial distribution of carbon tetrachloride along a column when a given amount was carried in by the air stream at two different initial concentrations (2% and 0·2%). The distribution is very nearly independent of the initial concentration. The experimental adsorption isotherm for carbon tetrachloride, given in Fig. 2(*a*), shows that there is rather little variation in the equilibrium amount adsorbed over the concentration range 2% to 0·2%. The observed constancy of distribution is therefore in agreement with the isotherm.

By the method of successive approximation explained above, the distribution of carbon tetrachloride during passage of a 0·2% stream was calculated, and gave good agreement with experimental results.

(c) *Water.* The isotherm for the adsorption of water on charcoal is of an unusual shape [Fig. 2(*b*)]. At partial pressures below about 6 mm. of water vapour (0·8%), the amount adsorbed is small and increases only slowly with pressure. Between about 10 mm. and 20 mm. it increases rapidly, and at 20 mm. (2·5%) saturation is nearly reached. The distribution of water in charcoal columns was investigated with air streams containing water at partial pressures corresponding to three significantly placed points on the isotherm. Two (1·9% and 1·6%) are on the steeply rising section. The third (0·9%) is on the lower part, corresponding to a much lower percentage adsorption. The experimental results are given in Fig. 5, where the same scale is used for all concentrations. The shape of the wave-front in the column changes from concave at small adsorptions to convex as saturation is approached.

FIG. 6.



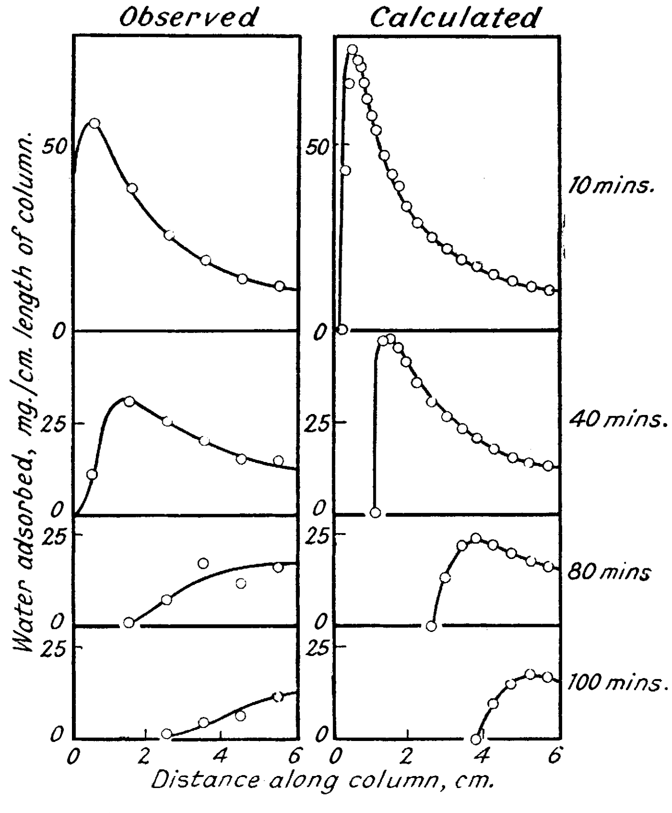
Adsorption isotherm for water inferred from observed distributions in the flow system (marked points). The continuous line gives the isotherm corresponding to complete equilibrium.

The distribution of water obviously differs greatly from that of the other vapours considered in this paper. There is immediate penetration of water vapour right through the column. This is a consequence of the very small slope of the initial part of the isotherm. Changes in the concentration of water vapour in the stream have more effect on the total amount taken up in the column than on its distribution.

The distribution of water along the column was calculated from the isotherm by a process of successive approximation similar to that already explained. With the data from which Fig. 5 was derived, the values plotted in Fig. 6 were calculated, the isotherm being shown as a continuous line. The calculated points lie quite near to the true isotherm, indicating that in the various distribution experiments there has been a close approach to equilibrium.

(d) *Cyanogen chloride.* The distributions of cyanogen chloride in a charcoal column after passage of 1·0% for 4 minutes and of 0·1% for 40 minutes were determined. A given amount of gas was found to be distributed over a greater length of the column when admitted at a lower concentration. In its behaviour, therefore, cyanogen chloride bears a closer resemblance to hydrogen cyanide than to water or carbon tetrachloride.

Fig. 7.



Changes in the distribution of water in a charcoal column on passage of a stream of air.

The calculated distribution of cyanogen chloride was in good agreement with the experimental results.

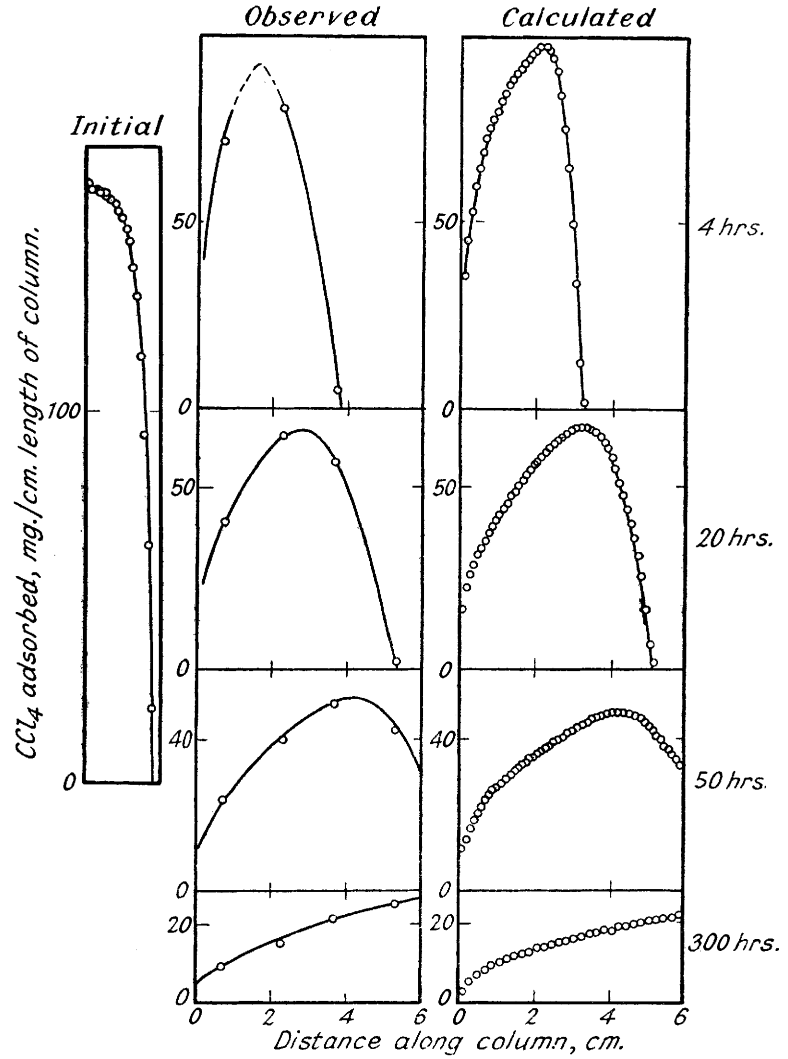
The Change in Distribution with Time during Desorption.

In this section we consider a charcoal column on to which a certain amount of gas has already been carried, and investigate the changes in distribution caused by subsequent passage of a stream of pure air.

Experiments with the four gases previously considered showed that the respective times required for the transference of comparable amounts differed by whole orders of magnitude. These very diverse rates of transfer can, however, be satisfactorily calculated from the isotherms by an extension of the method already described. To illustrate the procedure, the transfer of water from a single section of a column in a single interval of time will be calculated.

Consider the first 1 mm. section of a column on which are adsorbed 9·50 mg. of water. We wish to find the water content of this section after the passage of dry air at the standard rate for 3 minutes. The amount initially adsorbed corresponds to 21·0% water on the charcoal, and the initial vapour pressure of water over the section is therefore 14·46 mm. [from the isotherm, Fig. 2(*b*)]. If this pressure were maintained for 3 minutes, the charcoal would lose 8·16 mg. to the stream, leaving 1·34 mg. on the charcoal: this is a *maximum* estimate for the desorption. A water content of 1·34 mg. corresponds to 2·97% and a vapour pressure of 7·97 mm., which would lead to the *minimum* estimate for desorption, namely, 4·49 mg., leaving 5·01 mg. on the charcoal. Proceeding in this way :

FIG. 8.



Changes in the distribution of carbon tetrachloride in a charcoal column on passage of a stream of air.

9·50 mg. on charcoal ≡ 14·46 mm., or 8·16 mg. desorbed: 1·34 mg. on charcoal.
1·34 mg. on charcoal ≡ 7·97 mm. or 4·49 mg. desorbed : 5·01 mg. on charcoal.
½(1·34 + 5·01) = 3·18 on C ≡ 9·78 mm. or 5·52 mg. desorbed : 3·98 mg. on charcoal.
½(3·98 + 3·18) = 3·58 on C ≡ 10·60 mm. or 5·98 mg. desorbed : 3·52 mg. on charcoal.

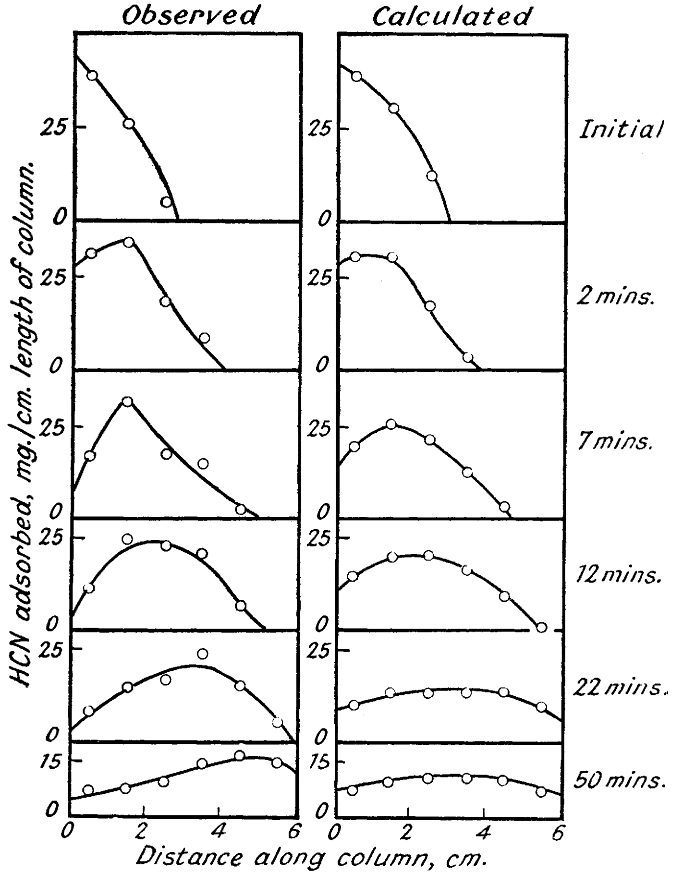
The final amount of water on this section is found in this way to be 3·55 mg., so that the air stream has picked up 5·95 mg. to give a mean partial pressure of water of 10·50 mm. This is the initial concentration of water vapour offered to the second element in the column.

Calculations of this type carried out for each successive element in the column give the transfers of water from section to section in the 3-minute interval chosen. By repeating the series for a succession of such intervals we eventually obtain a picture of the whole of the desorption process.

These calculations have been made for the four gases : water, carbon tetrachloride, hydrogen cyanide, and cyanogen chloride. The calculated curves for the distribution changes during the desorption are compared with the experimental results in Figs. 7, 8, 9, and 10. The results obtained will now be considered briefly.

Water.—On passing dry air into a charcoal column previously treated with a wet air stream for a short time, a steep maximum is rapidly set up in the distribution. This maximum moves through the column, decreasing in height and becoming more rounded. The amount of water in the later sections of the column remains almost constant until about 80% of the total water has been desorbed : this results in an almost constant concentration of water vapour in the effluent during this time. The calculated distributions agree well with the experimental data, except that the calculated maximum concentrations are somewhat greater than those observed—probably because the experimental results are averages of concentrations over 1 cm. sections while the calculations are based on much shorter elements. The areas under the two sets of curves, however, correspond closely, and the times for complete desorption—about 115 minutes (calculated) and 135 minutes (observed)—are in good agreement.

FIG. 9.

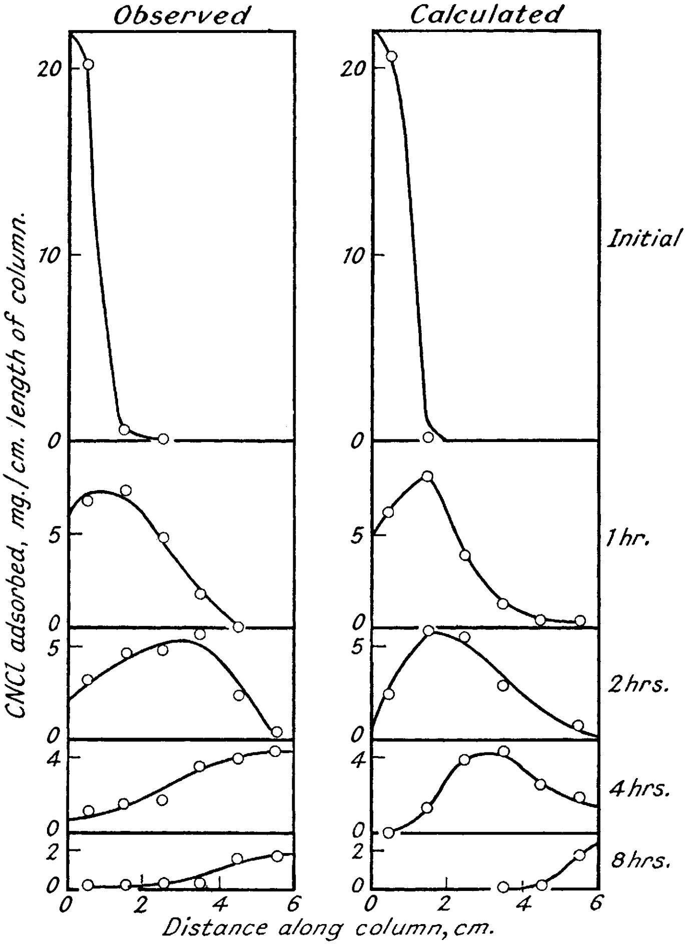


Changes in the distribution of hydrogen cyanide in a charcoal column on passage of a stream of air.

Carbon Tetrachloride.—The adsorption isotherm is such that, even when quite large amounts are adsorbed, the vapour pressure is small. The leading edge of the distribution curve of adsorbed carbon tetrachloride is therefore initially very steep. The change in the form of the distribution with time during the passage of air is qualitatively very similar to that observed with water. The time scale is, however, vastly greater. As will be seen from Fig. 8, appreciable amounts of carbon tetrachloride still remain in the intial layers of the column after air has been passing for 300 hours. Sensibly complete desorption is only attained after about 600 hours. Comparison of the experimental and calculated results reveals very good agreement.

Hydrogen Cyanide.—The change of distribution with time during desorption of hydrogen cyanide is similar to that observed with the other gases, but the calculations give a rather greater rate of progress than is actually observed. This discrepancy is almost certainly to be attributed to chemical reaction of the hydrogen cyanide which proceeds hand in hand with desorption. Even so, the calculations predict a time-scale for desorption which is fairly close to that observed experimentally.

FIG. 10.



Changes in the distribution of cyanogen chloride in a charcoal column on passage of a stream of air.

Cyanogen Chloride.—For cyanogen chloride the results indicate a behaviour intermediate between that of hydrogen cyanide on the one hand and carbon tetrachloride on the other. Thus the time-scale for desorption under the conditions employed is of the order of 10 hours. This is to be compared with about 1 hour for hydrogen cyanide and over 300 hours for carbon tetrachloride. The calculations give the correct order of magnitude of this time-scale, and reproduce fairly well the changes in shape of the distribution curve during the desorption process.

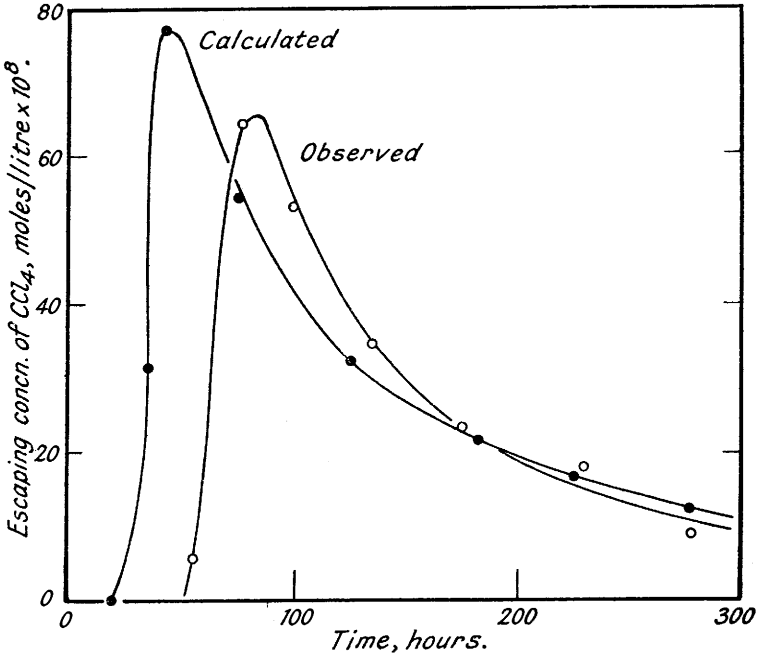
The Concentration of Gas in the Effluent Stream during Desorption.

When the adsorbed gas reaches the end of the column it will pass into the effluent stream. In general, there is an initial period during which no gas can be detected in the effluent; the concentration then rises rapidly to a maximum and finally decreases slowly in a more or less exponential manner.

We have seen that for practical purposes adsorption equilibrium is maintained during desorption in systems of the type we are considering. The concentration of gas in the effluent stream at any instant will therefore correspond to equilibrium with that adsorbed on the final layer of the column and may be calculated by the methods described in the last section.

In Figs. 11 and 12 are shown the observed and the calculated curves for the variation in effluent concentration with time during desorption from columns previously treated with carbon tetrachloride and with water. The agreement is close. For reasons already discussed, water vapour penetrates through the column, even in the brief initial treatment. This leads to a high concentration of water vapour in the effluent stream at the beginning of the desorption.

FIG. 11.



Variation with time of the effluent concentration of carbon tetrachloride during desorption.

Similar calculations have been made for hydrogen cyanide and cyanogen chloride. As already explained, the former reacts slowly on charcoal to give products which are not desorbed. As would be expected, therefore, the amount of hydrogen cyanide actually desorbed from a column is appreciably less than that calculated. The form of the calculated curve is, however, in general agreement with experiment. The same considerations, in general, apply to cyanogen chloride.

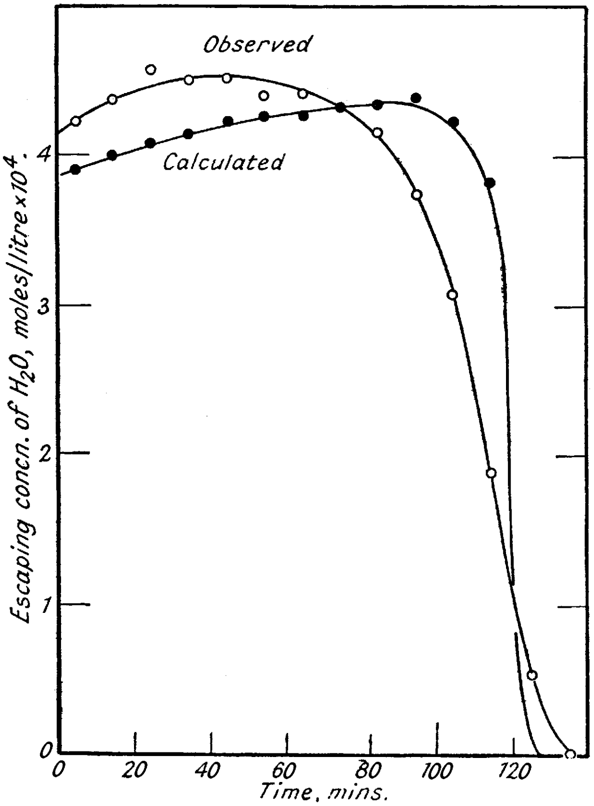
The Later Stages of Desorption.

During desorption the point of maximum adsorbed concentration moves through the column. The arrival of this maximum at the end of the column corresponds to the maximum concentration of gas in the effluent stream. The concentration of adsorbed gas is by this time fairly uniform along the column. The process of desorption would thereafter be expected to resemble that from homogeneously saturated charcoal in an adsorption balance.

Experiments with such a balance have shown that the behaviour of different gases on desorption conforms to one of three main types. These are exemplified severally by carbon tetrachloride, water, and hydrogen cyanide, and may be related directly to the adsorption isotherms. The idealisation of charcoal columns by the very small quantities of charcoal used in an experiment with an adsorption balance may constitute an over simplification, but for our purpose the two sets of conditions are sufficiently comparable.

The desorption of carbon tetrachloride is characterised by a linear decrease in the amount retained with the *logarithm of the time* of desorption. This means that there is a very rapid decrease in desorption rate with decreasing amounts of material remaining adsorbed. In practice the rate of desorption may become almost negligible while the amount adsorbed is still appreciable. The desorption of carbon tetrachloride from a column must, at least qualitatively, follow such a course. For example, in the experiment from which the results given in Fig. 11 were derived, the vapour originally admitted was completely adsorbed within the first 1·5 cm. of the column. On passage of air, 18 hours elapsed before carbon tetrachloride escaped from the end of the 6-cm. column. After 65 hours' desorption, the mean concentration on the final layers of the column was 13·43% by weight; after 89 hours it had fallen only to 12·27%. During the intervening period of 24 hours the total amount of carbon tetrachloride desorbed from the entire column was only 28·1 mg. In the air stream of 200 c.c./min. this corresponds to a dilution of about 10^5. Though this would appear to be a remarkably low rate of desorption from a completely penetrated column, it will be seen that it is to be expected from a consideration of the form of the desorption curve and isotherm. The two operative factors are the high maximum adsorption and the very rapid fall in the desorption rate with decreasing amount adsorbed, the latter being inherent in the linear relation between amount adsorbed and the logarithm of the time.

FIG. 12.



Variation with time of the effluent concentration of water vapour during desorption.

A sharp contrast with the behaviour of carbon tetrachloride is shown by that of water. Here there is a nearly linear relation between the amount remaining adsorbed and the time (in contrast with the *logarithm* of the time with carbon tetrachloride). This means that the rate of desorption is nearly constant over a considerable range, and decreases only when the amount remaining adsorbed is very small. We should therefore expect that in the desorption of water vapour the concentration in the effluent would first remain constant, and then fall very rapidly. As will be seen from Fig. 12, this situation is completely realised. The practical significance of this type of behaviour is obvious. Substances, such as water, having S-shaped adsorption isotherms, will be desorbed very readily.

Hydrogen cyanide shows an intermediate type of behaviour. The rate of desorption is approximately proportional to the amount remaining adsorbed. In a constant air stream the latter will therefore decrease in a more or less exponential manner. The falling branch of the experimental curves for the effluent hydrogen cyanide concentration are found to be of this type. The behaviour of cyanogen chloride is rather similar, though at lower pressures it becomes intermediate in character between hydrogen cyanide and carbon tetrachloride. This again is expected from its adsorption isotherm.

The close relation between the form of the desorption curves of the different substances and their adsorption isotherms is very clear. The nearly constant desorption rate of water depends essentially on the fact that, according to its isotherm, the vapour pressure over the adsorbent changes little over wide ranges of the amount adsorbed. The hydrogen cyanide isotherm is roughly linear: the vapour pressure over the charcoal, and hence the desorption rate is therefore proportional to the amount of hydrogen cyanide remaining adsorbed. Finally, with carbon tetrachloride, the vapour pressure over the surface falls more and more rapidly as the amount adsorbed is decreased. This leads to vanishingly small desorption rates from charcoal still containing appreciable quantities of adsorbed vapour.

The Redistribution of Adsorbed Gas by Diffusion.

After a brief treatment of a column with gas, the latter is largely confined to the initial layers. We have now to consider distribution changes resulting from simple diffusion when no air is passed through, and also the effect of such redistribution on subsequent desorption into an air stream. This has a bearing on several practical problems (such as the storage of a respirator after a short period of use in a contaminated atmosphere and subsequent use on a later occasion).

A rigorous mathematical treatment is impracticable. The diffusion of adsorbed gas along the column may, however, be calculated by an approximate method.

The rate of diffusion of one gas into another is given by Fick's equation $\mathrm{d}w/\mathrm{d}t = -D.\mathrm{d}c/\mathrm{d}l$, where $\mathrm{d}w/\mathrm{d}t$ is the weight of gas passing across a plane 1 sq. cm. in area per second through a concentration gradient of $\mathrm{d}c/\mathrm{d}l$, and D is the diffusion constant. In a packed column the distance which a molecule will have to diffuse in order to travel a distance of 1 cm. along the tube is greater than if the tube were empty. Similarly, the concentration gradient will be less along this extended path than that measured directly along the tube. To a rough approximation the path may be assumed to be 1·5 times as great, and the concentration gradient correspondingly less. These corrections have been taken into account by suitable adjustment of the values taken for D. Precise values for the diffusion constants in air of the gases used in the experimental work were not available. The value 0·1 cm.^{2} sec.$^{-1}$ was used for water and hydrogen cyanide. For cyanogen chloride and carbon tetrachloride the value 0·05 cm.^{2} sec.$^{-1}$ has been assumed. The cross-section area of the gas space in a packed column has been taken as 0·25 of that of the tube.

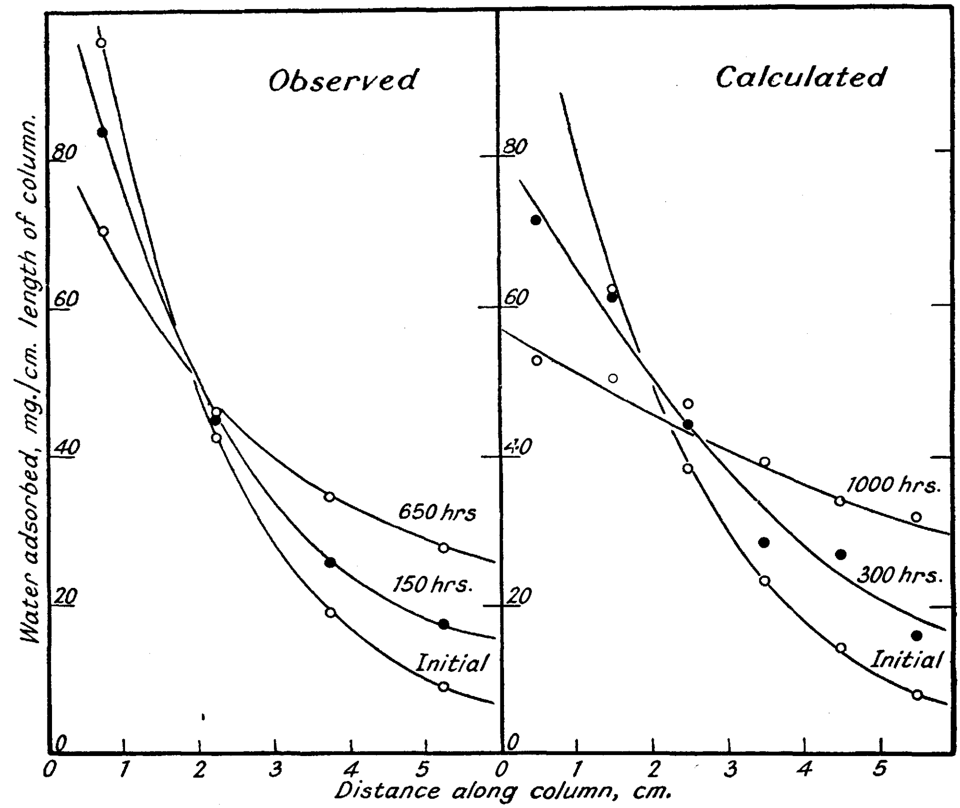
In the calculations of diffusion a differential method similar to that used in the preceding sections has been applied. Gas is assumed to be admitted to the column (its distribution being known by experiment or calculation), and from the isotherm the partial pressure over each element of the column is obtained. This gives the concentration gradient at all points. Diffusion is then allowed to take place for a given time interval, and the amount of gas which would diffuse from each element to the next is calculated from Fick's equation in its differential form. Adsorption equilibrium is assumed to be attained and the method of successive approximation used to obtain the amount of gas adsorbed on each element and the partial pressure over it. The concentration gradients corresponding to this new distribution are then calculated, and the process repeated for another interval of time. In this way we obtain a series of curves giving an approximate picture of the progressive diffusion of the adsorbed gas along the column.

Calculations by this method showed that redistribution of adsorbed hydrogen cyanide, water, cyanogen chloride, and carbon tetrachloride by diffusion alone would be expected to take place at about one fiftieth to one hundredth of the rate caused by the standard air stream previously considered.

The redistribution of adsorbed water by diffusion has been investigated experimentally by methods already described. The results are given in Fig. 13(*a*). Good agreement is shown with the calculated values in Fig. 13(*b*).

FIG. 13.

(*a*) (*b*)



Redistribution by simple diffusion of adsorbed water vapour.

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