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Review: Activated Carbon Filters in Respiratory Protective Equipment

Richard C. Brown

Health and Safety Laboratory, United Kingdom

The review considers first the nature of airflow through granular carbon filters and the relationship between pressure drop and airflow rate. Equilibrium adsorption is then summarized, with particular emphasis on the volume filling of micropores, on which most of the theory of activated carbon performance is based. The dynamics of adsorption is studied, and the analytical solution of the fundamental dynamic adsorption equation is given, leading to the development of various equations used in practice for the description of breakthrough. The most fundamental dynamic parameter, the rate constant for adsorption, is discussed, and the effects of concentration, granule diameter, and air stream velocity are summarized. Extracts of a number of experimental observations with reference to specific adsorbates are given, followed by an account of the adsorption of mixtures of compounds. The effect of relative humidity is discussed. This is followed by an account of non-destructive tests, and the review ends with a summary and an indication of possible fruitful areas for research.

activated carbon adsorption vapour filter respirator respiratory protection

1. INTRODUCTION

The subject of this review is the behaviour of activated carbon filters in respirators giving personal protection against gases and vapours. This forms only a part of the subject of activated carbon, comprehensive accounts of which are given in a number of texts (Jankowska, Swiatkowski, & Choma, 1991; Keltsev, 1976; Mantell, 1951). Those texts cover the history of activated carbon development, the raw materials used in its production, methods of carbonization and activation, the behaviour of the material as an adsorbent from both liquids and gases, the nature of the surface of the carbon, and the reactivity of surface groups.

There are clear analogies between filters used against gases and vapours and those used against particulates (Brown, 1993; Davies, 1973; Pich, 1966). In both cases, the two principal aspects of filter behaviour are the resistance of filters to airflow and their efficiency in removing hazardous substances from the air. The former is, in effect, the price paid for the latter, and its study is relatively straightforward. The latter forms by far the greater part of this review and comprises equilibrium adsorption theory, adsorption dynamics, the adsorption of binary mixtures of contaminants, the effect of humidity on adsorption, and experimental observations of the adsorption of a variety of chemical species.

2. PRESSURE DROP OF CARBON FILTERS

Most activated carbon filters used in respirators are in the form of cartridges containing 50 to 200 cm^3 of granules or canisters containing 250 to 2000 cm^3 (Breysse, White, Ryan, & Corn,

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Correspondence and requests for reprints should be sent to R. C. Brown, Health and Safety Laboratory, Broad Lane, Sheffield, S3 7HQ, United Kingdom.

1983). Some are made from sintered or bonded materials, and others comprise fibres that are mixed or coated with powdered carbon or actually made from carbon, a form particularly suitable for disposable respirators. The theory of airflow and pressure drop is most highly developed for assemblies of fibres. The pressure drop, Δp, across a filter of thickness, L, made from fibres of diameter, d, is

$$\Delta p = \frac{4\eta L U f(c)}{d^2} \tag{1}$$

η is the coefficient of dynamic viscosity of the air and U is its velocity; $f(c)$ is a function of the packing fraction, c, which is the fraction of the perceived volume of the filter taken up by the material of the fibres themselves. Its form depends on the model used, and the simplest successful model is that of Kuwabara (1959), in which

$$f(c) = \frac{c}{\left(-\frac{1}{2}\ln(c) + c - \frac{c^2}{4} - 0.75\right)} \tag{2}$$

A review of other models is given by Brown (1993), but all give $f(c)$ with broadly the same variation with c as that in Equation 2. Equations 1 and 2 show that the resistance of a filter is proportional to its thickness (which is obvious), and that it increases as the packing fraction increases and as the fibre diameter decreases. It also indicates that the pressure drop is directly proportional to the velocity of air through the filter, though this approximation is valid only if the following dimensionless parameter, the Reynolds number, Re, is small.

$$Re = \frac{dU\rho_g}{\eta} \tag{3}$$

In Equation 3, ρ_g is the density of the air. Because d is small (usually 20 μm or less in fibrous filters), Re is $\ll 1$, and the approximation of Δp proportional to U, enshrined in Darcy's law (Brown, 1993), is a good one.

Apart from the numerical constant and the functional form of $f(c)$, Equation 1 could be derived by dimensional analysis; and so could the Kozeny-Carman equation (Carman, 1937) which describes the pressure drop across granular beds, the form taken by most activated carbon filters.

$$\Delta p = \frac{150 L \eta U f(c)}{d^2} \tag{4}$$

In this case, $f(c)$ takes the form

$$f(c) = \frac{c^2}{(1-c)^3} \tag{5}$$

and d is identified with the diameter of a granule rather than that of a fibre. Equation 4 has the same dependence on the various parameters as Equation 1, but both c and d are higher for granular filters than for fibrous filters. A typical size for granules is 1 mm. The packing fraction of granular filters is difficult to measure; but that of a simple cubic array of spheres (by no means the most closely packed structure possible) is 0.52, whereas that of fibrous filters is

typically only a few percent. Trout, Breysse, Hall, Corn, and Risby (1986) found packing fractions of commercially available granular carbon filters of the same model to vary by a factor of about 1.3. It is most important that packing be tight, otherwise settling of granules and channelling of air through the loosely packed parts of the filter may occur.

Increases in c and d have opposite effects on pressure drop, but both will increase the Reynolds number, and this means that the linear relationship between Δp and U is a poorer approximation, both in theory and in practice, for granular filters. The increase of pressure drop with increasing velocity is more rapid than linear.

Ergun (1952) modified Equation 4 by the addition of a term quadratic in U.

$$\Delta p = \frac{150L\eta Uf(c)}{d^2} + \frac{1.75\rho LU^2 f(c)}{dc} \tag{6}$$

At high values of U, the second term in Equation 6 dominates and the first may be neglected, a situation more likely to be realized in large-scale filters than in respirators. In this situation, the equation becomes equivalent to the Leva correlation (Fair, Steinmeyer, Penny, & Crocker, 1985) for the special case of a dry packed bed.

Theoretical work (Brown, 1986; Miyagi, 1958) exploiting the upstream–downstream symmetry of a bed results in a correction term that is cubic in U. Both forms may be made to fit experimental data (Jefferies, 1974), and a graph of the experimentally observed relationships for a typical granular respirator filter is shown in Figure 1.

No simple model gives an exact account of the flow pattern through beds of irregular geometry like those found in practice, but Chi Tien (1989) described flow through regular arrays of spheres, referring to a number of models, specifically that of Snyder and Stewart (1966). A complication, which takes the study of active carbon filters further from that of simple packed beds, is the effect of granule shape. A thorough treatment of this is extremely difficult, but Jankowska et al. (1991) quoted results for cylindrical and irregular granules, neither of particularly well-defined shape, as respectively 2.8 and 3.3 times the resistance of spherical granules of the same nature.

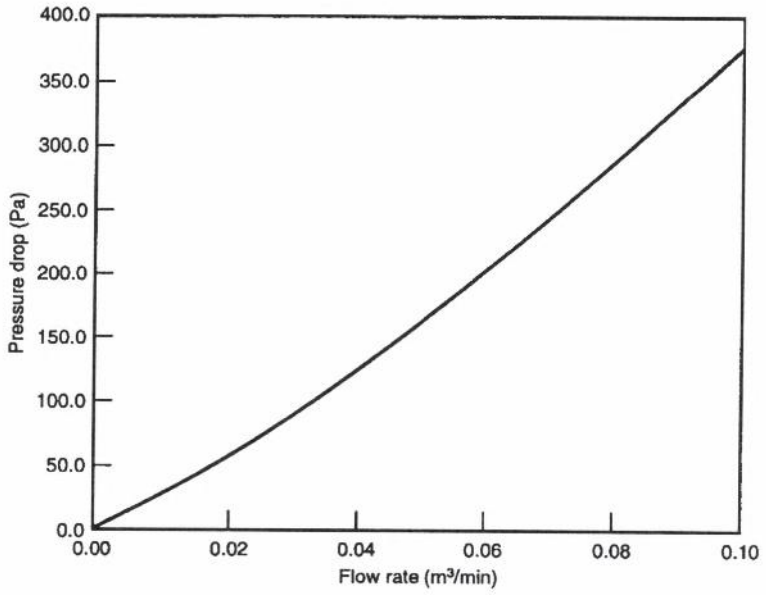

Figure 1. Pressure drop as a function of flow rate for a typical granular carbon filter.

3. ACTIVATED CARBON AS AN ADSORBENT

Adsorption of gases and vapours (a vapour is normally defined as the rarified phase of a substance that is liquid at normal temperatures) is a widespread phenomenon. In any situation where a solid surface is surrounded by a gas or vapour, a degree of adsorption will take place. The effectiveness of any material as an adsorbent depends on the affinity of its surface for potential adsorbates and its effective surface area. Activated carbon, being highly porous, has a large specific area (area per unit mass) mostly made up of pores which are generally classified into three groups: macropores, mesopores, and micropores. There is broad, but not perfect, agreement amongst authors concerning the size limits of the types of pore. The International Union of Pure and Applied Chemistry (IUPAC) recommends that pores greater than 50 nm in diameter should be termed macropores, and that pores less than 2 nm in diameter should be termed micropores, with the mesopores being of intermediate size (McEnaney, 1988). The macropores are sufficiently numerous to have a total specific area of 0.5 to 2.0 $m^2 g^{-1}$; whereas the micropores have a specific area of up to 2000 $m^2 g^{-1}$ and are considered to be slit-shaped (Dubinin, 1989). If the varieties of pore are classified according to their ability to capture molecules (Bering, Dubinin, & Serpinsky, 1966), the macropores are of such a size that their curvature is too low to affect their behaviour, their surfaces are effectively planar, whereas the micropores have sizes comparable with molecular dimensions. For this reason, the micropores comprise the greater part of the effective surface and dominate the behaviour of the carbon as an adsorbent.

The distribution of the pore sizes varies with the precursor material of the activated carbon. Carbon produced from saran (polyvinylidene chloride) has a structure consisting principally of homogeneous micropores (Dubinin, 1975). That produced from coal usually has a wide spread of pore sizes, and that from vegetable material is intermediate (Dubinin, 1989). If adsorption forces are strong, about 1 mg of vapour will be held on 1 m^2 of planar solid surface (Maggs, 1983). For materials with a microporous structure, such as carbon, the mass of vapour adsorbed can be in the range of 10 to 70% of the mass of the adsorbent.

4. EQUILIBRIUM ADSORPTION THEORY

Adsorption resembles condensation in that it has associated with it a latent heat. Chemisorption, which involves chemical reaction between the adsorbent and the adsorbate, involves a latent heat many times greater than that typical of physical adsorption. Whichever process is operative, ultimately an equilibrium situation will be reached, in which adsorption and desorption balance. For many surfaces, a unique relationship exists between the mass adsorbed per unit area of adsorbent and the partial pressure of the gas, at any particular temperature; and this relationship may be expressed graphically, as the adsorption isotherm. In some systems, hysteresis may occur, the degree of surface coverage dependent on whether the situation is approached from a higher or a lower partial pressure.

Five shapes of isotherm are defined empirically, as illustrated in Figure 2, and theories exist that give rise to each of the shapes. Most of the theories deal with systems that are simple in both surface geometry and energy of interaction between the adsorbent and the adsorbate, whereas activated carbon is highly complicated in both of these respects. In studies of activated carbon, the most widely used theory is the theory of volume filling of micropores (see following), but such theories do not apply to the larger pores. Theories based on planar adsorbent surfaces have been used by some workers in the field (Sircar, 1987), and these will be briefly reviewed first.

4.1. Adsorption at Planar Surfaces

The simplest theory of adsorption is that in which the vapour-absorbate system is considered to be analogous to a vapour-liquid system. By analogy with Henry's Law in the latter system, the adsorbed mass will be directly proportional to the partial pressure. This theory, which is

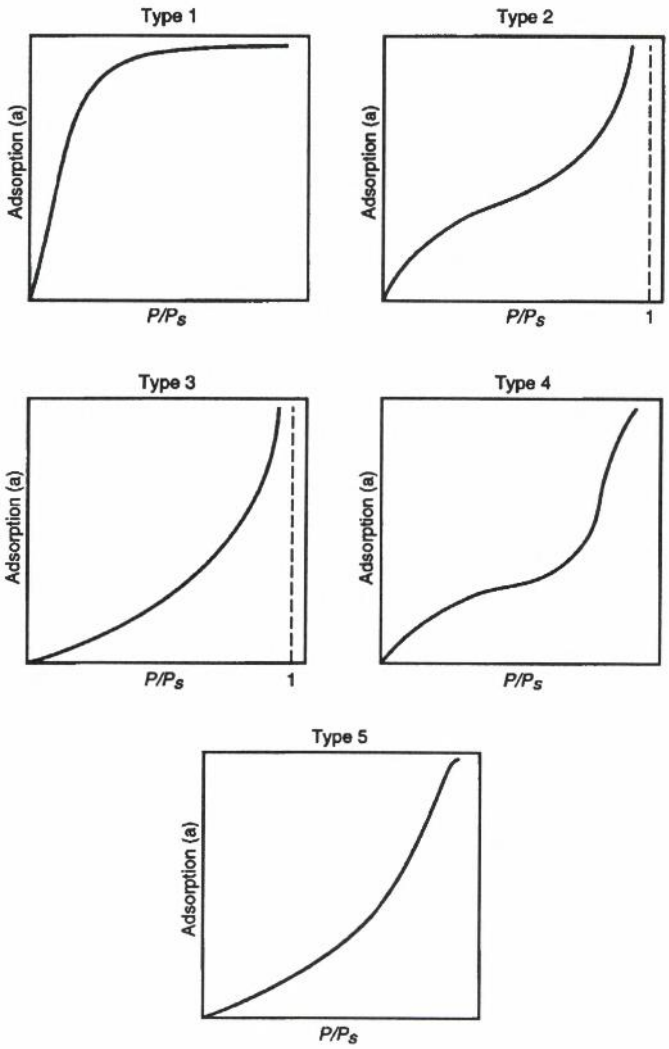

Figure 2. Adsorption isotherms of the five principal types.

almost axiomatic in the situation of low surface coverage, gives the linear relationship observed at sufficiently low pressures for many of the more sophisticated theories.

The first correction to this law results in the Langmuir isotherm (Langmuir, 1918), which takes account of finite surface area. As the fractional coverage approaches unity, the probability of adsorption decreases with the decrease of available area, whilst the probability of desorption increases with the adsorbed mass. Coverage of the surface is limited to a monolayer, which means that the surface can be saturated, and the mass of adsorbate approaches a limit as the pressure increases. The resulting isotherm, shown as Type 1 in Figure 2, is considered to be a good description of chemisorption.

The functional form of the relationship between equilibrium mass adsorbed, M_A, and pressure is

$$\frac{M_A}{M_{AS}} = \frac{\gamma P}{1 + \gamma P} \tag{7}$$

where M_{AS} is the mass adsorbed at saturation. Equation 7 is derived with the implicit assumption that all adsorption sites have the same latent heat of adsorption, though Langmuir developed the theory further to deal with the situation where the adsorption sites vary in their interaction energy with the adsorbate.

The saturation shown by Type 1 isotherms is not apparent in Types 2 or 3, for in these cases the volume of adsorbed material increases without limit as the vapour pressure approaches its saturation value. This behaviour comes about from the condensation of the vapour, and it can be described in terms of the formation of multilayers, using the so-called BET theory (Brunauer, Emmett, & Teller, 1938). The theory attributes a common heat of adsorption to all molecules in the same layer but allows this to vary from layer to layer. A simple and reasonable approximation is to consider that the first layer of molecules has a specific adsorption energy, and that that of all other molecules is equal to the molecular latent heat of vaporization. As the pressure of the gas approaches the saturation vapour pressure the gas condenses and the mass adsorbed increases without limit.

A modification of this allows isotherms of Types 4 or 5 to be described, by limiting the number of layers allowed to form, and in this instance, saturation behaviour is recovered, but not, of course, at monomolecular coverage.

Isotherms of Types 3 and 5 show a very low increase of adsorbed volume with pressure when pressure is low. This behaviour comes about when the energy of interaction between the adsorbate molecules and the adsorbent is weaker than that of the interaction between adsorbate molecules. When the converse in true, Types 2 and 4 result.

A further type of isotherm has been described by Pierce (1969). The shape of this is attributed to geometrical effects in the packing of molecules in the surface layer and subsequently adsorbed layers.

4.2. Volume Filling of Micropores

The theories that have been briefly summarized lead to mathematical expressions for an isotherm when the nature of the surface and its interaction energy distribution are known. In practice it is more likely that an isotherm will be observed experimentally and the fundamental constants deduced from it, particularly with complicated adsorbents like activated carbon. The characterization of each type of activated carbon with respect to each possible adsorbate by means of experiment is clearly an impossible task. An appealing approach, lying in between theory and exhaustive experiment, consists of the measurement of the adsorption isotherm using a limited number (perhaps only one) of adsorbates and the use of the parameters obtained to predict the behaviour of a wide range of adsorbates.

A detailed thermodynamic theory has been developed by Dubinin and coworkers (Bering et al., 1966; Dubinin, 1965, 1966, 1967, 1975, 1979, 1989; Young & Crowell, 1962) using concepts introduced by Polanyi (1932). The theory is based on the assumption of volume filling of micropores and relies heavily on the fact that the micropores are of molecular dimensions. In this situation, a considerable volume of adsorbate could be adsorbed without the formation of multilayers except, of course, outside the micropores, in a region that contributes relatively little to the adsorptive capacity. Furthermore, a molecule adsorbed in a micropore will be within molecular dimensions of a greater area of surface than will a molecule adsorbed on a surface of planar geometry, and so its energy of interaction will be considerably greater. That adsorption does, in fact, take place in molecular-sized pores rather than at a planar surface is confirmed by measurements of heats of adsorption, which are much greater for activated carbon than for the chemically similar but nonporous graphite.

Adsorption in pores means that the field of interaction of the surface extends throughout the region where adsorption takes place, which would not be the case for multilayer adsorption, and the enhanced adsorption potential means that gases may be strongly adsorbed in micropores at low pressures. Adsorption by multilayer formation has been considered to resemble condensation, in which the principal interaction is between adsorbate molecules,

whereas during volume filling of micropores, the dominant interaction is adsorbate–adsorbent, and for this reason it has been likened to the process of solution (Dubinin, 1975).

A further assumption in the theory is that the volume available for adsorption does not vary with the adsorbate used, and that the adsorbate exists in a highly compressed state, its volume being related to its volume in the normal liquid state (Dubinin, 1967). Both of these assumptions have strong experimental support. Finally, it is assumed that the adsorption energy does not vary with the degree of filling, which again would not be the case for multilayer adsorption.

The Polanyi theory assumed a conservative force field, whereas in the Dubinin theory, the fundamental parameter is A, the molar free energy of adsorption at equilibrium pressure P relative to the free energy of a chemically similar liquid at temperature T, in equilibrium with its saturated vapour at pressure P_S.

$$A = RT\left(\ln \frac{P_s}{P}\right) \tag{8}$$

A is assumed to be independent of temperature, and experiment shows that the degree of adsorption obeys the following functional form, where E is a characteristic energy of adsorption:

$$a \sim \exp\left[-\left(\frac{A}{E}\right)^2\right] \tag{9}$$

The form of the isotherm will be specific to the adsorbent, but the power of the theory is that, provided adsorption takes place as a result of van der Waals forces, that is to say provided that it is physical adsorption as normally construed, a specific constant can be defined for each adsorbate, expressing its affinity for the surface. This constant, β, is termed the affinity coefficient and is defined by

$$\beta = \frac{E}{E_0} \tag{10}$$

where E_0 is the characteristic energy of absorption of some reference material. The general form of the adsorption isotherm can be expressed as a relationship between A and M. The isotherm is measured experimentally for a reference material, benzene, which is ascribed as affinity coeffient of unity. That for any other material can be deduced, once its coefficient is known. The theory leads to an expression for the volume filling of the pores, or the quantity of adsorbed material, M.

$$M = M_0 \exp\left(-B\left[\frac{RT}{\beta}\ln\frac{P_s}{P}\right]^2\right) \tag{11}$$

where M_o is the limiting mass of adsorbate per unit volume and B is an index of the quality of the carbon as an adsorbent, normally termed the micro-porosity constant.

Equation 11 is strictly applicable only when the adsorbate is below its critical temperature, T_c. The theory has been extended (Dubinin, 1966) to higher temperatures, to give the following equation.

$$M = \frac{M_0 v}{b} \exp\left\{-\left[B\left(\frac{RT}{\beta}\right)^2 \ln\left(\frac{T}{T_c}\frac{P_c}{P}\right)^2\right]\right\} \tag{12}$$

where P_c is the critical pressure of the adsorbate, v is the molar volume, and b the van der Waals constant.

The affinity coefficient is related to the quotient of the molar volume of the material in question and that of the reference material v_o, or more accurately to the quotient of their parachors, bracketed in the following equation.

$$\beta = \left(\frac{m\sigma}{\rho}\right)\left(\frac{\rho_0}{m_0\sigma_0}\right) \tag{13}$$

ρ and ρ_0 are the densities of the experimental and reference materials (strictly the difference in densities of their liquids and vapours), m and m_0 their molecular weights, and σ and σ_0 their surface tensions. The surface tension of a material depends on the strength of intermolecular interactions and correlates well with the latent heat of vaporization. The special quality of the parachor is that it is only weakly dependent on temperature over a wide temperature range.

A discussion of adsorbate–adsorbent interaction has been given by Reucroft, Simpson, and Jonas (1971), who considered also the electrostatic interaction between polar molecules and a nonpolar surface (assumed to be a good model of a surface of carbon). If a molecule is highly polar, β should include the electronic polarizability, and Reucroft et al. used the expression given by the Lorenz-Lorentz equation (Fewkes & Yarwood, 1956 Jones & Rehrmann, 1972),

$$\beta = \frac{n^2 - 1}{n^2 + 2}\frac{m}{\rho}\frac{n_0^2 + 2}{n_0^2 - 1}\frac{\rho_0}{m_0} \tag{14}$$

where n and n_0 are the refractive indices of the test material and the reference material, respectively.

The dependence on refractive index should not be surprising since this parameter depends on the dielectric constant.

The study revealed that van der Waals forces should dominate, except when the adsorbate molecules are highly polar. It was found by experiment that the adsorption of different vapours correlated better with the parachors than with the Lorenz-Lorentz expression except in the case of highly polar molecules. If these were taken as a single group, with acetone chosen as the reference vapour, better correlation in this case would be obtained with Equation 14. Golovoy and Braslaw (1981) measured the equilibrium adsorption capacity of a number of solvents used in car body paints and found slightly better correlation with Equation 14 than with Equation 13.

On the other hand, Wood (1992) obtained good correlation in an exercise on experimentally measured isotherms using β calculated from Equation 13. He also attempted to correlate the microporosity constant, B, with the volume available for adsorption, with more limited success. Breysse, Cappabianca, Hall, and Risby (1987) measured the heats of adsorption of the three isomers of dichlorobenzene. The dipole moment of the o-isomer is 2.5 D, which puts it into the highly polar category, whereas that of the p-isomer is zero and that of the m-isomer is intermediate. The authors observed no significant differences in heats of adsorption and, therefore, concluded that this level of polarity did not seriously affect adsorption.

The strength of the Dubinin theory is its simplicity, though the author and coworkers pointed out its limitations. In particular, it is not applicable at very low ($< 4\%$) (Rozwadowski, Siedlewski, & Wojsz, 1979) or very high ($> 96\%$) levels of volume filling. Marsh and Rand (1970) pointed out that the distribution of adsorption free energies was sometimes bimodal, and Stoeckli and Houriet (1976) pointed out that B in Equation 12 was frequently found not to be constant. A modified theory was developed (Dubinin, 1975), in which the distribution of adsorption free energies was assumed not to be normal, as implicit in Equation 11, but to take the more general form of the Weibull distribution. The effect of this is that the power of

$\ln\left(\frac{P_s}{P}\right)$ can take any value. It was found that a value of 3 was appropriate for carbons obtained from polyvinylidene chloride, which has a narrow pore size distribution.

Similar results were obtained by Finger and Bulow (1979) and by Stoeckli, Kraehenbuehl, Ballerini, and de Bernardini (1989), suggesting a relatively small spread in pore sizes. Wojsz and Rozwadowski (1984) measured the index for a number of polar compounds and found that in general it was smaller than 2, and that it correlated inversely with the adsorption capacity, M_s. Dubinin (1989) quoted a limiting value of unity for the power in the case where the adsorbent is completely nonporous. Dubinin (1979) also generalized the equation for the situation where the micropores formed two well-defined populations, to give the result

$$M = M_{s1} \exp\left[-B_1\left(\frac{A}{\beta}\right)^2\right] + M_{s2} \exp\left[-B_2\left(\frac{A}{\beta}\right)^2\right] \tag{15}$$

5. ADSORPTION DYNAMICS

Equilibrium theory will give an account of the final state of an adsorbent exposed to an adsorbate in the gas phase, but it will not give any account of the rate at which that final state is reached. In practice, a contaminated gas is passed through an adsorbent bed in a finite time, and so the dynamics of the process of adsorption is critical. The process is described, quite generally, by the mass balance equation

$$U\frac{\delta C}{\delta x} = -\frac{\delta M}{\delta t} \tag{16}$$

which relates the spatial change in the concentration of adsorbate in the gas phase, C, to the temporal change in the concentration in the adsorbed phase, M. U is the velocity of the gas through the bed, which will be greater than its approach velocity, because of the finite packing fraction of the bed.

In spite of its apparent simplicity, Equation 16 does not have a simple general solution. It can, however, be solved for a homogeneous bed of finite capacity, when no desorption takes place. The most general case corresponding to this situation will be considered later, but first the hypothetical situation in which adsorption is instantaneous will be studied. In this case, each infinitesimal layer of adsorbent will be saturated in turn, the region of action being infinitesimally thin and all downstream regions being completely untouched by contaminant.

If the concentration of adsorbate in the gas stream is C_i and the saturation concentration of the bed is M_0, a front of saturation will pass through the bed at a velocity V where

$$V = \frac{UC_i}{M_0} \tag{17}$$

as indicated in Figure 3, and the effluent concentration will be zero, until a breakthrough time, t_B is reached, after which it will equal the approach concentration, as shown in Figure 4. The breakthrough time will be proportional to the length of the bed.

$$t_B = \frac{LM_0}{UC_i} \tag{18}$$

In practice this situation can never be realized, but it is a useful introduction to the study, and it describes the best possible performance of a filter bed of known adsorption capacity. In the

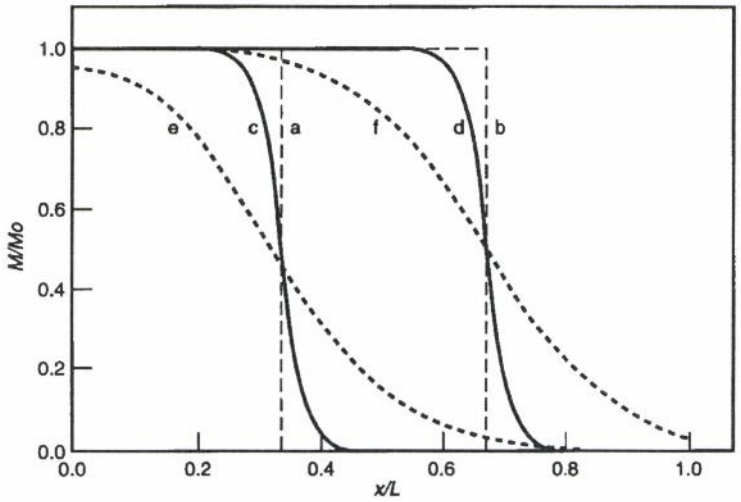

Figure 3. Concentration, at various times, of adsorbate in a bed of depth of L challenged with a moving gas stream at velocity, U, where the challenge concentration, C_o, and the equilibrium adsorption concentration, M_o, take unit values.

a) Instantaneous adsorption, $t = \frac{L}{3U}$

b) Instantaneous adsorption, $t = \frac{2L}{3U}$

c) $k = \frac{50U}{L}$, $t = \frac{L}{3U}$

d) $k = \frac{50U}{L}$, $t = \frac{2L}{3U}$

e) $k = \frac{10U}{L}$, $t = \frac{L}{3U}$

f) $k = \frac{10U}{L}$, $t = \frac{2L}{3U}$

simplest realistic situation, reaction can be described in terms of a rate constant, k, having dimensions t^{-1}. High values of k will correspond to readily adsorbed species; and the value of k may depend on the coefficient of diffusion of molecules in the gaseous phase and to the rate of diffusion, on the surface, of adsorbed molecules, because the adsorption sites will vary in their accessibility. Its value, however, will be assumed to be spatially and temporally invariant. It is assumed further that the rate of adsorption is proportional to the fraction of unoccupied adsorption space, $1 - \frac{M}{M_0}$, where M is the actual concentration of adsorbed material. This means that a partial differential equation can be written down for the change in concentration of adsorbate in the gas phase

$$\frac{\partial C}{\partial x} = -\frac{k}{U}\left(1 - \frac{M}{M_0}\right)C \tag{19}$$

Equation 19, along with the natural boundary conditions of the system, gives sufficient information to allow solution of the mass balance equation. The method of solution is given in

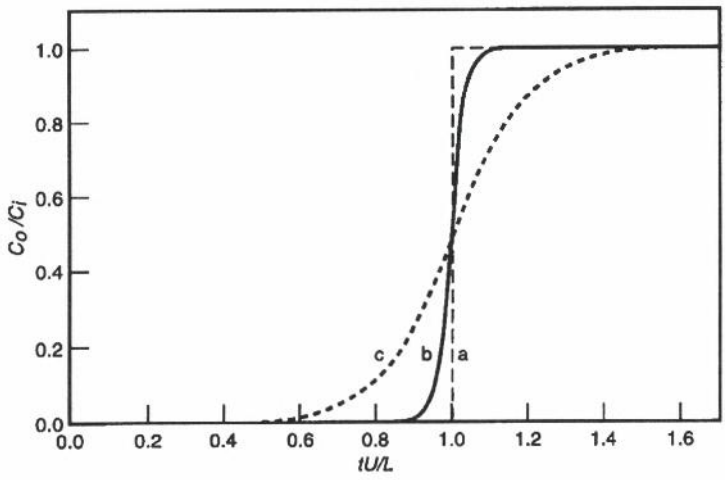

Figure 4. Concentration in the gas phase, as a function of time, of contaminant in the effluent from an adsorbent filter of depth, *L*, challenged with contaminant at unit concentration, in an air stream at velocity, *U*, and with unit equilibrium adsorption concentration.

a) Instantaneous adsorption

b) $k = \dfrac{50U}{L}$

c) $k = \dfrac{10U}{L}$

principle by Bohart and Adams (1920), and the results are, for the concentration in the gas phase,

$$C(x,t) = \frac{C_i}{\left\{1 + \exp\left(-\frac{kC_i t}{M_0}\right)\left[\exp\left(\frac{kx}{U}\right) - 1\right]\right\}} \tag{20}$$

and for the concentration of adsorbate,

$$M(x,t) = \frac{M_0 \exp\left(-\frac{kx}{U}\right)\left[\exp\left(-\frac{kC_i t}{M_0}\right) - 1\right]}{\left[1 + \exp\left(-\frac{kx}{U}\right)\exp\left(\frac{kC_i t}{M_0}\right) - 1\right]} \tag{21}$$

Curves of M as a function of x for various values of t are given in Figure 3, and curves of $C(L,t)$ are given in Figure 4. Their shapes, which depend critically on the value of k, contrast with that corresponding to idealized breakthrough conditions.

If $k \rightarrow \infty$, the step functions in Figures 3 and 4 are recovered, as would be expected, and if k is large but finite, Equation 21 can be simplified to

$$M(x,t) = \frac{M_0 \exp k\left(\frac{C_i t}{M_0} - \frac{x}{U}\right)}{\left[1 + \exp k\left(\frac{C_i t}{M_0} - \frac{x}{U}\right)\right]} \tag{22}$$

in which M is a function of $\left(\frac{C_i t}{M_0} - \frac{x}{U}\right)$ only, described by a sigmoid curve with a width inversely proportional to k, travelling through the filter bed at a velocity given by V in Equation 17. This region, where the concentration changes rapidly with position, is termed the *adsorption zone*. The region within the bed where the concentration of adsorbate is virtually equal to M_0 is sometimes termed the *saturation zone* (Ackley, 1985; Maggs, 1983).

When k is finite, there is no unique breakthrough time. t_B must be defined with reference to a particular quotient of the outlet concentration, C_0, and the inlet concentration (often 1%). This time can be obtained from Equation 20.

$$\frac{C_i}{C_0} = 1 + \exp\left(-\frac{kC_i t_B}{M_0}\right)\left[\exp\left(\frac{kL}{U} - 1\right)\right] \tag{23}$$

If a filter bed is sufficiently thin, this concentration will be reached immediately. The bed depth at which this occurs, the critical depth L_c can be obtained from Equation 24.

$$L_c = -\frac{U}{k}\ln\left(\frac{C_0}{C_i}\right) \tag{24}$$

5.1. Modifications to Adsorption Equation

Equation 23 is the exact consequence of the assumptions made in the previous working, but it can be reduced to a simpler and more useful form if the arguments of the exponentials are assumed to be significantly larger than unity, so that the unit constants in Equation 23 can be neglected. These are, in principle, the approximations made by Wheeler and Robell (1969) and by Jonas and Svirbely (1972). The result is the Wheeler equation:

$$t_B = \frac{M_0}{C_i U}\left[L + \frac{U}{k}\ln\left(\frac{C_0}{C_i}\right)\right] \tag{25}$$

Much subsequent work on the dynamics of adsorption has referred to this equation. The parameters that it embodies are well defined and easily measured, with the exception of M_0, the equilibrium mass of adsorbate per unit volume of filter, and k, the rate constant for adsorption, which must be obtained from experiment.

Equations 24 and 25 show that the breakthrough time should be directly proportional to the length of the bed minus the critical length, which is enshrined in the Mecklenburg equation (Ackley, 1985):

$$t_B = \frac{M_0}{C_i U}[L - L_c] \tag{26}$$

If, therefore, a range of values of t_B are measured for beds that vary in length only, the relationship should be linear, and the two parameters that are sufficient to describe a linear relationship enable the unknown parameters M_0 and k to be found. In such an experiment, Moyer (1987) found that the adsorption capacity increased with challenge concentration. This is consistent with the results of static adsorption experiments, since M_0 is related to C_i by way of the adsorption isotherms just discussed. The rate constant was found to vary among different batches of carbon.

An alternative to the Wheeler equation has been proposed by Yoon and Nelson (1984a):

$$t_B = \frac{M_0}{C_i U}\left[L + \frac{U}{k}\ln\left(\frac{C_0}{C_i - C_0}\right)\right] \tag{27}$$

A derivation of Equation 27 is given by the authors, but in fact it follows from Equation 23, which is exact within the approximations made in the Bohart-Adams theory. If the approximation is made only that the -1 on the extreme right in Equation 23 can be neglected relative to the exponential within the same brackets, the Yoon-Nelson equation follows. The Wheeler equation requires the further approximation of neglecting the other constant.

A slight rearrangement and substitution of terms in Equation 27 gives the form quoted by Busmundrud (1991) in terms of the volumetric flow rate, Q, the mass of the bed, W, and its density ρ_B.

$$t_B = \frac{M_0}{C_i Q}\left[W - \frac{\rho_B Q}{k}\ln\left(\frac{C_i - C_0}{C_0}\right)\right] \tag{28}$$

In addition, an essentially identical form is quoted by Balieu (1976a). Just as Equations 24 to 26 imply that the breakthrough time is approximately proportional to the bed depth, provided that the filtration velocity is constant, Equation 28 indicates that breakthrough time is approximately proportional to the mass of the bed, provided that volumetric flow rate is constant.

Balieu (1990) used a form of what is essentially Equation 27 to calculate the performance of a large-scale filter challenged with toluene vapour on the basis of tests carried out with small-scale simulations. The results conformed to the general form of the equation, and the values of M_0, taken from curve fits to the data, were used to plot part of the adsorption isotherm, which agreed well with the near saturation region of the Langmuir isotherm.

The mathematical theory described in this section requires the adsorption isotherm to have a particularly simple form. If this is not the case, the mathematical difficulty of the solution increases considerably, and it is most easily presented graphically (Klotz, 1946; Vermeulen, Levan, Hiester, & Klein, 1984). Precise solutions of this sort are more valuable from the point of view of process engineering, where reactions and concentrations can be controlled, than in the situation of respirator filters, where exposure is variable and frequently intermittent.

Vermeulen et al. (1984) described the general effect of the shape of the isotherm. If it is concave downwards, like the Langmuir isotherm, Type 1 in Figure 2, the adsorption conditions are said to be favourable. This means that ultimately there will develop an adsorption zone of constant thickness, which migrates through the bed at a constant velocity (provided that the challenge conditions are constant) without dispersion. If, however, the isotherm has the opposite shape, the conditions are unfavourable, and the width of the adsorption zone will increase as it passes through the filter.

6. FUNDAMENTAL DESCRIPTION OF RATE CONSTANT FOR ADSORPTION

Predictive methods have had fair success in the estimate of M_0, and if this could be extended to the rate constant, considerable practical benefit would result. The dynamic nature of the rate constant complicates the matter, and the adsorption of molecules by the carbon is a process that involves transport of the molecules to the surface, and redistribution of the adsorbate on the surface. Jonas (1978), in a study of impregnated carbon, broke down the complete sequence of possible surface reactions into seven steps: mass transfer or diffusion in the gas phase; surface diffusion; intragranular diffusion; physical adsorption; gas desorption; chemical reaction; and surface renewal. The value of the rate constant depends on which of the processes is rate limiting. Danby, Davoud, Everett, Hinshelwood, and Lodge (1946) had demonstrated that if the gas phase diffusion is the limiting step, k should be proportional to the coefficient of diffusion of the adsorbate molecules in air and to the square root of the velocity, but that it should not vary greatly amongst carbon types. If surface adsorption is rate limiting, it may vary

amongst different types of carbon. The authors published data for adsorbates falling into both of these categories.

Klotz (1946) postulated that when surface diffusion is rate limiting, k should depend on two dimensionless parameters, the Reynolds number, Re, and the Schmidt number, Sc, and that the functional relationship should be that obtained, from experiment, by Gamson, Thodos, and Hougen (1943)

$$k \sim Re^{-0.41}Sc^{-0.67} = \left(\frac{d\rho_g U_0}{\eta}\right)^{-0.41}\left(\frac{\eta}{\rho_g D}\right)^{-0.67} \tag{29}$$

The theory of bulk and surface transport and its interaction with the process of adsorption is treated with more rigour by Masamune and Smith (1964, 1965a) and by Thomas and Qureshi (1971).

However, according to the theory of Wheeler (1955; see also Jonas and Rehrmann, 1974), if it is the transport to the surface that limits the process, then the value of k, designated k_∞ in this situation, is given by

$$k_\infty = 10\left(\frac{U}{\overline{m}d^3\rho_g}\right)^{\frac{1}{2}} \tag{30}$$

where $\overline{m}$ is the mean molecular weight of the carrying gas, which can be taken as the mean molecular weight of air so far as respirators are concerned. Since m and P, atmospheric pressure, are virtually constant, k can be expressed as

$$k_\infty = 1.86U^{\frac{1}{2}}d^{-\frac{3}{2}} \tag{31}$$

In a series of experiments carried out with contaminant passing through beds at the relatively high velocity of 0.5 m s^{-1}, Jonas and Rehrmann (1973) measured the values of M_0 and k for five organic materials with molecular weights ranging from 61 to 140 and found that the values of k_∞ agreed very well with the theoretical value of 0.4 sec^{-1}, the mean value differing by only 2.6% from the theoretical value, and all 5 values being close together. With a single exception, the value of M_0 agreed well with that obtained from static experiments on the basis of the Dubinin theory.

Equations 30 and 31, which are empirical, do not have the form that standard filtration theory would predict, since, rather surprisingly, they do not contain the diffusion coefficient of the adsorbate, although the dependence on U and d are basically what would be expected. However, Sansone, Tewari, and Jonas (1979), Jonas, Tewari, and Sansone (1979), and Sansone and Jonas (1981) applied a predictive expression to the adsorption of a number of compounds and found that the experimental data could be interpreted consistently if the rate constant was assumed to be inversely proportional to the square root of the molecular weight of the adsorbate, which is the expected functional form of the coefficient of diffusion.

6.1. Velocity Dependence of Rate Constant

According to the simple theory developed in the previous section, the rate constant is likely to be velocity dependent at low flow velocities, since in this situation it will be limited by the rate of diffusion of molecules in the air. At high filtration velocities, the velocity dependence will be lost. The low velocity situation was studied by Jonas and Rehrmann (1974), who passed benzene through identical beds at a range of velocities from 0.02 to 0.5 m s^{-1}. In such a situation, the values k obtained by the curve-fitting procedure described above are signifi-

cantly smaller than the k_∞ value for velocities below about 0.1 m s^{-1}. In this situation, the authors were able to fit the following function to observed values of the rate constant:

$$k = \frac{\alpha + \delta}{1 + \frac{\alpha}{\delta} \exp[-(\alpha + \delta)\epsilon U]} \tag{32}$$

where, as $U \rightarrow \infty$ $k \rightarrow \alpha + \delta = k_\infty$. The results obtained for this system are illustrated in Figure 5.

The same equation was applied to the adsorption of dimethyl methylphosphonate (Rehrmann & Jonas, 1978) by the same type of carbon at a similar range of velocities. The functional form of Equation 32 was closely followed, but the numerical values of the coefficients fitted to the experimental data were different.

Wood and Moyer (1989) used a variety of velocities whilst keeping the challenge concentration constant. The adsorption capacity, given by the Wheeler equation, was found to be almost constant, whereas the rate constant increased with the filtration velocity, levelling off at high velocities, consistent with the presented theory.

Ackley (1985) found by experiment that the breakthrough curves measured at different velocities scaled in such a way that direct proportionality between breakthrough time and residence time was observed. This would be expected if the velocities used in the experiments were all sufficiently high for the rate constant to assume its limiting value, k_∞.

The adsorption capacity of the bed was found, by this author, to increase with increasing residence time. The reason for this appears to be that the capacity is measured at a breakthrough concentration of 0.1% as opposed to 100%, the latter measurement giving the equilibrium adsorption capacity, which should be independent of velocity. At a breakthrough concentration of less than 100%, much of the adsorption zone is contained within the bed and, according to Equation 22, the thickness of the zone is directly proportional to U and, therefore, inversely proportional to the residence time.

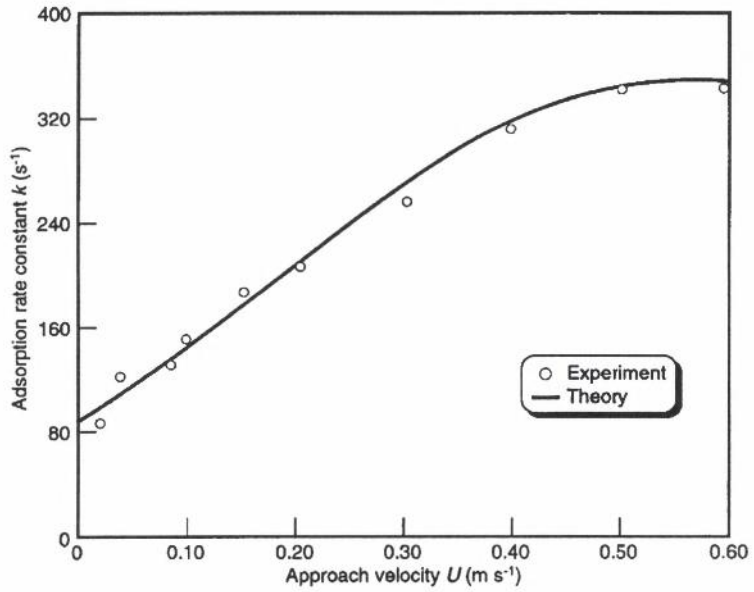

Figure 5. Dependence of rate constant for benzene on filtration velocity. (Reprinted from Rehrmann & Jonas, 1978, with kind permission from Elsevier Science, The Boulevard, Langford Lane, Kidlington, OX5 1GB, UK.)

6.2. Effect of Granule Size

In work just described (Rehrmann & Jonas, 1978) a range of carbons that differed in granule diameter (ranging from 0.19 to 1.44 mm) but, as far as possible, in no other way, were exposed to the adsorbate at velocities from 0.02 to 0.6 m s^{-1}. The adsorption capacity appeared to differ very little, but the rate constant varied considerably, showing increase to limiting forms when plotted as a function of velocity, as before, and varying with the reciprocal of the granule diameter. At every velocity, the rate constant was greater for carbons composed of smaller granules, and the velocity dependence was weaker for smaller granules. A higher rate constant, consistent with the theory above, was also observed for small-granuled carbon by Sansone et al. (1979). More rapid adsorption by small granules points toward their use in adsorbent filters, but a penalty is that the resistance to airflow of filters made up of such granules, given by Equation 4, is considerably greater.

This behaviour is consistent with the theory of diffusion-limited rate constant, but its verification requires measurements to be carried out on different specimens of carbon, and this inevitably introduces sample variation. No size dependence was observed in experiments of this type by Nelson and Harder (1976), nor by Wood and Stampfer (1993).

6.3. Effect of Temperature

Carbon used in respirators is rarely operated deliberately at air temperatures far from normal, but adsorption is itself an exothermic process, and so the likely increase in temperature of carbon as a result of adsorption and the effect of this on the predicted behaviour of carbon filters should be taken into account. Jonas, Boardway, and Meseke (1974) considered the effect that changes in temperature might have on the breakthrough times calculated from the Dubinin and Wheeler equations. Increase in temperature tends to reduce breakthrough time, and this effect is brought about by three processes: a decrease in effective rate constant, principally as a result of an increase in the rate of desorption; a decrease in the adsorption capacity; and a reduction in concentration as a result of thermal expansion of the carrier gas. Theory and experiment show that the first of these is by far the most important. A reduction in the breakthrough time of carbon tetrachloride at increased temperatures was reported by Tripathi and Ramachandran (1983). Previous work on the adsorption of methane (Lee & Weber, 1969) showed the general pattern of a reduction of t_B with increase in T. Nelson, Correia, and Harder (1976), from studies of the adsorption isotherm, showed that a 1 to 10 °C increase in temperature should cause a 1 to 10% decrease in filter service life.

6.4. Effect of Contaminant Concentration

Nelson and Harder (1976) exposed three types of activated carbon filters to nine organic vapours at concentrations of 50 to 2000 ppm. Plotting the logarithm of the breakthrough time against that of the concentration, they observed linear relationships, indicating simple negative power laws. The powers were the same for a single material whatever fraction of the input concentration was used to define breakthrough, and the slopes did not differ widely among the materials tested, which suggested that a good approximation to the relationship between breakthrough time and challenge concentration C_i was

$$t_B \sim C_i^{-n} \tag{33}$$

where the power n took values between 0.45 and 0.94, with an average of 0.67. Direct proportionality was observed between t_B and the residence time when the filtration velocity was varied. Lara and Lafond (1987) obtained values between 0.52 for methylene chloride and 1.04 for hexane.

The work was continued by Littleton and Feeney (1991), who sought relationships similar to Equation 33 for a wider range of compounds. The purpose was to extrapolate the observa-

tions of tests carried out at high challenge concentrations and completed relatively quickly to conditions in the workplace where exposure is to lower concentrations for longer periods. The authors attributed the lower values of n to desorption of the more volatile compounds (e.g., $n = 0.39$ for vinyl chloride, a gas) and supported this by observations of $n > 1.00$ for the chemisorbed species sulphur dioxide and chlorine.

6.5. Effect of Flow Pattern

The theory of flow rate has been discussed with reference to the value of the rate constant, k, that is, whether the diffusion-limited value, k_∞, can be assumed. If this is the case, the breakthrough time will be proportional to the residence time. If not, this linear relationship is not followed, but rather, the breakthrough time at higher velocities, although shorter than that at lower velocities, is larger than would be predicted.

The effect of a varying flow rate such as would be encountered during breathing has been compared with that of a constant flow rate at the same average velocity by Nelson and Harder (1972), who found no significant difference in performance. On the other hand, Jager and Bokhoven (1991) found that breakthrough time was significantly shorter for pulsating flow, for both physisorbed hexane and chemisorbed cyanogen chloride; and that this was especially serious for thin filters.

Hemenway, Fitzgerald, and Paret (1982) adopted a slightly different approach and obtained different results. They compared constant loading at relatively high concentration with intermittent loading for periods with the adsorbate at a concentration equal to that used in the constant loading experiment, and for equal periods with clean air. They expressed the results in terms of a decrease in the capacity of the bed and found this decrease to be approximately 16% for benzene and approximately 20% for carbon tetrachloride. The results were interpreted in terms of desorption from the bed, which was particularly noticeable during the clean air part of the cycle.

Hori, Tanaka, and Akayima (1990) and Hori and Tanaka (1992) did similar work but with a wider range of adsorbate and a variety of time intervals ranging from 5 to 30 min, comparing the results with those obtained in the situation of exposing the bed to a constant concentration equal to half of the peak concentration observed during the intermittent loading. The very nature of loading makes comparisons difficult, but the results suggested that the breakthrough times were shorter during intermittent loading and that the effect was more marked in the case of volatile adsorbates. Again desorption was involved, and the simple fact that finite outlet concentrations were observed during the clean air part of the cycle indicated that it was taking place.

Coover, Reist, and Hudgins (1982) carried out experiments using intermittent flow, in which volumes of air contaminated with carbon tetrachloride vapour or vinyl chloride were passed through the filter in one direction alternating with equal volumes of clear air in the opposite direction, to simulate breathing. They found that this increased the breakthrough time by a factor of 1.5 to 3.6. If the uncontaminated air was humidified, like exhaled air, the effect was less marked than with dry air but was still apparent. This effect of humidity will be considered in more detail later in this article.

7. ADSORPTION OF SPECIFIC COMPOUNDS

Ultimately, practical interest in adsorbent filters will relate to the extent of protection they offer against specific contaminants. In respect of this, an extensive study was carried out by Nelson and Harder (1974), who measured the penetration as a function of exposure of a range of vapours including aromatics, alcohols, acetates, alkanes, ketones, amines, and chlorinated compounds. In the work described earlier, adsorption has been correlated rigorously with the parachor and the molecular polarizability, but in this work, the boiling point was chosen, because this is a simple observable that depends on the intermolecular forces. Each class of compounds studied by Nelson and Harder included members with a variety of boiling points,

and it was found that the breakthrough time, t_B, was lowest for the most volatile member within each class, and that it increased with decreasing boiling point, to reach a maximum, and then to decrease once more. The behaviour of different classes of compounds could not be easily related. The boiling points correlated negatively with the vapour pressure and the coefficient of diffusion. In general, materials with a low boiling point broke through rapidly, but methanol, with its relatively high boiling point (64.7 °C) was unique in having a breakthrough time of less than 1 min, much lower than that of other materials of comparable volatility.

Similar measurements had been made by Freedman, Ferber, and Hartstein (1973), again on a range of compounds of various types. Particularly short breakthrough times were observed for methanol, methyl formate, acetaldehyde, and methyl bromide, when the challenge concentration was 1,000 ppm and breakthrough was registered at 5 ppm. Maggs and Smith (1975), however, used the last of these at a challenge concentration of 1,000 ppm with breakthrough defined as 1% and observed significantly longer breakthrough times. A feature of this compound is that it binds only weakly, and if partly used canisters are allowed to stand, the adsorbate will redistribute itself to become uniformly dispersed. The result of this will be instantaneous breakthrough once use of the canister is resumed.

Nelson and Harder (1974) sought to interpret the data in terms of Equations 12 and 26, the Dubinin equation and the Mecklenburg equation. The former gave adsorptive capacities comparable with those observed, but it consistently overestimated for the more volatile and underestimated for the less volatile in each class. The calculated breakthrough times tended to be overestimates of those observed, especially when the observed time was short. A further analysis of the same data (Yoon & Nelson, 1992), using Equation 27, resulted in reasonable agreement between theory and experiment for the breakthrough times.

Wood (1992, 1993) interpreted the data of Nelson and Harder (1974) using a modified form of Equation 11, in which β is given by the right-hand side of Equation 14 but is raised to the power 0.9, because this gives a better fit to the adsorption data. With this correction the measured breakthrough time correlated reasonably well with the calculated, being within 0.5 to 1.3 times its value.

In general, studies have tended to concentrate on compounds of known or suspected hazard and, therefore, of particular significance in hygiene studies. Moreover, in many instances all that is measured is the 1% breakthrough point rather than the complete breakthrough curve, going up to 100% penetration. The results are strictly applicable only to the particular filter canister or cartridge being used. They should, however, serve as a guide to what might be expected from filters of other types.

Stampfer (1982) tested canisters against a number of vapours at concentrations approximately equal to 50 times the TLV (threshold limit value, indicating the maximum permitted exposure level) pertaining at the time, the breakthrough concentration being set at the TLV itself. The tests were carried out at 80% relative humidity (RH) at temperatures of between 23 and 26% to give what might be assumed to be a worst likely case challenge. The results suggested that the canisters could be used with confidence for a period of 4 hr against chloroform, benzene, and acrylonitrile, for 8 hr against epichlorohydrin, and for 16 hr against propargyl alcohol, 1,2-dibromoethane, and acrolein, but could not be used with any confidence against chloromethyl methyl ether.

The performance of a number of filters against dichloromethane (methylene chloride) was measured by Moyer and Peterson (1993) for a range of challenge concentrations and at 50% and 80% controlled RH. Their results were comparable with those of Nelson and Harder (1974), giving breakthrough times of 10 to 20 min for typical cartridges containing 70 g or so of carbon. Only canisters with about 10 times this quantity of carbon were able to give protection for a reasonable time against this compound.

Henry (1981) measured the breakthrough times for formaldehyde vapour with a number of cartridge and canister respirators. Ordinary organic vapour respirator filters, containing carbon without impregnating agents, and challenged with approximately 3 ppm of formaldehyde vapour, gave breakthrough times (to 10%) at 30 to 130 min. The authors extrapolated the results to a challenge concentration of 50 ppm and predicted breakthrough times in single

figures. Again, canisters containing large masses of carbon gave protection for a greater period of time. The poor performance is consistent with the volatility of formaldehyde, a low molecular weight compound. Normal-sized canisters of the organic vapour or acid gas types gave protection for about 5 hr in these conditions, whereas acid gas canisters gave protection for 50 hr.

Simon, Fisher, and Davison (1987) measured the effectiveness of canisters and cartridges in the removal of chlorine dioxide, using a challenge concentration of approximately 500 ppm at 64 L/min, and defining breakthrough at 0.1% penetration. They found that breakthrough time was roughly proportional to the weight of the adsorbent, being 45 min with the lightest canister, which contained 81 g. Some of the filters were equilibrated for a period of 6 hr with air at 60 to 80% RH, but any effect that this might have had on the breakthrough time was lost within sample variation.

Several authors have studied the adsorption of isocyanates, which are relatively high molecular weight compounds but which, because they are respiratory sensitizers, have very low TLVs. Vasta (1985) studied the adsorption of hexamethylene isocyanate produced during spraying of enamels under a laboratory simulation of industrial conditions. The enamel consisted of the isocyanate mixed with esters, aromatic compounds, and, in one instance, a ketone. The respirator filter under test was placed in the position that it would occupy in working conditions. No breakthrough of isocyanate was observed, but after an extensive period of use, breakthrough of the solvents occurred.

Dharmarajan, Lingg, and Hackathorn (1986) studied the performance of cartridges and a disposable filtering facepiece against toluene diisocyanate, which is used in the manufacture of polyurethane. This compound has a ceiling exposure level of 0.02 ppm, well below its odour threshold. The authors challenged respirators with atmospheres containing the isocyanate at a level of between 0.2 and 11.0 ppm, for periods greater than 40 hr and in only 1 out of 12 tests measured breakthrough of 0.4% (still within the TLV). In all other instances, they measured no breakthrough within the detection limit of their instrument (0.0003–0.0009 ppm).

Moyer and Berardinelli (1987) considered the problem of methyl isocyanate, which is used in the manufacture of carbamate pesticides. They were concerned with the extremely high concentrations of this material that might result from the catastrophic loss of containment of a chemical reactor, and so they used challenge concentrations of up to 1,000 ppm of a material for which the TLV was 0.02 ppm. Typical breakthrough times for 1% concentration of this material were found to be 15 to 20 min at 1,000 ppm challenge, though rather lower at lower concentrations. An increase in relative humidity to 73% resulted in the detectable breakthrough occurring earlier, but the increase in concentration thereafter was considerably less rapid. The authors attributed this to a reaction at the carbon surface resulting in the production of methylamine, and they carried out tests using this compound, which confirmed the earlier results of Nelson and Harder (1974) that the breakthrough of methylamine, is rapid. The acceptability of adsorbent filters against isocyanates depends on the chemical species and the concentration.

Jones and Rehrmann (1972) studied the adsorption of two organophosphorus compounds, dimethyl methylphosphonate (DMMP) and isopropyl methylphosphono fluoridate (IMPF), on carbons both impregnated with metal ions and without impregnant. Their data fitted the Wheeler equation, with a linear relationship between breakthrough time and bed weight for both compounds on both types of carbon. The filtration velocity was approximately 0.5 m s^{-1}, and breakthrough times varied between 9 and 54 min for DMMP and between 5 and 36 min for IMPF with beds of 0.6 to 1.2 cm in depth. DMMP was slightly less effectively captured by impregnated carbon than by unimpregnated carbon and IMPF slightly more so. The Dubinin theory could be used to relate the performance of the two compounds, giving agreement within about 4% of the experimental values.

Further work on a range of pesticides, having between 7 and 13 carbon atoms per molecule, has been carried out by Wallace, Grover, and Westcott (1988). The work was aimed at tractor cab filters, and the conditions of test involved passing the contaminated gas through a 2.54 cm deep bed at a velocity of 0.67 m s^{-1}, both bed thickness and velocity being somewhat higher

than those normally encountered in respirators. The pesticide concentration was between 0.5 and 2.5 $\mu g\ m^{-3}$, and integrated collection efficiencies of the test beds, over a 12- to 48-hr exposure period, ranged from 93 to 100%.

Ackley (1987) measured breakthrough times for 1,3-butadiene in terms of the residence time model just described. With breakthrough defined as 10 ppm in the effluent, residence times of 0.2 s corresponded with breakthrough times of 30 min at a challenge concentration of 1,000 ppm, and 100 min at 100 ppm. The adsorbate was only weakly bound, and desorption could be brought about relatively easily with gas at a temperature of 25°C.

Miller and Reist (1977) exposed cartridges to vinyl chloride vapour at a concentration of 10 ppm and observed breakthrough defined as 1 ppm in the effluent after 45 min or less. In some instances, breakthrough was observed after only 2 or 3 min.

Beaumont and Garrido (1979) tested canisters with benzene and acrylonitrile and observed 1 ppm breakthrough times of several hours at a challenge concentration of 100 ppm for both compounds. The results for acrylonitrile were confirmed by Henry and Wilhelme (1979).

Johnston, Dyrud, and Shih (1989) tested samples of a filtering facepiece containing active carbon sorbent with ozone at 5 ppm, which is 50 times the TLV, the breakthrough time being defined as the time when 0.1 ppm of ozone was measured downstream of the filter. The tests were carried out at 64 L/min, and the authors observed breakthrough times of 126 ± 35 min with the carrier gas at ambient relative humidity. Because ozone is an oxidizing agent, chemical reaction at the surface is possible, but the results of chemical analysis showed only formaldehyde, and at a very low level, the source of which could have been extraneous to the experiment. The use of any protective device against ozone brings with it the benefit that ozone has a very low odour-detection threshold. Deitz and Bitner (1973) had previously reported the formation of carbon dioxide and carbon monoxide by the interaction of ozone with the carbon surface.

Wood (1981) measured the effectiveness of carbons in the adsorption of radioiodine compounds that could be encountered in a nuclear environment. Carbons impregnated with metal and ammonium salts (Whetlerized carbon), potassium iodide, and triethylenediamine (TEDA) were tested; and iodine, HI, and methyl iodide were used in the tests. Of the three chemical species, methyl iodide was invariably the most penetrating of any particular carbon, and so it was chosen for further tests. The TEDA-impregnated canisters were found to be the most effective and, for these, the adsorption of nonradioactive methyl iodide was found to compare very well with that of the compound containing the radioactive element; indicating that normal methyl iodide should be a suitable test agent. The vapour penetration at chosen times was found to vary exponentially with the bed contact time, in agreement with the Wheeler equation. Penetrations of 0.03 to 4.00%, depending on the canister type, were observed in the first 2 hr of use, whereafter the penetration rose, as expected.

Moore and Smith (1976) measured the effectiveness of acid gas type canisters in respirators for the protection of the wearer against sulphur dioxide at a copper smelter. Little detail was given, and the authors were as much interested in leakage into the respirator as with the filter penetration, but they observed protection factors between 6 and 50, corresponding respectively to upper limits of 17% and 2% for the integrated penetration of gas through the filter, though it was likely that the penetration was much less than these values. In work of a similar type, Cohen (1984) measured the protection factor of disposable masks used against mercury vapour. He observed protection factors between 9 and 63 with a harmonic mean of 22, but the behaviour of the adsorbent was not analyzed in detail.

Barnir and Aharoni (1975) and Aharoni and Barnir (1978) reported experiments on the interaction of impregnated carbon with cyanogen chloride. They compared the quantities of contaminated air that could be freed of the compound using carbon without adsorbent and with various ions on the surface, and concluded that both Cu^{2+} and Cr^{6+} were necessary but that silver ions were superfluous. Essentially similar results for the adsorption of cyanogen chloride and hydrogen cyanide were obtained by Reucroft and Chiou (1977). In further experiments, they showed that the ions influenced neither the adsorptive capacity nor the rate of adsorption, but that they limited desorption by catalyzing the breakdown of the compound into other molecules, including carbon dioxide.

Alder, Fielden, and Smith (1988) found that salts of cobalt and nickel each performed satisfactorily as impregnants for the adsorption of hydrogen cyanide and pointed out that impregnant crystals are situated in the mesopores of the carbon. The importance of sites of impregnant is discussed by Brown, Jayson, Thompson, and Wilkinson (1989) with reference to granular carbon, which contains both mesopores and micropores, and carbon cloth, which, essentially, contains micropores only. Chromium impregnants enter all pores, but divalent copper enters the mesopores only. This manifests itself in the effect of ageing of the carbon on the breakthrough time of cyanogen chloride, which is reduced by ageing in both types of carbon, and that of hydrogen cyanide, which is reduced by ageing only in the granular carbon.

Active carbon is used for the removal of certain other pollutants in ways other than respiratory protection; but data on these will be summarized here for the sake of completeness. Inert gases can be physisorbed on carbon, and Underhill, DiCello, Scaglia, and Watson (1986) described the adsorption of xenon, with particular reference to radioactive forms. They gave adsorption coefficients of 400 to 900 $cm^3\ g^{-1}$ (the volume presumably referring to the gas phase) for the carbons they examined and remarked that the adsorption can be enhanced by impregnating with silver, probably owing to the increase of van der Waals interaction associated with elements of high atomic number, but that impregnation with iodine does not improve performance. The pore size distribution appears to be critical, and the effect of moisture on the adsorption coefficient is considerable.

Chiou and Reucroft (1977) studied the adsorption of phosgene on Whetlerized carbon, carbon with copper and bromate impregnants, and unimpregnated carbon. The first was the best adsorbent, and the authors concluded that chromate or silver ions, present in the Whetlerized carbon, were principally responsible for the adsorption (cf. earlier). Haacke, Brinen, and Burkhard (1988) studied the adsorption of arsine, not with specific reference to respirators but, in principle, applicable to them. Copper and chromium ions were effective in ensuring the oxidation of the gas. Colabella, Stall, and Sorenson (1988) carried out experiments on the adsorption of both arsine and phosphine and found that oxidation of both species took place in the presence of oxygen on the surface. The authors also observed that at low flow rates the breakthrough time was independent of flow rate, which is consistent with a surface-reaction limited rate constant, as just described.

The potential use of adsorbents other than activated carbon in respirators has been considered by Hitchcock, Reist, and Coover (1981), who studied the adsorption of methanol, previously shown to have been very poorly adsorbed by activated carbon (Nelson & Harder, 1974). They examined a number of adsorbents and found that activated alumina was comparable to carbon, and silica gel was superior, with approximately six times the 10% breakthrough time. Matsumura, Yamabe, and Takahashi (1985) also observed that silica gel had a higher affinity for methanol vapour than did activated carbon. Further studies by Hitchcock et al. showed that a fine grade of silica gel was able to give 25 min of protection against methanol at a concentration of 2,000 ppm (10 times the TLV) at ambient relative humidity, but that this was seriously limited at high RH. The behaviour of the same adsorbent in the adsorption of ethanol was described by Masamune and Smith (1965b), who demonstrated the strong temperature dependence, at temperatures well above those that might be encountered in respirators.

Table 1 lists specific compounds against references, for convenience.

8. ADSORPTION OF MIXTURES

The challenge of a respirator filter by a single pure vapour may occur in the laboratory, but in an industrial situation vapour mixtures are the most likely challenge that a filter will receive. The interaction of mixtures of potential adsorbates with active carbon is a subject that, like the adsorption of pure compounds, can be treated in two parts: equilibrium theory and adsorption dynamics.

8.1. Equilibrium Theory

The fundamental property of mixtures of gases in equilibrium with an absorbed phase of qualitatively similar composition is that, like in liquid-vapour equilibrium, the composition of the two phases will be different. Figure 6 illustrates the situation with experimental data from Lewis, Gilliland, Cherton, and Cadogan (1950) for adsorbed ethylene-propylene mixture, in which the molar fraction of ethylene in the gas phase is plotted against the molar fraction of ethylene in the adsorbed phase in equilibrium with it. Carbons with very different adsorption capacities give essentially the same form. These authors made a number of observations relating to the pattern of adsorption applied to hydrocarbon mixtures but probably of much wider applicability. At constant partial pressure there is less adsorption from a mixture than from a pure gas, which indicates interference in the adsorption process. At constant total pressure the quantity adsorbed from the mixture lies between the values for each pure gas at the total pressure. The gas for which the adsorbent has the higher affinity in the pure state is preferentially adsorbed from the mixture. The greater the difference in boiling points of the two components of a mixture, the greater the difference in adsorption affinities.

The authors explained their results in terms of an empirical theory, by which the experimental data were found to conform to the general relationship

$$\frac{a_1}{a_{10}} + \frac{a_2}{a_{20}} = 1 \tag{34}$$

where a_1, and a_2 are the values of adsorption of the two components of a binary mixture, and a_{10} and a_{20} are the values taken by each when its partial pressure equals the total pressure of

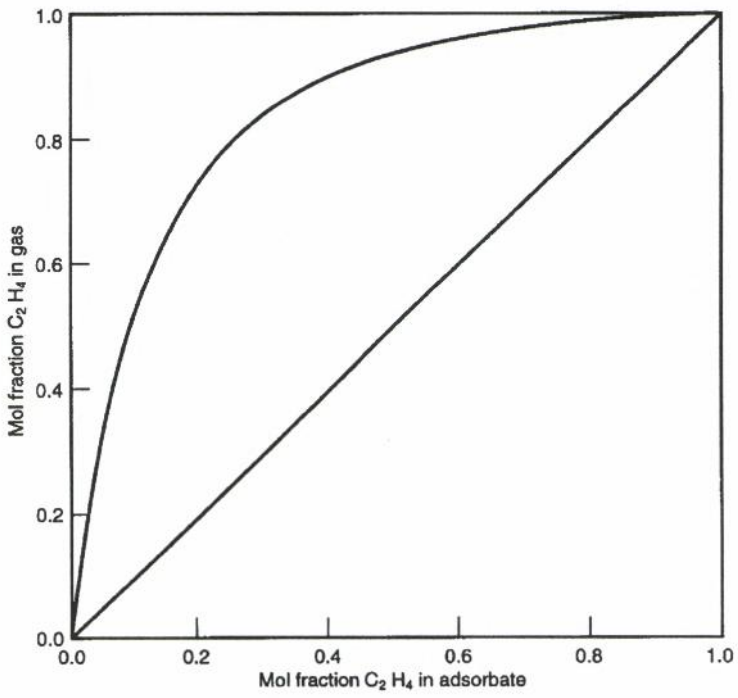

Figure 6. Equilibrium adsorption curve for an ethylene-propylene mixture with activated carbon absorbent. (Reprinted with permission from Lewis et al., 1950, © American Chemical Society, 1955).

the mixture. The authors defined a relative volatility of the two components, which is equal to the quotient of ratios of mole fractions in the vapour and adsorbed phase, respectively, and assumed that this does not vary with the composition of the mixture. In this way, good fits to most of their experimental data were obtained.

The thermodynamics of the process is discussed in more detail by Myers and Prausnitz (1965), Costa, Sotelo, Calleja, and Marron (1981), and Grant and Manes (1966). Bering, Dubinin, and Serpinsky (1966) and Dubinin (1975) generalized the theory of volume filling of pores to the situation where a binary mixture is adsorbed. In this situation, Equation 11 is modified to

$$a_1 + a_2 = \frac{M_0}{N_1 v_1 + N_2 v_2} \exp\left[-B\left(\frac{RT}{N_1\beta_1 + N_2\beta_2}\right)^2 \ln\left(\frac{P_{s12}}{P_{12}}\right)^2\right] \tag{35}$$

where N_1 and N_2 are the molar fractions of the components in the adsorption phase, P_{12} is the sum of the partial pressures of the two components in the vapour phase, and P_{s12} is the equilibrium pressure of the vapour over a liquid with the same composition as the adsorbate.

8.2. Dynamics of Binary Vapour Mixture Adsorption

To investigate dynamics, Jonas, Sansone, and Farris (1983) exposed filters to binary mixtures of vapours including benzene, chloroform, and carbon tetrachloride and interpreted their results in terms of the Wheeler equation and the Dubinin theory. The filters were loaded with the vapour until breakthrough of 1% of the challenge concentration occurred. The rate constants and adsorption capacities were then calculated from the experimental data. Within experimental variation, the observations were consistent with the adsorption space occupied by each component being proportional to its mole fraction in the mixture, and without observable competition between molecules of different species for the same adsorption site. Similar observations were made by the authors (Jonas & Sansone, 1986) when carbons were exposed to the same vapours sequentially rather that concurrently, though the authors did not claim to generalize the conclusions to all possible adsorbates.

When observations of this sort are extended to complete breakthrough, the picture changes. Thomas and Lombardi (1971) observed the breakthrough of mixtures of benzene and toluene, the latter of which is preferentially adsorbed. When the filter is exposed to the mixture, benzene breaks through first, but its concentration then rises to a level higher than in the challenge mixture. It reaches a plateau and then descends to the challenge concentration level, as the toluene breaks through. The reason for this is that when the adsorption space is largely unfilled, molecules of both species are adsorbed, but when the space is mostly filled, and desorption occurs, the situation tends towards a steady state, with a vapour mixture of one composition in equilibrium with an adsorbate mixture of another composition. As this situation is approached, the more weakly bound component, the benzene in this situation, is desorbed and so the concentration in the effluent exceeds that in the influent. As the adsorption space becomes filled, there becomes less benzene to be desorbed and so its concentration in the vapour phase drops. At the same time, there are fewer vacant sites or benzene-occupied sites for the toluene molecules, and so this compound breaks through. Similar observations, along with a theoretical interpretation, have been made by Siddiqi and Thomas (1982) for ethane-methane mixtures, which are not serious toxic hazards but, nevertheless, illustrate the basic behaviour of the carbon.

The binary mixtures m-xylene-acetone and styrene-acetone have been studied by Yoon, Nelson, Lara, Kamel, and Fregeau (1991, 1992). The carbon filters used in the experiments were subjected first to challenges of the individual vapours, and then to mixtures of various composition, so that breakthrough curves could be observed. A typical curve is shown in Figure 7. The data obtained on the single component exposure were used to plot theoretical curves which, however, required a further parameter, the maximum concentration reached by the more volatile compo-

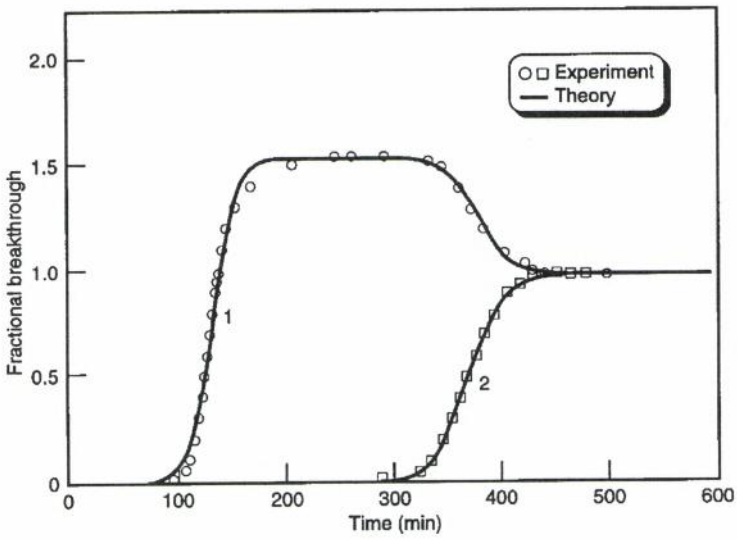

Figure 7. Breakthrough curves for acetone-m-xylene mixture:

1) acetone
2) m-xylene
(Reprinted with permission from Yoon et al., 1991. With the permission of the American Industrial Hygiene Association.)

nent during breakthrough. This, which should be related to the adsorption isotherms of the individual components, was obtained from experiment and, along with the other parameters, was used to predict the rest of the curves. On the basis of this, the curve-fitting procedure was found to be good. Furthermore, comparisons between the concentration value fitted to the experimental data and that calculated from experimental observations of breakthrough time and, therefore, adsorption capacity showed discrepancies of only a few percent.

In conclusion, it was found that the presence of a less volatile compound (xylene) reduced the breakthrough time of a more volatile component (acetone) compared with the value that the latter would take if the more volatile compound acted alone. In addition, the pattern of breakthrough is altered, and the total mass of volatile component adsorbed at saturation is reduced. The behaviour of the less volatile compound is virtually unaltered by the more volatile material. Essentially similar results for the acetone-styrene system had previously been obtained by Lara, Kamel, and Drolet (1989).

Swearengen and Weaver (1988) measured the adsorption of pure compounds and binary mixtures of materials used in paints, classifying them into compounds with low boiling points and small molecules, such as propan-2-ol, methyl ethyl ketone, and hexane, and compounds with large molecules such as n-butyl acetate and ethylbenzene. They measured breakthrough at 1% influent concentration, for the pure compounds and for binary mixtures on similar carbon samples. In general, the more volatile components showed accelerated breakthrough, but the breakthrough of the less volatile component was retarded in the small-molecule group and accelerated in the large-molecule group.

9. EFFECT OF HUMIDITY ON PERFORMANCE OF ACTIVATED CARBON

The effect of atmospheric water vapour on the behaviour of activated carbon is relatively small compared with certain other adsorbents such as silica gel and molecular sieve, particularly at

low relative humidities. It is for this reason that activated carbon is used as an adsorbent for a range of contaminants, whereas silica gel, for instance, is used as a desiccant. The adsorbent surface of the carbon is largely made up of the micropores (Dubinin, 1975), whereas relatively more of the surface of desiccants is contained in larger pores, where multilayer adsorption is possible. The final process of water adsorption at high RH is capillary condensation.

Freeman and Reucroft (1979) studied the adsorption part of water by unimpregnated carbon, Whetlerite, and carbon that had been pretreated with hydrogen cyanide. According to their theory, the initial adsorption centres for water molecules are surface oxides, and attachment to these gives the initial, slow, weight increase with relative humidity. At higher RH, as the surface coverage increases, the adsorbed water molecules themselves, with their potential to form hydrogen bonds, are the centres of attachment. (These bonds are strong enough to keep a substance with a molecular weight of 18 liquid at normal temperatures and cause a significant increase in water adsorption.) Whetlerites were shown to have a higher affinity for water than nonimpregnated carbons, which was attributed to the affinity of the water molecules for the ionic salts used as impregnants. Adsorbed hydrogen cyanide, however, hindered the adsorption of water vapour.

Burrage and Allmand (1938) showed that the adsorption of carbon tetrachloride from an air stream was usually made less efficient by the presence of water vapour; in particular, they observed that when experiments were carried out on carbon using a gas stream in equilibrium with it, as far as water vapour is concerned, both the adsorption capacity and the breakthrough time decreased as the relative humidity increased. In other situations the behaviour was not always consistent and repeatable, and it was concluded that the water vapour has two effects: It competes with the adsorbate, reducing the adsorption capacity; and it removes oxides from the carbon, which increases the capacity. The latter effect was also observed by McDermot and Arnell (1954),

Water vapour may, in addition, enhance adsorption by interacting with the adsorbate. Henry (1981) found that the breakthrough time for formaldehyde increased by about 50% when the relative humidity was increased to 80%, probably owing to the formation of a hydrated compound. Barnir and Aharoni (1975) observed that pre-adsorbed water increased the adsorption of cyanogen chloride by causing hydrolysis of the adsorbate. Matsumura et al. (1985) observed that the adsorption of methanol was enhanced by the presence of water vapour, and they attributed this simply to the methanol dissolving in the water.

Enhanced adsorption of a different sort was described by Davies and Legros (1986) for hydrogen sulphide, the adsorption of which is enhanced by the presence of oxygen, which oxidizes it to elemental sulphur.

Nelson et al. (1976) studied the effect of water vapour on adsorption, both when the filters were preconditioned at elevated RH and when they were exposed to contaminant vapour in an air stream at elevated humidity. They found that the latter had a greater effect but that the two processes acted in a cumulative fashion. At relative humidities below 50%, both effects were small, but at higher humidities than this, the breakthrough time decreased rapidly with increasing relative humidity, the effect probably being rather like the effect of loading with binary mixtures, described earlier. This behaviour parallels the normal hygroscopicity of the carbon, which increases in weight by only about 5% when the relative humidity is increased from zero to 50%, but which increases by about 30% when the relative humidity is 85%. The theory of the effect has been outlined by Balieu (1976b) in terms of the adsorption isotherms.

Maggs and Smith (1976) found a greater reduction in breakthrough times at increased relative humidity for anaesthetic vapours of low boiling point than for the less volatile types, consistent with easier competition between vapour and water for available adsorption sites in the former case.

Wood (1985) studied the effects of temperature and humidity on the adsorption of methyl iodide by TEDA-impregnated carbon, and by unimpregnated carbon. Temperature, absolute humidity (expressed as dew point, for instance), and relative humidity are interrelated, and the effect of each on any aspect of filter behaviour depends on which of the other parameters is held constant and which is allowed to vary. The penetration of methyl iodide through TEDA-

impregnated capsules was found to increase with increasing temperature and constant relative humidity (and, therefore, increasing absolute humidity). This was attributed to the deactivation of TEDA sites by the adsorbed water. The service life of canisters was, under the same conditions, found to decrease. However, at constant absolute humidity, the service life of the canisters was found to increase with increasing temperature (and, therefore, decreasing relative humidity).

Jonas, Sansone, and Farris (1985) studied the effect of moisture on the adsorption of chloroform measured in terms of its effect on the breakthrough time. They produced a water isotherm that was similar in all essential features to that of Nelson et al. (1976), indicating that the material was basically similar. The results of the study were that the breakthrough time of previously desiccated carbon was not affected by the relative humidity of the air carrying the chloroform, but that when the carbon was previously humidified, the breakthrough time was seriously reduced at relative humidities of more than about 60%. The authors quoted results obtained by other workers, using benzene, in which the water content of a benzene-laden stream did not affect its adsorption by a dry carbon bed. The behaviour was attributed to the very slow adsorption of water and the displacement of previously adsorbed water by the benzene. They also quoted results in which the adsorption of phosgene was enhanced by water vapour, which almost certainly caused hydrolysis of the phosgene.

Werner (1985) found that the effect of relative humidity was more marked at low influent concentrations. The adsorption of trichloroethylene by oven-dried (but not desiccated) carbon at various concentrations and relative humidities was measured, enabling the adsorption capacity to be calculated from the 50% breakthrough point, with the assumption of a symmetric breakthrough curve. There was a significant reduction in capacity at 25% RH, for the lowest influent concentrations, and the capacity was reduced at all concentrations when the RH was raised to 50%. In the worst case, 85% RH at the lowest contaminant concentration, the capacity of the bed was only 9% of its highest value. In addition, the author observed a broadening of the breakthrough curve (i.e., the time elapsing between, say, the 25% and the 75% breakthrough points).

A theoretical interpretation of Werner's results has been performed by Underhill (1987) in terms of the Dubinin theory, with the free energy of adsorption defined in terms of the isothermal work of compression (the compressibility of a material is known to correlate with both its surface energy and its latent heat of vaporization). A plot can be made of the adsorbed volume against the adsorption energy for both the adsorbate of interest and the water vapour. The corrected graph for the adsorption in the presence of water is obtained by subtracting the abscissa. The result is that the effect is greatest at low adsorbate partial pressure. If the same is done for water vapour at reduced relative humidity, the result is negligible change at high partial pressures of the adsorbate. This is explained by the large change in filled volume at small changes in adsorption potential when the latter is high, that is, when the concentration of adsorbate is low, and the contrary effect when the adsorbate concentration is high.

The breakthrough time at any relative humidity has been expressed in terms of that at RH = 50% in the form of the following simple function (Cohen, Zellers, & Garrison, 1990; Wood, 1987) applicable when temperature is held constant:

$$t_B(RH) = t_B(50)(\zeta + \lambda RH^n)^{-1} \tag{36}$$

where ζ and λ are constants, and the power n is found to be large. Equation 36 describes the behaviour well qualitatively, for it gives a small change in t_B with RH when the latter is small, and a much greater change when it is large, but the power varies considerably among data sets.

The quantitative effects of adsorbed water vapour on both the adsorption capacity and the rate constant for adsorption have been demonstrated by Hall, Breysse, Corn, and Jonas (1988), who exposed carbon filters to carbon tetrachloride vapour at relative humidities ranging from 0 to 90%. The rate constant was found to be virtually the same for values of RH up to 50%

but then to decrease linearly with increasing RH. The adsorption capacity showed an approximately linear decrease at all relative humidities.

These authors plotted the isotherm for water on carbon under conditions of both adsorption and desorption, which demonstrated considerable hysteresis. At 50% RH the mass of water existing as adsorbate per unit mass of carbon during the absorption of the cycle was about 5%, in agreement with the observations of other workers, but under desorption it was about 30%. This effect could explain discrepancies observed among the results of different workers in the field.

The linear decrease in rate constant was also noted by Yoon and Nelson (1988), and they also observed that plots of $\ln\left(\frac{C_0}{C_i - C_0}\right)$ against time, which should be linear according to Equation 27, are nonlinear at elevated humidity.

Isotherms during adsorption and desorption were observed by Hall et al. (1988) for a range of carbons, both new and aged. Ageing significantly increased the mass of adsorbed water on the adsorption limb at moderate relative humidity, but it had little effect at elevated humidity or during desorption. This behaviour was attributed to the formation of polar surface regions by oxidation during the ageing process, consistent with the observations of McDermot and Arnell (1954). The polar groups formed during ageing increased the breakthrough time for methanol, a polar compound, but had no effect on breakthrough time for hexane, a nonpolar compound (Adams, Hall, Holmes, & Newton, 1988). When the hexane was presented to the carbon in air at elevated RH, the breakthrough time was reduced, because the polarity of the surface increased the competitive adsorption of the water vapour and reduced that of the hexane. Hall and Holmes (1992) found that the formation of polar groups could be suppressed if the carbons were chlorinated, by treatment with chlorine or phosgene gas at a high temperature.

Detailed measurements of the displacement of pre-adsorbed water from carbon previously exposed to high humidity atmospheres, by chloropicrin vapour, were made by Hall and Holmes (1989). The water was desorbed as the contaminant vapour was adsorbed from the moving air stream, desorption coming to an end as complete breakthrough of the contaminant occurred. The breakthrough time was reduced as the conditioning relative humidity was increased, but also the shape of the breakthrough curve became asymmetric at high relative humidity, with a rapid increase in effluent concentration followed by a slow increase, similar to that observed by Yoon and Nelson (1988).

Yoon and Nelson (1990) studied the effects of high humidity on the concentration dependence of breakthrough times. The power relationship given in Equation 33 was preserved, but the numerical value of the power depended on the relative humidity. They found that the power was approximately 0.75 for both benzene and methyl chloroform at relative humidities of up to about 50%, but that it dropped to approximately 0.58 for both compounds at a relative humidity of 80%.

10. DESORPTION

Desorption has been mentioned with reference to adsorption isotherms, the theory of which centres around the existence of an equilibrium between adsorption and desorption. When a filter bed is subjected to a contaminant of constant concentration, the influence of desorption can be subsumed into the theory by means of a pseudo-first-order rate constant and need not be accounted for explicitly. When, however, a saturated bed is subjected to a flow of clean air, or if indeed a partly loaded bed is subjected to air containing the contaminant at a lower concentration than that with which it was loaded, desorption must be taken into account. This has been apparent qualitatively, in measurements made when the contaminant concentration is temporally variable (Coover, Reist, & Hudgins, 1982; Hemenway, Fitzgerald, & Paret, 1982; Hori & Tanaka, 1992).

Jonas (1978) and Jonas, Deitz, and Romans (1980) studied the desorption of methyl iodide from impregnated carbon and interpreted their results in terms of the counterparts of the Wheeler equation, for desorption,

$$t_r = \frac{M_0}{C_0 U}\left[L - \frac{U}{k_d}\ln(1-q)\right] \tag{37}$$

where t_R is the time at which a fraction, q, of the adsorption capacity of the filter has been regenerated. Equation 37 applies to a completely saturated bed challenged with clean air. The adsorption capacity, of the bed, M_0, and the rate constant for desorption, k_d can be obtained from experiment; and the authors introduced a new constant, the quotient of the rate contents for adsorption and desorption, defined as the retentivity of the bed, K. Values of K between 26 and 5,000 were observed.

Jonas and Sansone (1981) observed the desorption kinetics of carbon tetrachloride using beds that were only partly loaded and in which Equation 37 would not apply. When such beds are subjected to clean air, a combination of adsorption and desorption occurs, and the result is that the effluent concentration increases with time until a maximum is reached, after which there is a decrease. If a saturated bed is subjected to clean air, the effluent concentration decreases monotonically. Rate constants for both adsorption and desorption were obtained from the data, and their quotient gave a retentivity index similar in magnitude to that obtained above for methyl iodide. Maggs and Smith (1975) exposed filters that had been partly loaded with methyl bromide to clean air and observed high effluent concentrating immediately, indicating that internal rearrangement of the contaminant, without the agency of an air stream, had occurred.

11. ODOUR DETECTION

A question is raised from time to time on the suitability of odour detection by the wearer as an indication of a spent filter. It is, in fact, most unsuitable. The relationship between the odour threshold and the (then) TLV of substances was reviewed by Reist and Rex (1977), who observed that the odour threshold varied considerably among individuals and chose the 100% recognition level as their standard. They compared the observed thresholds with the occupational standards and divided materials into three classes: those in which the two levels are similar; those in which the odour threshold exceeds the TLV by a factor of less than 10; and those in which the discrepancy is greater than this. Occupational standards have changed since then, but from those compounds in which the Occupational Exposure Standards or Maximum Exposure Limit (Health & Safety Executive, 1995) is the same now as at the time of writing, styrene is placed in the first category, allyl alcohol in the second, and methanol in the third. In some situations, for example, with ozone, as examined by Johnston, Dyrud, and Shih (1989), the odour threshold is well below the TLV.

Vasta (1985) observed, during tests where filters were exposed to a highly toxic material, hexamethylene isocyanate, that breakthrough of the (much less toxic) carrier solvents occurred first, and one of these reached a concentration above the normal human odour-detection limit before any isocyanate breakthrough was registered. It was suggested that this observation meant that the respirators could reasonably be used against isocyanates in this situation with the solvents serving as indicators. If this were accepted, it might point to the use of odoriferous breakthrough indicators with harmful compounds (i.e., nontoxic materials with low odour thresholds, a principle formerly employed in the United Kingdom where domestic fuel gas, which used to contain high levels of carbon monoxide, was deliberately made bad smelling so that leaks would be obvious). Research would be needed, to ensure that human response was adequate, and the situations in which the method could be employed would be very limited.

12. PERFORMANCE TESTS

In practice, the performance of a respirator depends on both the efficiency of the filter and the quality of seal between the respirator and the wearer's face. The latter has been covered in two recent reviews (Brown, 1992; Johnson, Myers, Colton, Birkner, & Campbell, 1992). The work of the previous sections indicated that correlations could be obtained between the performance of a filter tested against one contaminant with its performance against another, and the test agents currently used in a number of countries have been reviewed by Breysse, White, Ryan, and Corn (1983).

Such tests, whilst giving a complete picture of the quality of the carbon, involve the destruction of its adsorptive capacity. They can be employed by filter manufacturers on a routine basis whereby a small representative sample of each batch of filters is tested to destruction, so that quality can be monitored. Wood and Ackley (1989) outlined a protocol for the testing of filters so that information could be maximized and effort minimized. The procedure was designed for situations where the real contaminant was known or where the ideal test agent had been identified. The protocol involved contaminant concentrations of 10, 100, and 1,000 times the permitted exposure level, RH of 0, 50, and 85%, volume flow rates of 32, 64, and 128 L/min, temperatures of 15, 25, and 35 °C, and either a single canister or two in series.

Cohen and Garrison (1989) suggested the use of sorbent tubes with pumps to simulate filters during field trials. The criteria of filter acceptability were those discussed in this review.

12.1. Nondestructive Tests

Destructive tests allow only a sample of filters from each batch to be tested, and the assumption must be made that these are representative. Particulate filters used in respirators in the United Kingdom are routinely subjected to a nondestructive test, BS 4400 (British Standards Institution, 1969), as part of quality control, and a similar procedure for adsorptive filters would be valuable.

Maggs (1972) proposed two types of nondestructive test. The first involved subjecting the filter to a pulse of a weakly adsorbed material and examining the time dependence of its concentration in the effluent gas. A number of test agents were used, and many showed promise, provided that there was no competition between the adsorbate and water; the weakly bound test adsorbates tend to be more seriously affected by moisture than the more tightly bound real pollutants. Methyl bromide, however, was found to be relatively unaffected. The second test protocol involved subjecting the filter to a very small pulse of a real contaminant. The effluent concentration would be given by Equation 20 with $t = 0$, $x = L$, since any effect of load on the behaviour of the filter could be neglected.

Other workers in the field have tended to concentrate on the use of a weakly adsorbed gas. Kladnig, Weiss, and Jonas (1980) used both methane and ethane as test agents on filters that had been loaded with dimethyl methyl phosphonate up to a known fraction of their adsorptive capacity. A linear relationship was observed between the residual capacity and the time taken for the peak of a concentration pulse of the test gas to pass through the filter (corrected for the normal transit time without adsorption) except at very low residual capacity. The emergent pulse was also broader when the residual adsorptive capacity was higher. Ethane was preferred as a test agent because its pulse breakthrough time was much greater, relative to the normal transit time, than that of methane, making estimates of residual capacity more accurate.

This work was furthered by Sacco, Chung, and Aksoy (1982) using the same test agents. They expressed the results in terms of a reduced residence time, which is the quotient of the corrected residence time and the normal transit time, allowing comparisons among filters to be made, irrespective of the filter geometry. The pulse of test agent is likely to become broadened as it passes through the filter, as a result of three effects (Deemter, Zuiderweg, & Klinkenberg, 1956). Lack of homogeneity in the filter structure means that not all possible airflow paths will have the same transit time; this effect is independent of the air velocity in

the Stokes Flow regime, corresponding to Equation 4. Adsorption-desorption effects will broaden the pulse more as the air velocity is increased. Longitudinal diffusion effects, neglected in most simple studies, will increase as the air velocity is reduced. The result is that there is an optimal test velocity. Sacco et al. (1982) used a velocity of 1.05 cm s^{-1} to give the best resolution. In addition to contaminant load, they studied the effect of relative humidity on residual adsorptive capacity and found the effect to be linear at low RH and less than linear at high RH, which they attributed to multilayer formation.

Jonas and Sansone (1984), using ethane as the test gas and carbon partly loaded with carbon tetrachloride, observed a linear relationship between the dimensionless time parameter above and the residual adsorptive capacity.

Underhill (1988) used argon as a test gas in filters partly loaded with carbon tetrachloride and observed results basically similar to those with ethane, described earlier. The results obtained on different batches of unloaded carbon were, in addition, found to correlate with the adsorption of the higher atomic weight inert gases krypton and xenon, which occur as radioactive isotopes.

13. CONCLUSIONS

Moyer (1983) has reviewed the factors that need to be taken into account when the use of a respirator with a carbon filter is considered. Respiratory protection of this form is not considered suitable for substances that are immediately dangerous to life or health, and problems occur when they are used with materials that have either a low odour threshold or a particularly high heat of adsorption. Nevertheless, they prove useful and acceptable in a wide range of situations.

A considerable amount of research has been carried out on activated carbon. The references cited in this review are those most relevant to respirator filters, but they are only a small fraction of the total of published work on the subject. The study has been placed on a sound scientific basis, though the greatest fundamental problem is the individual variability among samples of activated carbon.

Simple expressions exist, relating the basic structural parameters of a filter and the velocity, the viscosity, and the density of the air to the pressure drop, but there is no simple analytical theory that gives a satisfactory description of the flow pattern, even through highly regular arrays of particles in contact.

The theory of adsorption, developed for clean and perfect surfaces, cannot be applied directly to carbon, because of the complicated surface geometry. The most useful approach is the theory of volume filling of micropores which, in spite of its approximate nature, its limitations, and the rather poorly justified approximations made in its derivation, does at least allow generalizations to be made. Since it is not practicable to test a respirator in all possible situations of use, a good means of predicting behaviour in one situation from observations of behaviour in another is valuable. The Dubinin equation facilitates this, using physical parameters such as parachor (which is related to surface tension) and refractive index (which is related to molecular polarizability), both of which give a measure of the strength of the adsorbate-adsorbent interaction. Useful as the prediction is, it is important that proper account be taken of the likely error (Wood, 1993).

The performance of a filter exposed to a moving stream of contaminated air depends on adsorption kinetics, and the only simple analytical solution of the mass balance equation is the Wheeler equation (with its various modifications). This equation is strictly applicable only in a relatively small range of situations, but it frequently happens that an equation is a good description of the situation well outside the range of parameters where it can be rigorously justified, and the Wheeler equation is very widely used.

The dynamic equation introduces a constant describing the rate at which adsorption takes place. The form taken by the rate constant depends upon whether the rate limiting process is diffusion or surface interaction. In the situation where diffusion in the gaseous phase is rate

limiting, the derivation of the rate constant will need to take account of the flow pattern near the surface, just as in the theory of diffusional deposition in particulate filters. The rate constant can be obtained from experimental results, and there is scope for further fundamental work on this parameter.

A number of (related) experimental observables appear in the Wheeler equation, of which the most important is breakthrough time, the time taken for the concentration of the contaminant leaving the filter to equal a chosen fraction, usually 1%, of the (constant) concentration with which the filter is challenged. This depends on the depth of the filter, the quality of the carbon, and the velocity at which the contaminated air passes through; and also on the chemical nature of the contaminant and its concentration.

Breakthrough usually occurs at a lower total load when the contaminant is presented at a lower concentration, and in fact breakthrough time varies approximately as the concentration raised to a fractional power. This means that predictions of long-term behaviour made on the basis of short-term tests with high concentrations of contaminant must be applied with care.

The behaviour of filters with respect to one component of a mixture of contaminants cannot be predicted from that of the component acting in isolation at its own partial pressure because of competition among the various components for adsorption sites. However, semiquantitative predictions can be made if proper account of the behaviour of all components is taken.

The relative insensitivity of the behaviour of activated carbon to humidity when the latter is low or moderate is one reason for its wide use as an adsorbent, but at relative humidities greater than about 50%, the effect is significant. It is further complicated by hysteresis in the moisture regain cycle of the carbon, and by the greater moisture uptake of aged samples. Usually the effect of water is to reduce the efficiency of the filter, but in certain instances it increases the efficiency in contaminant removal by promoting hydrolysis.

Desorption need not be explicitly considered in the theory of adsorption from a stream of constant contaminant concentration. However, for intermittent exposure with clean air episodes, it must be included, because experimental observations show breakthrough at a lower concentration in the latter situation. Desorption may occur in still air, and diffusion may cause the adsorbate, formerly concentrated at the leading face of the filter, to be redistributed in a more uniform pattern.

Future work on adsorbent filters might usefully be inclined towards field studies of filter performance, because these have lagged behind laboratory work, and more effort here is likely to be fruitful. A long-standing problem is that of the specification of filter lifetime. Recognition of breakthrough by detection of the odour of a contaminant by the respirator wearer is unacceptable. In many instances the odour threshold is above the permitted exposure concentration, and even when this is not the case, individual olfactory deficiency may cause certain people to be vulnerable. Firm guidance based on field studies or, preferably, a sound physical or chemical indication system, is necessary. A problem with indicators is, however, that the obvious place to situate them is at the breakthrough point, the downstream face of the filter, where they are invisible to the wearer.

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TABLE 1. Index of Authors Reporting on Adsorption of Specific Adsorbents

Adsorbate	Reference
Acetaldehyde	Freedman, Ferber, & Hartstein (1973)
Acetic acid	Freedman, Ferber, & Hartstein (1973)
Acetronitrile	Freedman, Ferber, & Hartstein (1973)
Acetamide	Sansone & Jonas (1981)
Acrylonitrile	Sansone & Jonas (1981); Nelson & Harder (1974); Yoon & Nelson (1992)
Allyl acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
Allyl chloride	Nelson & Harder (1974); Yoon & Nelson (1992)
Allyl alcohol	Nelson & Harder (1974); Yoon & Nelson (1992)
Acetone	Vasta (1985); Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984a); Wood & Moyer (1989); Nelson & Correia (1976)
Acetic anhydride	Nelson & Harder (1974); Yoon & Nelson (1992)
Acrolein	Stampfer (1982)
Benzene	Jonas, Tewari, & Sansone (1979); Freedman, Ferber, & Hartstein (1973); Sansone & Jonas (1981); Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984b); Jonas & Rehrmann (1974); Nelson & Correia (1976)
Butane	Freedman, Ferber, & Hartstein (1973)
Butanol	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Butyl formate	Freedman, Ferber, & Hartstein (1973)
sec-Butylamine	Jonas, Tewari, & Sansone (1979)
sec-Butanol	Nelson & Harder (1974); Yoon & Nelson (1992)
sec-Butyl acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
Butyl acetate	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
2-Butanone	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Butylamine	Nelson & Harder (1974); Yoon & Nelson (1992)
Bromobenzene	Nelson & Harder (1974); Yoon & Nelson (1992)
Carbon tetrachloride	Jonas, Tewari, & Sansone (1979); Sansone & Jonas (1981); Nelson & Harder (1974); Yoon & Nelson (1992); Ackley (1985); Yoon & Nelson (1984b); Nelson & Correia (1976)
bis Chloromethyl ether	Sansone & Jonas (1981)
Chloromethyl methyl ether	Sansone & Jonas (1981)
Chloroform	Jonas, Tewari, & Sansone (1979); Freedman, Ferber, & Hartstein (1973); Sansone & Jonas (1981); Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984a); Nelson & Correia (1976)
Cyanogen chloride	Aharoni & Barnir (1978)
Chlorine dioxide	Simon, Fisher, & Davison (1987)
Cumene	Nelson & Harder (1974); Yoon & Nelson (1992)
p-Cymene	Nelson & Harder (1974); Yoon & Nelson (1992)
2-Chloropropane	Nelson & Harder (1974); Yoon & Nelson (1992)
1-Chloropropane	Nelson & Harder (1974); Yoon & Nelson (1992)
2-Chloro-2-methylpropane	Nelson & Harder (1974); Yoon & Nelson (1992)
1-Chlorobutane	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
2-Chloro-2-methylbutane	Nelson & Harder (1974); Yoon & Nelson (1992)
1-Chloropentane	Nelson & Harder (1974); Yoon & Nelson (1992)
Chlorocyclopentane	Nelson & Harder (1974); Yoon & Nelson (1992)
Chlorobenzene	Nelson & Harder (1974); Yoon & Nelson (1992)
1-Chlorohexane	Nelson & Harder (1974); Yoon & Nelson (1992)
O- Chlorotoluene	Nelson & Harder (1974); Yoon & Nelson (1992)
1-Chloroheptane	Nelson & Harder (1974); Yoon & Nelson (1992)
3-(Chloromethyl) Heptane	Nelson & Harder (1974); Yoon & Nelson (1992)
Cyclopentanone	Nelson & Harder (1974); Yoon & Nelson (1992)
Cyclohexanone	Nelson & Harder (1974); Yoon & Nelson (1992)
Cyclohexane	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Cyclohexene	Nelson & Harder (1974); Yoon & Nelson (1992)

TABLE 1. ***(continued)***

Adsorbate	Reference
1,3,5-Cycloheptatriene	Nelson & Harder (1974); Yoon & Nelson (1992)
Cyclooctane	Nelson & Harder (1974); Yoon & Nelson (1992)
Cyclohexylamine	Nelson & Harder (1974); Yoon & Nelson (1992)
Chlorine	Bohart & Adams (1920)
p-Dioxane	Jonas, Tewari, & Sansone (1979); Sansone & Jonas (1981)
1,2 Dibromo-3-chloropropane	Sansone & Jonas (1981)
1,1 Dibromoethane	Sansone & Jonas (1981); Nelson & Harder (1974); Yoon & Nelson (1992)
1,2 Dibromoethane	Sansone & Jonas (1981); Nelson & Harder (1974); Yoon & Nelson (1992)
1,2 Dichloroethane	Jonas, Tewari, & Sansone (1979); Sansone & Jonas (1981); Nelson & Harder (1974); Yoon & Nelson (1992)
Deppoxy butane (meso)	Sansone & Jonas (1981)
1,1 Dimethyl hydrazine	Sansone & Jonas (1981)
1,2 Dimethyl hydrazine	Sansone & Jonas (1981)
Dimethyl sulphate	Sansone & Jonas (1981)
Dichloromethane	Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984b); Nelson & Correia (1976)
trans-1,2-Dichloroethylene	Nelson & Harder (1974); Yoon & Nelson (1992)
1,1-Dichloroethane	Nelson & Harder (1974); Yoon & Nelson (1992)
cis-1,2-Dichloroethylene	Nelson & Harder (1974); Yoon & Nelson (1992)
1,2-Dichloropropane	Nelson & Harder (1974); Yoon & Nelson (1992)
cis, trans-1, 3-Dichloropropene	Sansone & Jonas (1981)
1,4-Dichlorobutane	Nelson & Harder (1974); Yoon & Nelson (1992)
O-Dichlorobenzene	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
1,3-Dimethylbutyl acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
Diisobutyl ketone	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
2,3-Dimethylbutane	Nelson & Harder (1974); Yoon & Nelson (1992)
Decane	Nelson & Harder (1974); Yoon & Nelson (1992)
Diethylamine	Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984b); Nelson & Correia (1976)
Dipropylamine	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Diisopropylamine	Nelson & Harder (1974); Yoon & Nelson (1992)
Dibutylamine	Nelson & Harder (1974); Yoon & Nelson (1992)
Dimethylamine	Nelson & Harder (1974); Yoon & Nelson (1992)
Epichlorohydrin	Nelson & Harder (1974); Yoon & Nelson (1992)
Ethyl formate	Freedman, Ferber, & Hartstein (1973)
Ethanol	Nelson & Harder (1974); Yoon & Nelson (1992)
Ethyl bromide	Freedman, Ferber, & Hartstein (1973)
Ethyl iodide	Freedman, Ferber, & Hartstein (1973)
Ethylene oxide	Freedman, Ferber, & Hartstein (1973)
Ethylenimine	Sansone & Jonas (1981)
Epichlorohydrin	Stampfer (1982)
Ethyl benzene	Nelson & Harder (1974); Yoon & Nelson (1992)
2-Ethyl-1-butanol	Nelson & Harder (1974); Yoon & Nelson (1992)
Ethyl chloride	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Ethyl acetate	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
5-Ethylidene-2-norbornene	Nelson & Harder (1974); Yoon & Nelson (1992)
Ethylamine	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
2-Ethoxyethanol	Nelson & Harder (1974); Yoon & Nelson (1992)
2-Ethoxyethyl acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
Formaldehyde	Henry (1981)
Hexane	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984b); Nelson & Correia (1976)
Heptane	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Hydrazine	Sansone & Jonas (1981)

TABLE 1. ***(continued)***

Adsorbate	Reference
Hexamethylene diisocyanate	Vasta (1985)
Hexyl acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
Hydrogen chloride	Bohart & Adams (1920)
3-Heptanone	Nelson & Harder (1974); Yoon & Nelson (1992)
2-Heptanone	Nelson & Harder (1974); Yoon & Nelson (1992)
Hydrogen sulphide	Davies & Legros (1986)
Ispopropyl acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
Isopropanol	Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984b); Nelson & Correia (1976)
Isopropenyl acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
Isopentyl acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
Isopropylamine	Nelson & Harder (1974); Yoon & Nelson (1992)
Methylene chloride	Moyer & Peterson (1993)
2-Methoxyethyl-acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
2-Methoxyethanol	Nelson & Harder (1974); Yoon & Nelson (1992)
Methylamine	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Methylcyclohexane	Nelson & Harder (1974); Yoon & Nelson (1992)
5-Methyl-3-heptanone	Nelson & Harder (1974); Yoon & Nelson (1992)
3-Methyl cyclohexanone	Nelson & Harder (1974); Yoon & Nelson (1992)
4-Methylcyclohexanone	Nelson & Harder (1974); Yoon & Nelson (1992)
Methylcyclopentane	Nelson & Harder (1974); Yoon & Nelson (1992)
4-Methyl-2-pentanone	Nelson & Harder (1974); Yoon & Nelson (1992)
Methyl acetate	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984a); Yoon & Nelson (1984b); Nelson & Correia (1976)
Methyl chloride	Nelson & Harder (1974); Yoon & Nelson (1992)
Methyl chloroform	Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984a); Yoon & Nelson (1984b); Nelson & Correia (1976)
3-Methyl-1-butanol	Nelson & Harder (1974); Yoon & Nelson (1992)
4-Methyl-2-pentanol	Nelson & Harder (1974); Yoon & Nelson (1992)
Mesitylene	Nelson & Harder (1974); Yoon & Nelson (1992)
Methyl bromide	Maggs & Smith (1975); Freedman, Ferber, & Hartstein (1973)
Methanol	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Methyl formate	Freedman, Ferber, & Hartstein (1973)
Methyl iodide	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992)
Methyl methane sulphonate	Sansone & Jonas (1981)
Methyl isocyanate	Moyer & Berardinelli (1987)
Methyl ethyl ketone	Vasta (1985)
Mesityl oxide	Nelson & Harder (1974); Yoon & Nelson (1992)
1-Naphthylamine	Sansone & Jonas (1981)
2-Naphthylamine	Sansone & Jonas (1981)
N-Nitrosodiethylamine	Sansone & Jonas (1981)
N-Nitrosodimethylamine	Sansone & Jonas (1981)
N-Nitroso-N-methylurethane	Sansone & Jonas (1981)
N-Nitrosopiperidine	Sansone & Jonas (1981)
N-Nitrosodipropylamine	Sansone & Jonas (1981)
Nonane	Nelson & Harder (1974); Yoon & Nelson (1992)
1-Nitropropane	Nelson & Harder (1974); Yoon & Nelson (1992)
Octane	Freedman, Ferber, & Hartstein (1973)
Ozone	Johnston, Dyrud, & Shih (1989)
Pyridine	Jonas, Tewari, & Sansone (1979); Nelson & Harder (1974); Yoon & Nelson (1992)
Pentane	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)

TABLE 1. ***(continued)***

Adsorbate	Reference
Propanol	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992)
Propyl formate	Freedman, Ferber, & Hartstein (1973)
Propyl acetate	Freedman, Ferber, & Hartstein (1973); Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Proprionaldehyde	Freedman, Ferber, & Hartstein (1973)
1,3-Propane sultone	Sansone & Jonas (1981)
β-Propiolactone	Sansone & Jonas (1981)
Propylenimine	Sasone & Jonas (1981)
Propargyl alcohol	Stampfer (1982)
2-Pentanol	Nelson & Harder (1974); Yoon & Nelson (1992)
Pentanol	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Perchloroethylene	Nelson & Harder (1974); Yoon & Nelson (1992); Nelson & Correia (1976)
Pentachloroethane	Nelson & Harder (1974); Yoon & Nelson (1992)
Pentyl acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
2-Pentanone	Nelson & Harder (1974); Yoon & Nelson (1992)
3-Pentanone	Nelson & Harder (1974); Yoon & Nelson (1992)
2,4-Pentanedione	Nelson & Harder (1974); Yoon & Nelson (1992)
Propylamine	Nelson & Harder (1974); Yoon & Nelson (1992)
Sulphur dioxide	Ackley (1985)
Safrole	Sansone & Jonas (1981)
Toluene diisocyanate	Dharmarajan, Lingg, & Hackathorn (1986)
Toluene	Vasta (1985); Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984a); Nelson & Correia (1976)
Trichloroethylene	Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984a); Nelson & Correia (1976)
1,1,2-Trichloroethane	Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984a); Nelson & Correia (1976)
1,2,3-Trichloropropane	Nelson & Harder (1974); Yoon & Nelson (1992); Yoon & Nelson (1984a); Nelson & Correia (1976)
1,1,2,2-Tetrachloroethane	Nelson & Harder (1974); Yoon & Nelson (1992)
2,2,4-Trimethylpentane	Nelson & Harder (1974); Yoon & Nelson (1992)
2,2,5-Trimethyhexane	Nelson & Harder (1974); Yoon & Nelson (1992)
Triethylamine	Nelson & Harder (1974); Yoon & Nelson (1992)
Urethane	Sansone & Jonas (1981)
Valeraldehyde	Freedman, Ferber, & Hartstein (1973)
Vinyl chloride	Sansone & Jonas (1981); Bohart & Adams (1920); Yoon & Nelson (1984b); Nelson & Correia (1976)
Vinyl acetate	Nelson & Harder (1974); Yoon & Nelson (1992)
m-Xylene	Nelson & Harder (1974); Yoon & Nelson (1992)

List of Symbols

a_1	adsorption of component 1 (dimensionless)
A	molar free energy of adsorption (joule $mole^{-1}$)
b	van der Waals constant (m^3)
B	microporosity constant ($joule^{-2}$ $mole^2$)
c	packing fraction (dimensionless)
C	concentration in gas phase (kg m^{-3})
C_i	C at inlet of filter (kg m^{-3})
C_o	C at outlet of filter (kg m^{-3})
d	fibre/granule diameter (m)
D	coefficient of diffusion (m^2 s^{-1})
$f(c)$	function relating c to Δp (dimensionless)
k	rate constant for adsorption (sec^{-1})
k_∞	k as $U \rightarrow \infty$ (sec^{-1})
k_d	rate constant for desorption (sec^{-1})
K	retentivity of filter (dimensionless)
L	filter depth (m)
L_c	critical depth (m)
m	molecular weight (dimensionless)
$\overline{m}$	mean molecular weight (dimensionless)
M	mass of adsorbate/unit volume of filter (kg m^{-3})
M_A	mass of adsorbate/unit area (kg m^{-2})
M_{As}	M_A at saturation of area (kg m^{-2})
M_o	M at equilibrium (kg m^{-3})
M_s	M_o at saturation vapour pressure, adsorption capacity (kg m^{-3})
n	refractive index (dimensionless)
N_1	molar fraction of component 1 (dimensionless)
P	pressure (Pa)
P_s	saturation vapour pressure (Pa)
q	fractional regeneration of filter (dimensionless)
Q	volumetric flowrate (m^3 s^{-1})

R	gas constant (joule $mole^{-1}$ C^{-1})
Re	Reynolds number (dimensionless)
Sc	Schmidt number (dimensionless)
t_B	breakthrough time (s)
t_R	characteristic time for desorption (s)
T	absolute temperature (K)
U	air velocity (ms^{-1})
v	molar volume (m^3)
V	velocity of adsorption front (ms^{-1})
W	mass of adsorbent (kg)
α	constant in Equation 32 (s^{-1})
β	affinity coefficient (dimensionless)
γ	constant in Langmuir theory (Pa^{-1})
δ	constant in Equation 32 (s^{-1})
Δp	pressure drop across filter (Pa)
ϵ	constant in Equation 32 (s^2 m^{-1})
ζ	constant in Equation 36 (dimensionless)
η	coefficient of viscosity (kg m^{-1} s^{-1})
λ	constant in Equation 36 (dimensionless)
ρ	density of adsorbate (kg m^{-3})
ρ_g	density of air (kg m^{-3})
ρ_B	bulk density of filter (kg m^{-3})
σ	surface tension (joule m^{-2})