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ANALYTICAL ASPECTS RELATING TO THE ESTIMATION OF CARBON FILTER PERFORMANCE FOR MILITARY APPLICATIONS

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14. ABSTRACT-LIMIT 200 WORDS The ability to estimate the gas capacity of carbon-based filters in military applications is important to the engineering and design communities. These design aspects factor into the configuration, performance, and service aspects of the filter. This effort was undertaken to conduct a detailed review of analytical developments that have been pursued in the past with respect to breakthrough estimation, to provide a rationale for the various parameters used in current breakthrough relationships, and to demonstrate the analytical complexity that results from fundamental mass balance expressions. This complexity is often addressed through several simplifying assumptions and the use of correlative relationships to estimate the breakthrough of carbon-based adsorbent systems used in military applications. The analytical developments contained herein are based on fundamental engineering principles and concepts relating to mass conservation. The dynamics associated with the transfer of energy are not considered in this report. This review effort focused on contaminant materials having relatively low room-temperature vapor pressures and exhibiting Type I Brunauer, Edward, and Teller (BET) isotherms. Many compounds that exhibit such property characteristics are effectively removed by activated carbon substrates through a mechanistic pathway termed physical adsorption.					
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EXECUTIVE SUMMARY

The ability to estimate the gas capacity of carbon-based filters in industrial and military applications is important to the engineering and design communities. These design aspects factor into the configuration, performance characteristics, and service aspects of the filter. A common goal of these efforts is to be able to quantify and track the transmission of a compound (typically a contaminant) as it traverses the adsorbent bed from the inlet to the effluent.

Within the field of adsorption modeling and science, extensive efforts have been undertaken and continue to be pursued in developing analytical tools to enable the engineering community a means to gauge filter performance. The analytical models are founded on the basic engineering principles of mass, energy, and momentum conservation. The essential element of these approaches is to establish a fundamental conservation relationship over a differential volume element and then integrate the resultant differential expressions over the entire volume of the reactor vessel to characterize the performance of the adsorber. Although the development of the basic differential conservation relationships is relatively straightforward, the development of closed-form solutions to these resultant conservation expressions can be quite formidable. Advances in modern analytical capability enable numeric solutions to be obtained; however, closed-form analytical solutions for even relatively simplified adsorption processes can be quite complex. Because of these substantial analytical obstacles, engineering and design engineers must often rely on correlative approaches to characterize filter performance.

The following analytical model has been used (and continues to be used) to estimate the breakthrough capacity of carbon-based filters against low-volatility compounds of military interest:

$$t_b = [(W_e A \rho_b)/(Q C_o)] (L - M_z) \quad (\text{ES-1})$$

where

$$M_z = \{[(\varphi_s d_p)/[6(1 - \epsilon)]]\} [(\varphi_s d_p u \rho)/\mu]^{0.41} [\mu/(\rho D)]^{0.67} \ln(C_o/C_b) \quad (\text{ES-2})$$

The development of these relationships seems to trace back to efforts conducted by G. S. Bohart and E. Q. Adams during the 1920s through their investigations with the transmission of chlorine through carbon beds. These relationships are based on the assumption that bulk diffusion from the vapor phase to the adsorbed phase represents the rate-controlling removal process.

The purpose of the current effort is to provide a developmental basis and rationale for the relationships given by eqs ES-1 and ES-2. The approach taken in this review effort was to demonstrate the complexity of the basic mass balance relationships, the need to employ simplifying assumptions, and the use of accepted correlative relationships to develop the relationships given by eqs ES-1 and ES-2. This review is intentionally very detailed in the mathematical developments. A further intent of this effort was to provide a historical lineage of the currently used breakthrough relationships to the analytical developments of the past.

During the conduct of this review effort, there were analytical developments that were not thoroughly understood by this author. These knowledge gaps are attributable in part to mathematical as well as experience limitations. The areas that were not well understood included the detailed form of eq ES-3 (eq 195 within the report) and the analytical development and progression that followed eq ES-4 (eq 232 within the report). It was surmised that a pressure factor was inadvertently omitted from the Dole and Klotz relationship given by ES-3. Dimensional consistency arguments and an analytical development were conducted to support this contention.

$$[(p_o p_{lm,B})/\Delta p_m] = \ln(C_o/C_b) \quad \text{ES-3}$$

$$t_b = [(\rho_b W_e)/(u C_o (MW)_i)] \left\{ L - \int_{C_o}^{C_b} [1 - (W_i/W_e)] (\partial C_i / \partial z)^{-1} dC_i - \int_0^L (W_o/W_e) dz \right. \\ \left. + [(u C_o (MW)_i)/(\rho_b W_e)] \int_{C_o}^{C_b} [C_i(L)/C_o] (\partial C_i / \partial t)^{-1} dC_i \right\} \quad \text{ES-4}$$

The energetic aspects and prior loading history (or service environment) of the adsorbent are important considerations with adsorption processes. Each of these aspects would be expected to contribute to the characterization of the transmission of a contaminant through the carbon bed. Because of the added analytical complexity associated with the energy balances and prior loading considerations, this review only focused on fundamental mass balance requirements. Energy considerations would likely have to be considered with design efforts requiring a high degree of refinement. These issues were beyond the scope of this review.

PREFACE

The work described in this report was started in May 1995 and completed in September 2011.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release.

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The author wishes to acknowledge the contributions and support of the late Robert W. Morrison ("Bob," a former employee of the Research and Technology Directorate of the U.S. Army Edgewood Chemical Biological Center [ECBC]) as well as other members, both past and current, of the Chemical, Biological, Radiological, and Nuclear (CBRN) Filtration Team of the Research and Technology Directorate (of ECBC) for fostering an interest in trying to better understand the analytical developments and history relating to carbon filtration. In years past, Bob provided considerable guidance and background information on the origins of the analytical relationships that are used to estimate filter capacities. Bob, as well as his former colleagues of the CBRN Filtration Team, provided (and continue to provide) considerable support to personnel within the ECBC Engineering Directorate on numerous issues relating to adsorbent-based filtration.

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ANALYTICAL ASPECTS RELATING TO THE ESTIMATION OF CARBON FILTER PERFORMANCE FOR MILITARY APPLICATIONS

1. BACKGROUND

The estimation of filtration capabilities for carbon-based military filters is typically based on the characteristics of the compound that is targeted for removal from a contaminated airstream. An important metric relating to the removal of a compound from a contaminated airstream is the room-temperature vapor pressure of the material. In many instances, compounds with room-temperature vapor pressures below 10 torr are efficiently removed on activated carbonaceous adsorbents through a process known as physical adsorption. This grouping of materials covers the known H, G, and V classes of chemical warfare compounds. With vapor pressures greater than approximately 100 torr, impregnants are incorporated into the pore structure of the activated carbon, and the removal mechanisms are generically classified as chemisorption.

This report will review the analytical foundations upon which the carbon filter performance for military applications is based. As indicated earlier, considerable effort has already been put forth in this area, and to that end, the content presented here represents more of a compilation of past efforts rather than anything new or novel. The review does expand upon mathematical developments, to provide sufficient background so as to be understood by the design community.

The foundation upon which the performance estimations are based rests with fundamental mass balance relationships that are typically developed in differential form. Solution to the resultant differential mass balances would yield vapor-phase concentrations as a function of both time and position within an adsorbent bed. As is demonstrated, closed-form analytical solutions to the resultant differential mass balance relationships are complex; therefore, simplifying assumptions are necessary. Even when the simplifying assumptions are invoked, analytical solutions to the differential mass balance expressions can be formidable.

2. ANALYTICAL CONSIDERATIONS OF DIFFERENTIAL VOLUME ELEMENTS AND DIRECTIONAL GRADIENTS

The intent of this section is to consider differential volume elements and the flow fields associated with such elements for varying geometries. For rectilinear geometries, an orthogonal volume element can often be used, whereas for radial flow geometries, a volume element having cylindrical characteristics would be appropriate. The M48A1 and M98 gas filters used with collective protection applications are examples of radial flow filters.

A note relating to the nomenclature convention used throughout this review is needed at this stage. The following nomenclature terminology and interpretation were used throughout this report:

- $N_{ix}(x)$ represents the molar flux of component i in the x -direction evaluated at position x .
- $N_{ix}(x + \Delta x)$ represents the molar flux of component i in the x -direction evaluated at position $(x + \Delta x)$.
- $N_i(t, r, \theta, z)$ represents the molar flux of component i evaluated at time t and coordinate position (r, θ, z) .
- $N_i(t + \Delta t, r + \Delta r, \theta + \Delta \theta, z + \Delta z)$ represents the molar flux of component i evaluated at time $(t + \Delta t)$ and coordinate position $(r + \Delta r, \theta + \Delta \theta, z + \Delta z)$.

This nomenclature convention was chosen in an effort to explicitly define the variable dependency as well as the evaluation conditions of the affected parameters. In cases where the functional dependency and/or evaluation conditions are unambiguous, this explicit descriptor notation is omitted.

The development of the mass balance relationships in this review effort is based on the characterization of differential volume elements with respect to a fixed reference frame. This is in contrast with the characterization of the volume elements relative to a reference frame that undergoes positional displacements.

2.1 Differential Volume Element Considerations with Three Mutually Perpendicular Axes

Figure 1 depicts an orthogonal differential volume element in free space having three mutually perpendicular axes.

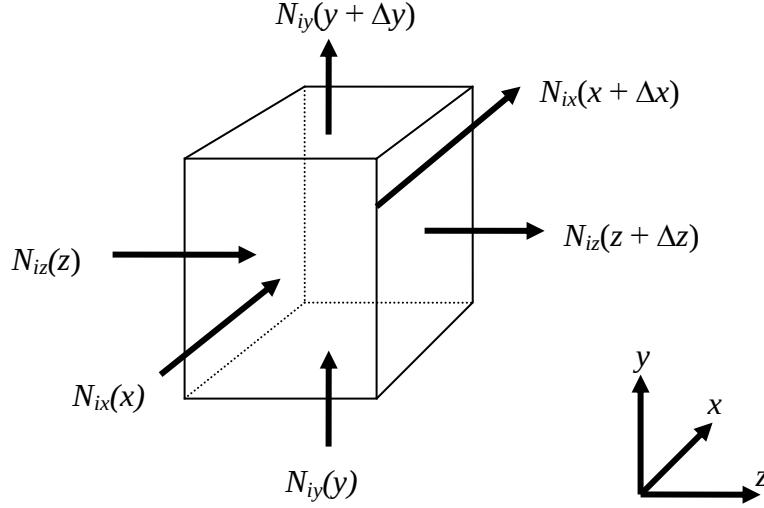


Figure 1. Three mutually perpendicular molar fluxes in a Cartesian coordinate system.

The volume of the differential element depicted in Figure 1 is $\Delta x \Delta y \Delta z$.

A generic mass balance for component i based on a reacting system can be written as

$$(\partial M_i / \partial t) = \sum (m_i)_{\text{in}} - \sum (m_i)_{\text{out}} + (MW)_i R_i \Delta x \Delta y \Delta z \quad (1)$$

where R_i represents the molar rate of generation (or consumption) of component i within the volume element expressed on a per-volume basis. The sum of the mass flows of component i into the differential volume element can be expressed by

$$\begin{aligned} \sum (m_i)_{\text{in}} &= (MW)_i N_{ix}(x) \Delta y \Delta z + (MW)_i N_{iy}(y) \Delta x \Delta z + (MW)_i N_{iz}(z) \Delta x \Delta y \\ &= (MW)_i [\Delta y \Delta z N_{ix}(x) + \Delta x \Delta z N_{iy}(y) + \Delta x \Delta y N_{iz}(z)] \end{aligned} \quad (2)$$

The sum of the mass flows of component i exiting the differential volume element can be expressed by

$$\begin{aligned} \sum (m_i)_{\text{out}} &= (MW)_i N_{ix}(x + \Delta x) \Delta y \Delta z + (MW)_i N_{iy}(y + \Delta y) \Delta x \Delta z \\ &\quad + (MW)_i N_{iz}(z + \Delta z) \Delta x \Delta y \\ &= (MW)_i [\Delta y \Delta z N_{ix}(x + \Delta x) + \Delta x \Delta z N_{iy}(y + \Delta y) \\ &\quad + \Delta x \Delta y N_{iz}(z + \Delta z)] \end{aligned} \quad (3)$$

Substituting the relationships given by eqs 2 and 3 into eq 1 gives the following expression after some simplification:

$$(\partial M_i / \partial t) = -(\text{MW})_i \left\{ \Delta y \Delta z [N_{ix}(x + \Delta x) - N_{ix}(x)] + \Delta x \Delta z [N_{iy}(y + \Delta y) - N_{iy}(y)] \right. \\ \left. + \Delta x \Delta y [N_{iz}(z + \Delta z) - N_{iz}(z)] \right\} + (\text{MW})_i R_i \Delta x \Delta y \Delta z \quad (4)$$

The vapor phase concentration of component i within the differential volume element is taken to be homogeneous and characterized by a uniform molar concentration of C_i . The mass of component i within the differential volume element is then given by

$$M_i = (\text{MW})_i C_i \Delta x \Delta y \Delta z \quad (5)$$

Equation 5 can be differentiated with respect to time, which yields

$$(\partial M_i / \partial t) = (\text{MW})_i C_i [\partial(\Delta x \Delta y \Delta z) / \partial t] + \Delta x \Delta y \Delta z \left\{ \partial[(\text{MW})_i C_i] / \partial t \right\} \\ = (\text{MW})_i C_i [\partial(\Delta x \Delta y \Delta z) / \partial t] + \Delta x \Delta y \Delta z (\text{MW})_i (\partial C_i / \partial t) \quad (6)$$

The full expansion of eq 6 will yield terms of the form

$$\Delta y \Delta z [\partial(\Delta x) / \partial t], \Delta x \Delta z [\partial(\Delta y) / \partial t], \text{ and } \Delta x \Delta y [\partial(\Delta z) / \partial t]$$

In the following development, it is assumed that the derivatives of the differentials are negligible relative to the first-order derivatives. Mathematically, this requires that the following holds true:

$$[\partial(\Delta x) / \partial t], [\partial(\Delta y) / \partial t], \text{ and } [\partial(\Delta z) / \partial t] \ll (\partial C_i / \partial t)$$

With this assumption, eq 6 is approximated by

$$(\partial M_i / \partial t) \approx (\text{MW})_i \Delta x \Delta y \Delta z (\partial C_i / \partial t) \quad (7)$$

Substituting the relationship given by eq 7 into eq 4 and dividing through by the quantity $[\Delta x \Delta y \Delta z (\text{MW})_i]$ gives

$$(\partial C_i / \partial t) = - \left\{ [N_{ix}(x + \Delta x) - N_{ix}(x)] / \Delta x \right\} - \left\{ [N_{iy}(y + \Delta y) - N_{iy}(y)] / \Delta y \right\} \\ - \left\{ [N_{iz}(z + \Delta z) - N_{iz}(z)] / \Delta z \right\} + R_i \quad (8)$$

In the limit as Δx , Δy , and Δz collapse to zero, eq 8 takes on the form

$$(\partial C_i / \partial t) = - [(\partial N_{ix} / \partial x) + (\partial N_{iy} / \partial y) + (\partial N_{iz} / \partial z)] + R_i \quad (9)$$

Each of the three orthogonally directed flux terms given in eq 9 is comprised of a bulk flow component as well as a dispersive (or diffusive)-based contribution. The dispersive-based contribution is typically based on a Fickian diffusion-type relationship (i.e., Fick's first law of diffusion). The dispersive contribution attempts to capture deviations from ideal plug-based flow. The following generic relationship characterizes the molar flux through each of the orthogonally directed axes:

$$\begin{aligned}(N_{ij})_{\text{total}} &= (N_{ij})_{\text{convective bulk flow}} + (N_{ij})_{\text{diffusion contribution}} \\ &= u_j C_i - \mathfrak{D}_{ij} (\partial C_i / \partial j)\end{aligned}\tag{10}$$

Differentiation of eq 10 with respect to a generic directional axis gives the following series of relationships:

$$(\partial N_{ij} / \partial j) = [\partial (u_j C_i) / \partial j] - \left\{ \partial [\mathfrak{D}_{ij} (\partial C_i / \partial j)] / \partial j \right\}\tag{11}$$

If it can be assumed that the directionally oriented velocities are constant, then eq 11 can be expressed as

$$(\partial N_{ij} / \partial j) = u_j [\partial C_i / \partial j] - \left\{ \partial [\mathfrak{D}_{ij} (\partial C_i / \partial j)] / \partial j \right\}\tag{12}$$

Equation 12 can be further simplified if it can be assumed that a constant-dispersion coefficient can be used to characterize the molar flux of i in each of the three orthogonal directions. The directional flux gradients can then be expressed as follows for each of the three coordinate axes:

$$(\partial N_{ix} / \partial x) = u_x (\partial C_i / \partial x) - \mathfrak{D}_{ix} (\partial^2 C_i / \partial x^2)\tag{13}$$

$$(\partial N_{iy} / \partial y) = u_y (\partial C_i / \partial y) - \mathfrak{D}_{iy} (\partial^2 C_i / \partial y^2)\tag{14}$$

and

$$(\partial N_{iz} / \partial z) = u_z (\partial C_i / \partial z) - \mathfrak{D}_{iz} (\partial^2 C_i / \partial z^2)\tag{15}$$

Substituting the relationships given by eqs 13–15 into eq 9 gives

$$\begin{aligned}(\partial C_i / \partial t) + u_x (\partial C_i / \partial x) + u_y (\partial C_i / \partial y) + u_z (\partial C_i / \partial z) \\ = \mathfrak{D}_{ix} (\partial^2 C_i / \partial x^2) + \mathfrak{D}_{iy} (\partial^2 C_i / \partial y^2) + \mathfrak{D}_{iz} (\partial^2 C_i / \partial z^2) + R_i\end{aligned}\tag{16}$$

Equation 16 can be further simplified by assuming that the directional dispersion coefficients are equal to one another. If a uniform, nondirectional dispersion coefficient depicted by $\mathfrak{D}_L$ can be used to characterize the transport of i within the system, eq 16 can be expressed as

$$\begin{aligned}
& (\partial C_i / \partial t) + u_x (\partial C_i / \partial x) + u_y (\partial C_i / \partial y) + u_z (\partial C_i / \partial z) \\
& = \mathcal{D}_L [(\partial^2 C_i / \partial x^2) + (\partial^2 C_i / \partial y^2) + (\partial^2 C_i / \partial z^2)] + R_i
\end{aligned} \tag{17}$$

Equation 17 represents the differential mass balance for component i for a system that is devoid of an adsorbent packing. The expression was developed from a simple geometry with inherent assumptions. One can observe that the relationship is rather complex if the gradients are retained for each of the three orthogonal directions. It is often assumed that the superficial flow velocities in the non-principal flow directions can be considered as negligible relative to the primary flow direction. Taking the principle flow direction to be along the z -axis and assuming that the concentration gradients in the x - and y -directions are negligible, eq 17 simplifies to

$$(\partial C_i / \partial t) + u_z (\partial C_i / \partial z) = \mathcal{D}_L (\partial^2 C_i / \partial z^2) + R_i \tag{18}$$

Although eq 18 represents a simplified form of the differential mass balance, it is still quite formidable for many practical applications. The following section addresses the analytical development for a differential volume element having cylindrical characteristics. Many of the same assumptions that were used for the orthogonally based coordinate system are also used for the cylindrical coordinate system.

2.2 Differential Volume Element Considerations for a Cylindrical Coordinate System

Figure 2 depicts a differential volume element in a cylindrical coordinate system.

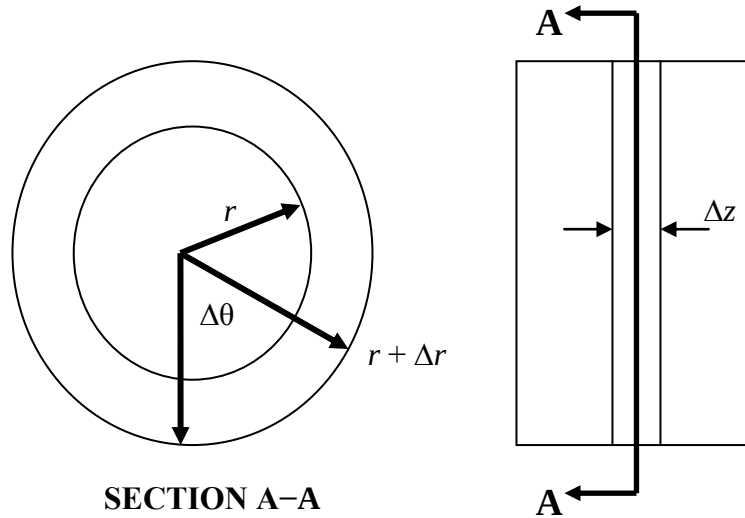


Figure 2. The coordinates associated with a cylindrical system.

The three coordinate directions of concern in a cylindrical coordinate system are the radial (r), angular (θ), and axial (z) directions. The volume of the differential element that is considered with the cylindrical coordinate system is given by

$$\Delta V_{\text{cyl}} = \Delta S \Delta z \Delta r \quad (19)$$

or

$$\Delta V_{\text{cyl}} = r \Delta \theta \Delta z \Delta r \quad (20)$$

The mass of component i within the differential volume element is given by

$$M_i = (\text{MW})_i C_i \Delta V_{\text{cyl}} \quad (21)$$

Differentiating eq 21 with respect to time gives

$$(\partial M_i / \partial t) = (\text{MW})_i \left\{ C_i [\partial(\Delta V_{\text{cyl}}) / \partial t] + \Delta V_{\text{cyl}} (\partial C_i / \partial t) \right\} \quad (22)$$

As was the case for Cartesian coordinate system development, the derivative of the differential is assumed to be negligible relative to the first-order derivative, such that

$$[\partial(\Delta V_{\text{cyl}}) / \partial t] \ll (\partial C_i / \partial t)$$

With this assumption, eq 22 is approximated as

$$(\partial M_i / \partial t) \approx (\text{MW})_i \Delta V_{\text{cyl}} (\partial C_i / \partial t) = (\text{MW})_i r \Delta \theta \Delta z \Delta r (\partial C_i / \partial t) \quad (23)$$

where the relationship given by eq 20 has been substituted for (ΔV_{cyl}) in eq 23. The net mass flows associated with each of the three directions are then considered as follows.

2.2.1 Net Rate of Mass Flow of Component i Associated with the Radial Direction

The mass flow associated with the radial direction is taken to be in the outward direction. The area associated with this flow is $(r \Delta \theta)(\Delta z)$. The cross-sectional area associated with this directional flux varies with radial position. The following expression describes the rate of mass flow of component i entering the differential volume element at position r :

$$(m_i)_r = (\text{MW})_i N_{ir}(r) [r(r) \Delta \theta \Delta z] \quad (24)$$

An expression for the rate of mass flow of component i exiting the differential volume element at position $(r + \Delta r)$ is then given by

$$(m_i)_{r+\Delta r} = (\text{MW})_i N_{ir}(r + \Delta r) [r(r + \Delta r) \Delta \theta \Delta z] \quad (25)$$

A note of clarification with respect to the nomenclature convention used in eqs 24 and 25 and throughout this review effort is emphasized here. Through the examples that follow, this nomenclature approach is demonstrated. The following nomenclature and interpretation was used throughout:

- $N_{ir}(r)$: represents the molar flux of component i in the radial direction evaluated at radial position r .
- $N_{ir}(r + \Delta r)$: represents the molar flux of component i in the radial direction evaluated at radial position $(r + \Delta r)$.
- $r(r)$: represents the radial position from a central reference evaluated at radial position r .
- $r(r + \Delta r)$: represents the radial position from a central reference evaluated at radial position $(r + \Delta r)$.
- $N_{ir}(r) r(r)$: represents the *product* of the molar flux of component i in the radial direction and the radius, both evaluated at radial position r .
- $N_{ir}(r + \Delta r) r(r + \Delta r)$: represents the *product* of the molar flux of component i in the radial direction and the radius, both evaluated at radial position $(r + \Delta r)$.

The net rate of mass flow of component i associated with the r -direction is the difference between the influent and effluent rates or the difference between eqs 24 and 25. The result is given by

$$\begin{aligned} [(m_i)_r]_{\text{net}} &= (m_i)_r - (m_i)_{r+\Delta r} \\ &= -(\text{MW})_i \Delta \theta \Delta z [r(r + \Delta r) N_{ir}(r + \Delta r) - r(r) N_{ir}(r)] \end{aligned} \quad (26)$$

2.2.2 Net Rate of Mass Flow of Component i Associated with the θ -Direction

The area associated with this angular flow is $(\Delta r \Delta z)$. The cross-sectional area associated with this directional flux is invariant with respect to the angular position. The following expression describes the rate of mass flow of component i entering the differential volume element at position θ :

$$(m_i)_\theta = (\text{MW})_i \Delta r \Delta z N_{i\theta}(\theta) \quad (27)$$

An expression for the rate of mass flow of component i exiting the differential volume element at position $(\theta + \Delta \theta)$ is then given by

$$(m_i)_{\theta+\Delta\theta} = (\text{MW})_i \Delta r \Delta z N_{i\theta}(\theta + \Delta \theta) \quad (28)$$

The net rate of mass flow of component i associated with the θ -direction is the difference between the influent and effluent rates or the difference between eqs 27 and 28. The result is given by

$$\begin{aligned} [(m_i)_\theta]_{\text{net}} &= (m_i)_\theta - (m_i)_{\theta+\Delta\theta} \\ &= -(MW)_i \Delta r \Delta z [N_{i\theta}(\theta + \Delta\theta) - N_{i\theta}(\theta)] \end{aligned} \quad (29)$$

2.2.3 Net Rate of Mass Flow of Component i Associated with the z -Direction

The area associated with the axially directed flow is $(r \Delta\theta \Delta r)$. The cross-sectional flow area associated with this directional flux does not vary in the axial direction. The following expression describes the rate of mass flow of component i entering the differential volume element at position z :

$$(m_i)_z = (MW)_i r \Delta\theta \Delta r N_{iz}(z) \quad (30)$$

An expression for the rate of mass flow of component i exiting the differential volume element at position $(z + \Delta z)$ is then given by

$$(m_i)_{z+\Delta z} = (MW)_i r \Delta\theta \Delta r N_{iz}(z + \Delta z) \quad (31)$$

The net rate of mass flow of component i associated with the z -direction is the difference between the influent and effluent rates or the difference between eqs 30 and 31. The result is given by

$$\begin{aligned} [(m_i)_z]_{\text{net}} &= (m_i)_z - (m_i)_{z+\Delta z} \\ &= -(MW)_i r \Delta\theta \Delta r [N_{iz}(z + \Delta z) - N_{iz}(z)] \end{aligned} \quad (32)$$

2.2.4 Composite Mass Balance for Component i : Cylindrical Volume Element

A generic mass balance for component i based on the cylindrical coordinate system depicted in Figure 2 for a reacting system can be expressed in an analogous manner to that for the orthogonal coordinate system. The generic mass balance is given by

$$(\partial M_i / \partial t) = \sum (m_i)_{\text{in}} - \sum (m_i)_{\text{out}} + (MW)_i R_i r \Delta\theta \Delta z \Delta r \quad (33)$$

As expressions for the directional mass flows of component i have been developed, eq 33 can be equivalently expressed through the following relationship:

$$\begin{aligned}
(\partial M_i / \partial t) &= \sum (m_i)_{\text{net}} + (MW)_i R_i r \Delta \theta \Delta z \Delta r \\
&= [(m_i)_r]_{\text{net}} + [(m_i)_\theta]_{\text{net}} + [(m_i)_z]_{\text{net}} \\
&\quad + (MW)_i R_i r \Delta \theta \Delta z \Delta r
\end{aligned} \tag{34}$$

Substituting expressions given by eqs 23, 26, 29, and 32 into the mass balance relationship given by eq 34 yields

$$\begin{aligned}
(\partial C_i / \partial t) &= -(1/r) \left\{ [r(r + \Delta r) N_{ir}(r + \Delta r) - r(r) N_{ir}(r)] / \Delta r \right\} \\
&\quad - (1/r) \left\{ [N_{i\theta}(\theta + \Delta \theta) - N_{i\theta}(\theta)] / \Delta \theta \right\} \\
&\quad - \left\{ [N_{iz}(z + \Delta z) - N_{iz}(z)] / \Delta z \right\} + R_i
\end{aligned} \tag{35}$$

In the limit as Δr , $\Delta \theta$, and Δz collapse to zero, eq 35 takes on the following form:

$$(\partial C_i / \partial t) + (1/r) [\partial(r N_{ir}) / \partial r] + (1/r) (\partial N_{i\theta} / \partial \theta) + (\partial N_{iz} / \partial z) = R_i \tag{36}$$

A useful comparison of eq 36 can be made with respect to a similarly developed relationship appearing in a standard reference text. Equation 36 is consistent with the relationship given in Table 18.2-1 (eq B) of the textbook *Transport Phenomena* (ref 1).

2.2.5 Relating Molar Flux and Directional Flux Gradients to Concentration and Diffusivity Parameters

The molar flux and directional flux gradients have forms consistent with the expressions given by eq 11. These relationships expressed in terms of a cylindrical coordinate system are as follows:

$$[\partial(r N_{ir}) / \partial r] = [\partial(r u_r C_i) / \partial r] - \mathfrak{D}_{ir} \left\{ \partial[r (\partial C_i / \partial r)] / \partial r \right\} \tag{37}$$

$$(1/r) (\partial N_{i\theta} / \partial \theta) = (1/r) [\partial(u_\theta C_i) / \partial \theta] - \mathfrak{D}_{i\theta} [(1/r^2) (\partial^2 C_i / \partial \theta^2)] \tag{38}$$

and

$$(\partial N_{iz} / \partial z) = [\partial(u_z C_i) / \partial z] - \mathfrak{D}_{iz} (\partial^2 C_i / \partial z^2) \tag{39}$$

The relationship for the angular flux gradient (eq 38) is addressed more fully in Appendix A. With the flux gradient relationships given by eqs 37, 38, and 39, it has been assumed that the directional dispersion coefficients are constant-valued.

Substitution of the relationships given by eqs 37, 38, and 39 into eq 36 yields the following expression:

$$\begin{aligned}
& (\partial C_i / \partial t) + [\partial(r u_r C_i) / \partial r] + (1/r) [\partial(u_\theta C_i) / \partial \theta] + [\partial(u_z C_i) / \partial z] \\
& = R_i + \mathfrak{D}_{ir} \left\{ \partial[r (\partial C_i / \partial r)] / \partial r \right\} + \mathfrak{D}_{i\theta} [(1/r^2) (\partial^2 C_i / \partial \theta^2)] + \mathfrak{D}_{iz} (\partial^2 C_i / \partial z^2)
\end{aligned} \tag{40}$$

If the directional dispersion coefficients are assumed to be equal to one another, such that

$$\mathfrak{D}_{ir} = \mathfrak{D}_{i\theta} = \mathfrak{D}_{iz} = \mathfrak{D}_L$$

then eq 40 simplifies to

$$\begin{aligned}
& (\partial C_i / \partial t) + [\partial(r u_r C_i) / \partial r] + (1/r) [\partial(u_\theta C_i) / \partial \theta] + [\partial(u_z C_i) / \partial z] \\
& = R_i + \mathfrak{D}_L \left\{ \left\{ \partial[r (\partial C_i / \partial r)] / \partial r \right\} + [(1/r^2) (\partial^2 C_i / \partial \theta^2)] + (\partial^2 C_i / \partial z^2) \right\}
\end{aligned} \tag{41}$$

The full expansion of eq 41 gives the following relationship:

$$\begin{aligned}
& (\partial C_i / \partial t) + u_r (\partial C_i / \partial r) + (u_\theta / r) (\partial C_i / \partial \theta) + u_z (\partial C_i / \partial z) \\
& + C_i [(u_r / r) + (\partial u_r / \partial r) + (1/r) (\partial u_\theta / \partial \theta) + (\partial u_z / \partial z)] \\
& = R_i + (\mathfrak{D}_L / r) (\partial C_i / \partial r) + \mathfrak{D}_L [(\partial^2 C_i / \partial r^2) + (1/r^2) (\partial^2 C_i / \partial \theta^2) + (\partial^2 C_i / \partial z^2)]
\end{aligned} \tag{42}$$

With the assumption of a constant mass density, continuity requires that the following relationship holds (see Appendix B for development) relative to a fixed spatial reference frame:

$$(u_r / r) + (\partial u_r / \partial r) + (1/r) (\partial u_\theta / \partial \theta) + (\partial u_z / \partial z) = 0 \tag{43}$$

With the relationship given by eq 43, eq 42 simplifies to

$$\begin{aligned}
& (\partial C_i / \partial t) + u_r (\partial C_i / \partial r) + (u_\theta / r) (\partial C_i / \partial \theta) + u_z (\partial C_i / \partial z) \\
& = R_i + (\mathfrak{D}_L / r) (\partial C_i / \partial r) + \mathfrak{D}_L [(\partial^2 C_i / \partial r^2) + (1/r^2) (\partial^2 C_i / \partial \theta^2) + (\partial^2 C_i / \partial z^2)]
\end{aligned} \tag{44}$$

Recognizing that the following relationship holds:

$$\begin{aligned}
& (\mathfrak{D}_L / r) \left\{ \partial[r (\partial C_i / \partial r)] / \partial r \right\} = (\mathfrak{D}_L / r) [r (\partial^2 C_i / \partial r^2) + (\partial C_i / \partial r)] \\
& = \mathfrak{D}_L (\partial^2 C_i / \partial r^2) + (\mathfrak{D}_L / r) (\partial C_i / \partial r)
\end{aligned} \tag{45}$$

Equation 44 can be rewritten as

$$\begin{aligned}
& (\partial C_i / \partial t) + u_r (\partial C_i / \partial r) + (u_\theta / r) (\partial C_i / \partial \theta) + u_z (\partial C_i / \partial z) \\
& = R_i + \mathcal{D}_L \left\{ \left\{ (1/r) \left\{ \partial [r (\partial C_i / \partial r)] / \partial r \right\} \right\} + (1/r^2) (\partial^2 C_i / \partial \theta^2) + (\partial^2 C_i / \partial z^2) \right\}
\end{aligned} \tag{46}$$

On a term-by-term basis, eq 46 is consistent with eq (B) in Table 18.2-2 (page 559) of *Transport Phenomena* (ref 1). The analytical complexity of eq 46 is readily apparent. The relationship was developed with the following assumptions:

- the directional dispersion coefficients are constant-valued and equal to one another,
- the overall mass density of the system is constant, and
- the reference frame of the differential volume element is spatially fixed with respect to its coordinate axes.

2.3 Closing Commentary

The analysis conducted on the differential volume elements in the Cartesian and cylindrical coordinate systems was performed to demonstrate the analytical complexity that arises when one considers the directional fluxes associated with each coordinate system. The preceding analyses were also simplified in that the volume elements were devoid of adsorbent packing. With an adsorbent packing, considerations relating to the void fraction and bulk density would have to be incorporated into the analytical expressions. The reaction rate terms appearing in the relationships would also have to be considered in a rigorous analytical analysis of the mass balance expressions. Depending on the mechanistic details associated with the chemical reactionary process, these rate expressions would add analytical complexity to the relationships.

A goal of the preceding discussion was to provide justification and rationalization for using analytical expressions based on gradients in a singular direction. For fixed cross-sectional area geometries in which an orthogonal coordinate system may be appropriate, the principle directional gradient would be in the direction of primary flow consistent with an orthogonally oriented axis. The gradients and velocities associated with the non-principle flow axes are often assumed to be negligible relative to the primary flow axis. Taking z to be the primary flow axis with a Cartesian coordinate system, eq 18 would typically be used:

$$(\partial C_i / \partial t) + u_z (\partial C_i / \partial z) = \mathcal{D}_L (\partial^2 C_i / \partial z^2) + R_i \tag{18}$$

The relationship given by eq 18 would also apply to a cylindrical coordinate system in which the cross-sectional flow area normal to the principle flow direction was constant (i.e., axial flow).

Through similar reasoning with a radial flow system in a cylindrical coordinate system, gradients and velocities in the angular and axial directions are often

considered to be negligible relative to the gradients and velocity associated with the primary or radially directed flow. Assuming that the directional gradients associated with the angular and axial directions are negligible relative to the gradients in the radial direction, eq 46 simplifies to

$$(\partial C_i / \partial t) + u_r (\partial C_i / \partial r) = R_i + (D_L / r) \{ \partial [r (\partial C_i / \partial r)] / \partial r \} \quad (47)$$

Despite these simplifying assumptions, eq 47 retains significant analytical complexity. A further simplification to eq 47 can be made if the dispersive effects associated with the flow of i can be neglected. In that case, $D_L = 0$, and eq 47 becomes

$$(\partial C_i / \partial t) + u_r (\partial C_i / \partial r) = R_i \quad (48)$$

3. CONSIDERATIONS ON THE PARAMETERS USED IN ADSORBENT-BASED FILTRATION SYSTEMS

3.1 Void Fraction

The void fraction, depicted by ϵ , is simply the ratio of the void volume to the total volume of an adsorbent packing. The total volume is comprised of the bulk material volume of the adsorbent as well as the interstitial volume about the individual bulk particles. The void fraction does not include the intraparticle volume associated with the pore structure within the individual granular particles. The intraparticle volumes associated with the porous networked structure contribute significantly to the characteristics of carbon-based adsorption; however, the void fraction is more of a bulk-packing characteristic. Some useful relationships associated with the void fraction are:

$$\begin{aligned} \epsilon &= \text{void volume/total volume} \\ &= V_{\text{void}} / V_{\text{total}} \\ &= V_{\text{void}} / (V_{\text{ads}} + V_{\text{void}}) \end{aligned} \quad (49)$$

Other groupings involving the void fraction that factor into subsequent analytical developments are

$$(V_{\text{ads}} / V_{\text{tot}}) = 1 - \epsilon \quad (50)$$

and

$$(V_{\text{ads}} / V_{\text{void}}) = (1 - \epsilon) / \epsilon \quad (51)$$

3.2 Dense Packing of Ideal Spheres

A void fraction of 0.39 is typically assumed for the adsorbent loadings of 12×30 granular activated carbon. For very high-efficiency, vapor-phase contaminant reductions, dense packing of the adsorbent is required.

Three typical lattice arrangements are often used to model atomic and molecular structures. These include the body-centered-cubic (BCC), the hexagonal-close-packed (HCP), and the face-centered-cubic (FCC) arrangements. Of the three, the HCP and FCC arrangements provide a more dense packing than the BCC arrangement. The HCP arrangement can be likened to an ABAB... sequential layering of ideal spheres, whereas the FCC arrangement can be likened to an ABCABC... sequential layering of ideal spheres, in which additional layerings are placed in the interstitial depressions created by the preceding coplanar layering of spheres.

In the following analysis, it was assumed that the carbon particles were comprised of ideal, uniform spheres, packed in an FCC arrangement.

3.2.1 Unit Cell Considerations

Figure 3 provides a description of the lattice sites that were considered in this analysis.

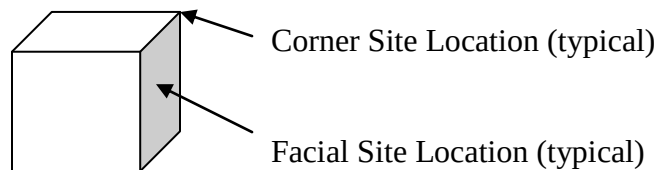


Figure 3. Lattice site depictions of an FCC unit cell.

The solids volume associated with a singular unit cell of an ideal FCC lattice arrangement (depicted in Figure 3) is determined as follows:

$$\begin{aligned} \text{Corner spheres:} \quad & (8 \text{ corners/unit cell}) \times [(1/8 \text{ sphere})/\text{corner}] \\ & = 1 \text{ sphere/unit cell} \end{aligned}$$

$$\begin{aligned} \text{Facial spheres:} \quad & (6 \text{ faces/unit cell}) \times [(1/2 \text{ sphere})/\text{face}] \\ & = 3 \text{ spheres/unit cell} \end{aligned}$$

The net number of spheres associated with the corner sites of an FCC unit cell is 1, and the net number of spheres associated with the facial planes of an FCC unit

cell is 3. Therefore, a total of four spheres are associated with the unit cell of an ideal FCC lattice arrangement:

Number of spheres associated with FCC unit cell = 4

The solids volume associated with a unit cell is therefore 4× the volume of a singular sphere, or

$$V_{\text{solids}} = 4 \times (4/3) \pi r^3 = (16/3) \pi (d/2)^3 = (2/3) \pi d^3 \quad (52)$$

The volume of an FCC unit cell is determined through consideration of a face plane. A representative face plane is depicted in Figure 4.

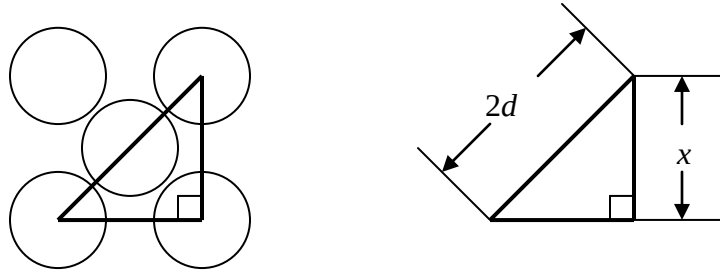


Figure 4. Representative face plane of an FCC unit cell arrangement.

The spheres located along the diagonals of Figure 4 are in direct contact in an FCC unit cell arrangement. These diagonal spheres form the hypotenuse of a right triangle formed by the sides of unit cell. With this direct contact, the hypotenuse of the right triangle formed has a length of $2d$. The sides of the FCC unit cell have the dimension given by x , which can be solved in terms of the sphere diameter to yield

$$x = 2^{1/2} d$$

The total volume of the FCC unit cell can be expressed in terms of the diameter of the sphere, yielding

$$V_{\text{fcc unit cell}} = x^3 = 2^{3/2} d^3 \quad (53)$$

3.2.2 Void Fraction Considerations

In this section, the definition of a void fraction (ϵ) is used in conjunction with the relationships developed for the FCC unit cell arrangement. The void fraction, as used in adsorbent packings, was provided by eq 49, and can be expressed as

$$\epsilon = \text{void volume/total volume}$$

Because the summation of the void and solids volume constitutes the total volume of the unit cell, the void volume can be expressed as

$$V_{\text{void volume}} = V_{\text{total volume}} - V_{\text{solids volume}} \quad (54)$$

Substituting the relationship given by eq 54 into eq 49 gives the following expressions:

$$\begin{aligned} \varepsilon &= (V_{\text{total volume}} - V_{\text{solids volume}}) / V_{\text{total volume}} \\ &= 1 - [(V_{\text{solids volume}}) / (V_{\text{total volume}})] \end{aligned} \quad (55)$$

With the volume of the solids given by eq 52 and the total volume of the FCC unit cell given by eq 53, these relationships can be substituted into eq 55, which yields the following:

$$\begin{aligned} \varepsilon &= 1 - \{[(2/3) \pi d^3] / (2^{3/2} d^3)\} \\ &= 1 - (2^{-1/2} 3^{-1} \pi) = 1 - [\pi / (3 2^{1/2})] \\ &= 0.2595 \end{aligned}$$

3.2.3 Ideal FCC Void Fraction Considerations

The following observations are made with respect to this modeling consideration:

- a. Assuming an ideal spherical geometry for the lattice locations of the FCC unit cell, the void fraction is independent of the diameter of the sphere.
- b. The FCC packing is assumed to be ideal and represents a most efficient packing arrangement of ideal homogeneous spheres.
- c. The 0.2595 void fraction for this idealized case compares favorably to the 0.39 void fraction, which is used in the analytical predictions for 12 × 30 mesh carbon granules.

3.2.4 Geometric Parameter (**a**)

The estimation of a mass transfer zone (MTZ) thickness per the Gamson, Hougen, and Thodos correlation (ref 2) contains the parameter **a**. The Dole and Klotz article (ref 3) indicates that **a** is the “superficial surface of the granule (ignoring pore structure) per unit volume of bed”. Similarly, in Perry’s *Chemical Engineering Handbook* (ref 4; pages 16–19), a similar parameter, **a_p**, is given, where **a_p** is the “outer surface area of particles per unit volume of contacting system (solid plus fluid), equal to 6 (1 – ε)/d_p.” The analysis that follows continues with the ideal packing of homogeneous spheres in a close-packed FCC lattice arrangement.

The following relationship can be obtained from eq 55:

$$V_{\text{total volume}} = [1 / (1 - \epsilon)] V_{\text{solids volume}} \quad (56)$$

The surface area of the ideal, uniform spheres within an FCC unit cell arrangement is determined as

$$(4 \text{ spheres/unit cell}) \times (4 \pi r^2/\text{sphere}) = 16 \pi r^2 = 16 \pi (d/2)^2$$

$$\text{or} \quad (57)$$

$$A_{\text{solids}} = 4 \pi d^2/\text{unit cell}$$

The volume of the solids in an FCC lattice arrangement was previously determined and is given by eq 52 as

$$V_{\text{solids}} = (2/3) \pi d^3/\text{unit cell}$$

Substituting eq 52 into eq 56 yields the following relationship:

$$V_{\text{total volume}} = [1 / (1 - \epsilon)] \{ (2/3) \pi d^3/\text{unit cell} \} \quad (58)$$

The expressions given by eqs 57 and 58 are then substituted into the definition of parameter **a** (or **a_p**) as given in the Klotz reference and the Perry and Chilton's *Chemical Engineers' Handbook*, to yield the following series of relationships:

$$\begin{aligned} \mathbf{a} = \mathbf{a}_p &= A_{\text{solids}}/V_{\text{total volume}} \\ &= \{ 4 \pi d^2/\text{unit cell} \} / \{ [1 / (1 - \epsilon)] \{ (2/3) \pi d^3/\text{unit cell} \} \} \\ &= [4 \times 3 (1 - \epsilon)] / (2 d) = 6 (1 - \epsilon)/d \end{aligned} \quad (59)$$

Equation 59 is the targeted relationship.

3.3 Bulk Density Considerations

There is a need to differentiate between the density of the adsorbent and the bulk density of the adsorbent packing. The two are related through the void fraction. The intent of this section is to detail the specific analytical relationship.

The density of the adsorbent is simply the mass of the adsorbent granules divided by the volume that the particles would displace exclusive of the void volume. Because the adsorbent-loading parameters (which are described in the following sections) are based on the amount of the adsorbent, packing considerations must be considered.

Activated carbon adsorbents are comprised of a heterogeneous mixture of irregularly shaped particles. Each of these particles in turn has an intraparticle network of pores. As used in the following development, the adsorbent density is taken to be the mass of the individual particle divided by the apparent volume of the individual particle. This “apparent” density, as used here, does not take into account the intraparticle volume associated with the porous framework that exists within the individual coarse particles. With this understanding, an apparent adsorbent density can be expressed through the relationship

$$\begin{aligned}\rho_{\text{ads}} &= \text{mass of adsorbent/volume of adsorbent} \\ &= M_{\text{ads}}/V_{\text{ads}}\end{aligned}\tag{60}$$

The bulk density of the adsorbent represents the volume occupied by the adsorbent as well as the void volume associated with the packing arrangement. It can be described through the relationship

$$\begin{aligned}\rho_b &= \text{mass of adsorbent/total volume} \\ &= M_{\text{ads}}/V_{\text{tot}}\end{aligned}\tag{61}$$

Equating the total mass of adsorbent in eqs 60 and 61 yields

$$(\rho_b/\rho_{\text{ads}}) = V_{\text{ads}}/V_{\text{tot}}\tag{62}$$

From eq 50, the ratio of the adsorbent volume to the total volume goes as $(1 - \epsilon)$. Substituting the relationship given by eq 50 into eq 62 then yields

$$\rho_b = (1 - \epsilon) \rho_{\text{ads}}\tag{63}$$

3.4 Equilibrium Adsorbate Loading Parameters

Adsorbate loading parameters are often specified on a per-volume or per-mass basis. The two are related through bulk property characteristics through the following development.

The adsorbate loading on an adsorbent volume basis can be expressed by

$$\begin{aligned}q_i &= \text{mass of adsorbate/volume of adsorbent} \\ &= M_i/V_{\text{ads}}\end{aligned}\tag{64}$$

The adsorbate loading on an adsorbent mass basis can be expressed as

$$\begin{aligned}W_i &= \text{mass of adsorbate/mass of adsorbent} \\ &= M_i/M_{\text{ads}}\end{aligned}\tag{65}$$

Dividing eq 64 by eq 65 gives the following relationship:

$$q_i/W_i = M_{\text{ads}}/V_{\text{ads}} = \rho_{\text{ads}} \quad (66)$$

Substituting the relationship given by eq 63 into eq 66 yields

$$q_i/W_i = \rho_b/(1 - \epsilon)$$

$$\text{or} \quad (67)$$

$$W_i = q_i [(1 - \epsilon)/\rho_b]$$

Differentiating eq 67 with respect to time gives

$$(\partial W_i/\partial t) = \partial \{ q_i [(1 - \epsilon)/\rho_b] \} / \partial t \quad (68)$$

If the void fraction and the bulk density are taken to be invariant, then eq 68 simplifies to

$$(\partial W_i/\partial t) = [(1 - \epsilon)/\rho_b] (\partial q_i/\partial t) \quad (69)$$

3.5 Uniformity of Adsorption Wave Contour for Strongly Adsorbed Materials

Figure 5 depicts the contours of an advancing adsorption wavefront with the progression of time along the length of an adsorbent bed for a strongly adsorbed material. The contours represent snapshots in time of the advancing wavefront where the elapsed time $t_1 < t_2 < t_3 < t_4$. The position L_T represents the length (or depth) of the adsorbent bed.

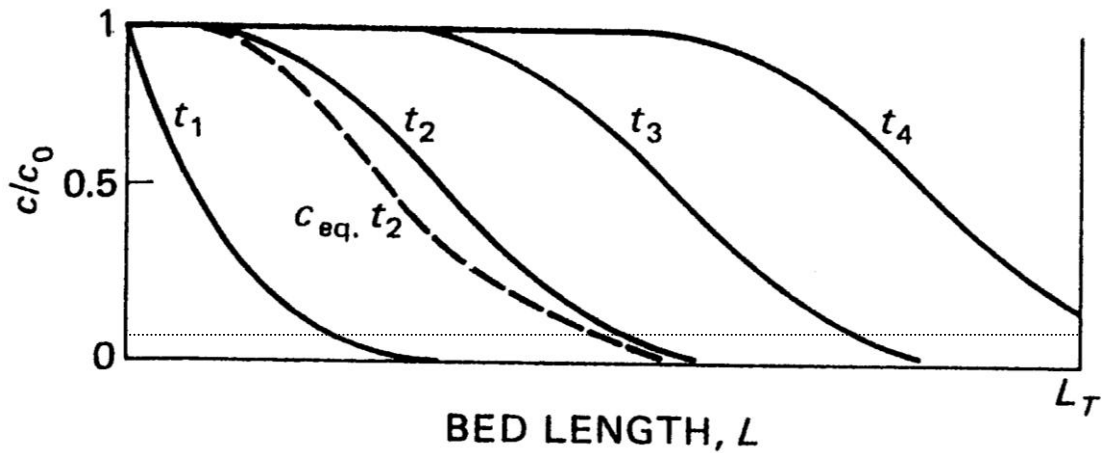


Figure 5. Depiction of advancing adsorption wavefront with time for a strongly adsorbed compound (from ref 5).

The adsorption wave contour depicted by t_1 is observed to differ from those depicted by t_2 , t_3 , and t_4 . This is because the adsorption wave has not had sufficient time and duration within the column to fully develop. The contours depicted by t_2 , t_3 , and t_4 are more uniform and consistent with respect to one another. These contours reflect a more fully developed and propagating wavefront.

A hypothetical breakthrough concentration is depicted as the dashed line just above the concentration ratio $C/C_o = 0$. The thickness of the MTZ encompasses that region of the bed length where the concentration ratio C/C_o departs from a value of 1.0 and extends to the dashed line of the breakthrough concentration ratio along a fixed time contour. As depicted in the Figure 5 plot, a breakthrough concentration would have been reached between the elapsed time periods of t_3 and t_4 . As time extends beyond t_4 , the adsorbent bed will eventually reach a state of full saturation as its residual adsorptive capacity diminishes with time.

There are three regions of note in the Figure 5 plot. These include the region in which a state of saturation has been achieved on the adsorbent, the region in which active mass transfer is occurring, and the region beyond the MTZ that retains full residual adsorptive capacity. The saturated region of the advancing adsorption wavefront is depicted by the relatively flat region of the contour extending along the length of the column where the concentration ratio $C/C_o = 1$. This region of the adsorbent has reached its maximum adsorption loading capacity (equilibrium limit) and can no longer effect any reductions in the vapor phase concentration. The second or active MTZ region is characterized by the downward-sloping portions of the time contours. The width of the time contours along the length axis correlates to the thickness of the MTZ that is bounded by the relative concentration ratios established by $C/C_o < 1$ and $C_b/C_o = 1$. This is the region in which there is an active transfer of adsorbate from the vapor phase to a condensed or adsorbed phase. The region to the right of the MTZ represents the segment of the adsorbent bed thickness that retains residual adsorption capacity provided that a concentration breakthrough condition has not been reached.

In the following analytical development, it is assumed that there is a singular MTZ thickness that fully characterizes the propagation of the adsorption wavefront as it traverses the thickness of the bed. This assumption is taken to apply to adsorbent beds of a constant cross-sectional flow area as well as for cylindrical systems with a positionally dependent cross-sectional flow area. This notion of a constant MTZ thickness as the adsorbent bed is traversed represents an idealized conceptualization. It further assumes that sufficient bed depth is available in which a uniform adsorption wavefront can fully develop.

4. DEVELOPMENT OF A COMPONENT MASS BALANCE FOR A REACTING SYSTEM IN A RADIAL FLOW SYSTEM

In Section 2, it was demonstrated that analytical complexity arises upon retention of the flow characterizations associated with each directional flow with commonly encountered geometries. In Section 3, a foundation was provided for the parameters often encountered in an adsorbent-based filtration system. In Section 4, a differential mass balance is developed for a reacting system with radially directed flow in a cylindrical coordinate system. This development builds upon the approaches established earlier and incorporates the parameters associated with an adsorbent fill. Figure 6 depicts the system that was considered in this development.

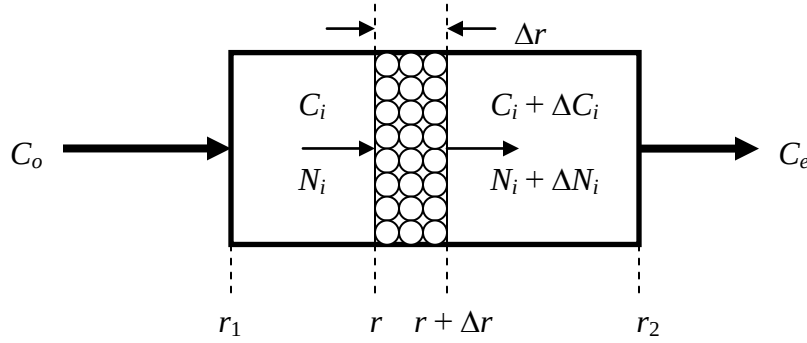


Figure 6. Radial flow adsorbent system.

Referring to Figure 6, the bed depth of the radial flow filter is $(r_2 - r_1)$, and a challenge concentration of species i (C_o) is introduced into the filter at radial position r_1 . An effluent concentration of species i (C_e) exits the filter at radial position r_2 . It is assumed that species i is consumed within the filter at a molar rate depicted by R_i , where R_i is defined on a per-volume basis.

The height of the cylinder taken along the axial coordinate is h . The cross-sectional area associated with the principle flux direction is therefore $A = 2\pi r h$.

The volume of the differential element depicted in Figure 6 is given as

$$\begin{aligned}\Delta V_{\text{cyl}} &= (\Delta S) (\Delta z) (\Delta r) \\ &= (r \Delta \theta) (\Delta z) (\Delta r)\end{aligned}\tag{70}$$

In accordance with the arguments presented in Section 2.3, it is assumed that the flows associated with the angular (θ) and axial (z) directions are negligible relative to the radially directed flow, which is taken to be the principle flow direction. Given this premise, the volume of the differential element depicted in Figure 6 and expressed by eq 70 can be expressed by

$$\Delta V_{\text{cyl}} = (2\pi r h) \Delta r$$

or

$$\Delta V_{\text{cyl}} = A \Delta r$$

(71)

4.1 Rate of Mass Flow of Species i Entering the Differential Volume Element at Radial Position r

An analytical relationship for the rate of mass flow of species i entering the differential volume element will be developed in terms of a mass flux. The analytical expression is

$$(m_i)_{\text{in}} = (\text{MW})_i [N_i(r) A(r)]_{\text{adsorbent}} \quad (72)$$

The mass flux given by eq 72 represents a total or effective flux that exists within the adsorbent packing. The area that appears in eq 72 is more appropriately associated with the area through which species i is transferred within the vapor phase through the packing in the radial direction. As such, this area represents a restricted area due to the presence of the solid adsorbent packing. The appropriate area expression in eq 72 should be the restricted area. With this notion, eq 72 is more appropriately expressed as

$$\begin{aligned} (m_i)_{\text{in}} &= (\text{MW})_i (N_i A)_{\text{adsorbent}} = (\text{MW})_i N_i(r) \varepsilon A(r) \\ &= (\text{MW})_i \varepsilon N_i(r) A(r) \end{aligned} \quad (73)$$

4.2 Rate of Mass Flow of Species i Exiting the Differential Volume Element at Radial Position $r + \Delta r$

By analogy, with the development of eq 73, the rate of mass flow of species i which exits the differential volume element at radial position $(r + \Delta r)$ can be expressed as

$$(m_i)_{\text{out}} = (\text{MW})_i [N_i(r + \Delta r) A(r + \Delta r)]_{\text{adsorbent}} \quad (74)$$

Adjusting the area to account for the packing of adsorbent, eq 74 takes on the following forms:

$$\begin{aligned} (m_i)_{\text{out}} &= (\text{MW})_i [N_i(r + \Delta r) \varepsilon A(r + \Delta r)] \\ &= (\text{MW})_i \varepsilon [N_i(r + \Delta r) A(r + \Delta r)] \end{aligned} \quad (75)$$

4.3 Mass of Species i within the Differential Volume Element

The mass of species i within the differential volume element is comprised of the mass in the adsorbed state and the vapor phase. An analytical expression that characterizes the mass of species i within the differential volume element is developed through the following relationships:

$$\begin{aligned}
 M_i &= (M_i)_{\text{adsorbed phase}} + (M_i)_{\text{vapor phase}} \\
 &= V_{\text{tot}} (V_{\text{ads}}/V_{\text{tot}}) q_i + [(M_i)_{\text{vap}}/V_{\text{void}}] V_{\text{void}} \\
 &= [A(r) \Delta r] (1 - \epsilon) q_i + (\text{MW})_i C_i (\epsilon V_{\text{tot}}) \\
 &= [A(r) \Delta r] (1 - \epsilon) q_i + (\text{MW})_i C_i \epsilon [A(r) \Delta r]
 \end{aligned} \tag{76}$$

The molar concentration of species i in the vapor phase is based on the void or interstitial volume within the adsorbent packing.

4.4 Rate of Change of Mass of Species i within the Differential Volume Element

An expression relating the rate of change in mass of species i within the differential volume element can be obtained by differentiating eq 76 with respect to time. This differentiation is accomplished as follows:

$$\begin{aligned}
 (\partial M_i / \partial t) &= \partial [A \Delta r (1 - \epsilon) q_i] / \partial t + \partial [(\text{MW})_i C_i \epsilon A \Delta r] / \partial t \\
 &= (1 - \epsilon) \Delta r [\partial (A q_i) / \partial t] + (\text{MW})_i \epsilon \Delta r [\partial (A C_i) / \partial t]
 \end{aligned} \tag{77}$$

The relationship given by eq 77 was obtained by assuming that the void fraction is constant and the derivatives of the differentials are negligibly small relative to the first-order derivatives. Expanding the derivatives in eq 77 yields the following equivalent form of the expression:

$$\begin{aligned}
 (\partial M_i / \partial t) &= (1 - \epsilon) \Delta r [A (\partial q_i / \partial t) + q_i (\partial A / \partial t)] \\
 &\quad + (\text{MW})_i \epsilon \Delta r [A (\partial C_i / \partial t) + C_i (\partial A / \partial t)]
 \end{aligned} \tag{78}$$

4.5 Rate of Consumption of Species i Due to a Chemical Reaction on the Adsorbent Surface

A generic reaction rate term is used to describe the rate of disappearance of species i on the adsorbent surface. This reaction rate term is based on a per-volume basis and is a function of several variables. A suggested form of the rate of reaction relationship is given by eq 79 as

$$(m_i)_{\text{rxn}} = (\text{MW})_i R_i (A \Delta r) \quad (79)$$

4.6 Analytical Mass Balance Development for Species i

The component mass balance expression can be expressed as

$$(\partial M_i / \partial t) = (m_i)_{\text{in}} - (m_i)_{\text{out}} - (m_i)_{\text{rxn}} \quad (80)$$

Equation 80 is a relationship relating the accumulation of mass of species i within the differential volume element to the mass input, the mass output, and a mass consumption term. The dynamic loading and desorption of species i to and from the surface of the adsorbent, respectively, are addressed through the surface-loading term appearing in eq 78.

Substitution of eqs 73, 75, 78, and 79 into eq 80 yields the following relationship:

$$\begin{aligned} (1 - \epsilon) \Delta r [A (\partial q_i / \partial t) + q_i (\partial A / \partial t)] + (\text{MW})_i \epsilon \Delta r [A (\partial C_i / \partial t) + C_i (\partial A / \partial t)] \\ = (\text{MW})_i \epsilon N_i(r) A(r) - (\text{MW})_i \epsilon [N_i(r + \Delta r) A(r + \Delta r)] - (\text{MW})_i R_i (A \Delta r) \end{aligned} \quad (81)$$

Division of eq 81 by $[(\text{MW})_i \epsilon \Delta r]$ yields

$$\begin{aligned} [1/(\text{MW})_i] [(1 - \epsilon)/\epsilon] [A (\partial q_i / \partial t) + q_i (\partial A / \partial t)] + [A (\partial C_i / \partial t) + C_i (\partial A / \partial t)] \\ = - \left\{ \{ [N_i(r + \Delta r) A(r + \Delta r)] - N_i(r) A(r) \} / \Delta r \right\} - (R_i / \epsilon) A(r) \end{aligned} \quad (82)$$

In the limit as Δr collapses to zero, eq 82 takes on the form

$$\begin{aligned} [1/(\text{MW})_i] [(1 - \epsilon)/\epsilon] [A (\partial q_i / \partial t) + q_i (\partial A / \partial t)] + [A (\partial C_i / \partial t) + C_i (\partial A / \partial t)] \\ = - [\partial (N_i A) / \partial r] - (R_i / \epsilon) A(r) \end{aligned} \quad (83)$$

Noting the following relationships for a cylinder with a constant height h ,

$$A = 2\pi h r$$

$$(\partial A / \partial t) = 2\pi h (\partial r / \partial t)$$

and

$$[\partial (N_i A) / \partial r] = 2\pi h [N_i + r (\partial N_i / \partial r)]$$

Equation 83 can therefore be expressed in the following equivalent form:

$$\begin{aligned}
& [1/(MW)_i] [(1 - \epsilon)/\epsilon] [r (\partial q_i/\partial t) + q_i (\partial r/\partial t)] + [r (\partial C_i/\partial t) + C_i (\partial r/\partial t)] \\
& = -N_i - r (\partial N_i/\partial r) - r (R_i/\epsilon)
\end{aligned} \tag{84}$$

or

$$[1/(MW)_i] [(1 - \epsilon)/\epsilon] [\partial(r q_i)/\partial t] + [\partial(r C_i)/\partial t] + [\partial(r N_i)/\partial r] + r (R_i/\epsilon) = 0 \tag{85}$$

4.7 Comparison of Equation 85 to Reference Relationship

It is instructive at this point to compare eq 85 to a reference relationship that is provided in a modern text on the analytical aspects associated with adsorption processes. Such a reference expression is provided by eq 7.5 in the text *Principles of Adsorption and Adsorption Processes* by D. M. Ruthven (ref 6). This equation served as a comparative reference for many of the analytical developments contained in this review effort. The Ruthven relationship (ref 6) is consistent with the following relationship:

$$-\mathfrak{D}_L (\partial^2 C_i/\partial z^2) + [\partial(v C_i)/\partial z] + (\partial C_i/\partial t) + [1/(MW)_i] [(1 - \epsilon)/\epsilon] (\partial q_i/\partial t) = 0 \tag{86}$$

The Ruthven expression is based on plug flow in a singular direction, which is characterized by a uniform dispersion coefficient $\mathfrak{D}_L$. The relationship is further based on a nonreacting system having a constant cross-sectional flow area.

For a constant cross-sectional area, the r terms within eq 85 can be considered as constants and can therefore be removed from the derivative terms. The r variables in eq 85 would essentially divide out, leaving the following relationship:

$$[1/(MW)_i] [(1 - \epsilon)/\epsilon] (\partial q_i/\partial t) + (\partial C_i/\partial t) + (\partial N_i/\partial r) + (R_i/\epsilon) = 0 \tag{87}$$

In a nonreacting system, $R_i = 0$, and eq 87 becomes

$$[1/(MW)_i] [(1 - \epsilon)/\epsilon] (\partial q_i/\partial t) + (\partial C_i/\partial t) + (\partial N_i/\partial r) = 0 \tag{88}$$

The molar flux gradient $(\partial N_i/\partial r)$ is replaced with $(\partial N_i/\partial z)$ because an axial system with a constant cross-sectional area is being considered. Equation 88 therefore becomes

$$[1/(MW)_i] [(1 - \epsilon)/\epsilon] (\partial q_i/\partial t) + (\partial C_i/\partial t) + (\partial N_i/\partial z) = 0 \tag{89}$$

The relationship represented by eq 89 corresponds to an axial flow equivalent to eq 85 for a nonreactive system having a constant cross-sectional area.

The total flux with respect to the axial direction is based on eq 10. For the particular system under consideration, the following relationship applies:

$$N_{iz} = v_z C_i - \mathfrak{D}_{iz} (\partial C_i / \partial z) \quad (90)$$

Assuming that a homogeneous coefficient ($\mathfrak{D}_L$) can be used, and removing the directional subscript from the molar flux, eq 90 can be re-expressed as

$$N_i = v_z C_i - \mathfrak{D}_L (\partial C_i / \partial z) \quad (91)$$

Differentiating eq 91 with respect to z and assuming that the dispersion coefficient is constant-valued yields

$$(\partial N_i / \partial z) = [\partial (v_z C_i) / \partial z] - \mathfrak{D}_L (\partial^2 C_i / \partial z^2) \quad (92)$$

Substituting the expression given by eq 92 into eq 89 yields

$$-\mathfrak{D}_L (\partial^2 C_i / \partial z^2) + [\partial (v_z C_i) / \partial z] + (\partial C_i / \partial t) + [1 / (\text{MW})_i] [(1 - \mathfrak{E}) / \mathfrak{E}] (\partial q_i / \partial t) = 0 \quad (93)$$

Equation 93 is the Ruthven relationship as given by eq 86.

4.8 Molar Flux Term of Equation 85

This term can be expanded through the generic flux relationship given by eq 10. From eq 10, the following expression applies for the radially directed molar flux:

$$N_i = v_r C_i - \mathfrak{D}_L (\partial C_i / \partial r) \quad (94)$$

Using the molar flux relationship given by eq 94, the following partial derivative is obtained:

$$\begin{aligned} [\partial (r N_i) / \partial r] &= v_r C_i + r v_r (\partial C_i / \partial r) + r C_i (\partial v_r / \partial r) \\ &\quad - r \mathfrak{D}_L (\partial^2 C_i / \partial r^2) - \mathfrak{D}_L (\partial C_i / \partial r) \end{aligned} \quad (95)$$

The relationship given by eq 95 can be substituted into eq 85, which would yield a rather complex expression.

4.9 Basis of the Adsorbent Loading

It is often useful to express the adsorbent loading term on a mass basis such as W_i . This is done because gravimetric methods are often more precise than volumetric-based determinations. The relationship between the loading terms q_i and W_i was developed in eq 67. Using eq 67 as a basis, the following relationship can be written:

$$r q_i = [\rho_b / (1 - \mathfrak{E})] (r W_i) \quad (96)$$

Assuming that the bulk density and the void fraction are constant, eq 96 is differentiated with respect to time to

$$[\partial(r q_i)/\partial t] = [\rho_b / (1 - \epsilon)] [\partial(r W_i)/\partial t] \quad (97)$$

Substituting the relationship given by eq 97 into eq 85 yields

$$[1/(MW)_i] (\rho_b/\epsilon) [\partial(r W_i)/\partial t] + [\partial(r C_i)/\partial t] + [\partial(r N_i)/\partial r] + r (R_i/\epsilon) = 0$$

4.10 Notes on $(\partial A/\partial t)$, $(\partial r/\partial t)$, and Positional References

The rate of change of mass within the differential volume element can be considered from two reference perspectives. In one perspective, the volume element is spatially displaced from position r to $(r + \Delta r)$. The analytical development with this frame of reference gives rise to the $(\partial A/\partial t)$ terms of eq 78. The rate of change of mass within the volume element with respect to time and displacement would be given by eq 78.

With the second reference frame, one is interested in the rate of change of mass relative to a fixed spatial reference. This situation would arise if one were monitoring the effluent properties relative to a fixed reference location. With respect to a fixed spatial reference, the area would be constant-valued and the derivative $(\partial A/\partial t) = 0$. With $(\partial A/\partial t) = 0$, it follows that $(\partial r/\partial t) = 0$. With $(\partial r/\partial t) = 0$, eq 84 can be expressed as

$$[1/(MW)_i] [(1 - \epsilon)/\epsilon] [r (\partial q_i/\partial t)] + [r (\partial C_i/\partial t)] + [\partial(r N_i)/\partial r] + r (R_i/\epsilon) = 0 \quad (98)$$

or

$$[1/(MW)_i] (\rho_b/\epsilon) [r (\partial W_i/\partial t)] + [r (\partial C_i/\partial t)] + [\partial(r N_i)/\partial r] + r (R_i/\epsilon) = 0 \quad (99)$$

Information relating to partial and total derivatives as well as reference frames is expanded upon in Appendix C.

4.11 Closing Commentary

The utility of the various forms of eqs 85 and 99 for practical engineering design purposes is formidable. The causes of this analytical complexity stem from the need to characterize the molar flux with position and loading parameters with respect to time, the need to characterize the reaction rate in terms of its independent variables, and the relative motion of the volume element with respect to a fixed spatial reference (if applicable). The dynamics associated with the changing cross-sectional area can be simplified somewhat by consideration of the reference frame; however, the resultant expressions still retain a degree of analytical complexity.

It must be recalled that the analytical development contained in this section addressed the radial components of the flux and assumed that the molar fluxes and gradients associated with the nonprinciple flow directions were negligible relative to their counterparts in the radial direction.

For very precise efforts, computational algorithms can be developed to arrive at numerical solutions to equations of the form of eqs 85 and 99. For practical engineering purposes, much simpler analytical approaches are often used; however, these simplified approaches are necessarily limited in their ability to truly model the performance characteristics of actual filters. It must also be remembered that the energetic aspects associated with physical adsorption and chemisorption were not considered in this review effort.

5. EFFORT BY BOHART AND ADAMS

An early effort to characterize the performance of carbon against an airstream contaminated by chlorine was undertaken by Bohart and Adams (ref 7). This early work was extensive, as Bohart and Adams conducted numerous experimental trials and developed analytical expressions in an effort to characterize the breakthrough characteristics of chlorine through carbon beds. Their analytical expressions provided a means to predict the concentration of chlorine with both position and time. With a room temperature vapor pressure considerably higher than 10 torr, chlorine is removed through a chemisorption process within the adsorbent system.

Bohart and Adams (ref 7) assumed a simplistic rate expression in which the rate of loss of residual capacity of the carbon for the chlorine challenge vapor ($\partial a/\partial t$) was proportional to the product of a first-order rate constant (k), the localized residual capacity of the carbon for the chlorine (a), and the localized vapor phase concentration of the chlorine with axial position (C_i). Their fundamental rate expression took on the form

$$(\partial a/\partial t) = -k a C_i \quad (100)$$

As the ability of the carbon to remove chlorine diminished with time, the residual loading capacity of the adsorbent would decrease in accordance with eq 100. At a condition of full consumption, or saturation of the adsorbent, the residual loading capacity would have a value of zero.

To describe the change in chlorine concentration within the vapor phase as a given fluid element traversed the bed in an axial direction, Bohart and Adams proposed the following rate relationship:

$$(\partial C_i/\partial z) = -(k/v) a C_i \quad (101)$$

where v represents the rate of supply of chlorine that saturates the carbon bed. As used in this definition, v can be likened to the propagation of the adsorption wave as it traverses

the adsorbent column. It is not directly related to the superficial velocity of the airflow that enters the column.

Some distinction on the use of adsorbate loading parameters should be emphasized here. The loading parameters q_i and W_i , as used in previous sections, related to the loading of the adsorbent with time. Their values would generally increase with time. Bohart and Adams based their analytical development on the notion of a residual loading capacity that would tend to decrease with time. As such, the parameter a is to be differentiated from the parameters q_i and W_i .

The relationship given by eq 101 relates the change in concentration of the chlorine concentration in the vapor phase to an axial position (constant cross-sectional area is assumed). Inspection of eq 101 indicates a similarity to the steady-state design equation used in simplified expressions for an ideal plug flow reactor (PFR) system with first-order reaction kinetics. With ideal PFR systems, the flow effects associated with dispersion and deviations from ideal flow behavior (i.e., axial mixing of adjacent volume elements) are not considered. Further assumptions of an ideal PFR system are that each volume element takes the same amount of time to traverse the reactor from the inlet to the outlet and that there is uniformity throughout the element in the radial direction. With the ideal steady-state design relationship for such systems, composition changes in the vapor phase concentration of i are spatially dependent and time invariant. A representative steady-state PFR design relationship can be expressed by

$$(\partial C_i / \partial z) = -(A/Q) R_i \quad (102)$$

Assuming that the reaction rate term is first-order in concentration, then $R_i = k C_i$, and eq 102 takes on the form

$$(\partial C_i / \partial z) = -(A/Q) k C_i \quad (103)$$

The generic similarities between the ideal PFR design expression and eq 101 are noted.

Through a series of variable transformations, magnitude estimations, and rationalizing arguments, Bohart and Adams give the following relationships to characterize the transmission of chlorine through carbon beds of constant cross-sectional area:

$$(C_i / C_o) = 10^{t''} / (10^{z''} - 1 + 10^{t''}) \quad (104)$$

and

$$(a/a_o) = 10^{z''} / (10^{z''} - 1 + 10^{t''}) \quad (105)$$

where

$$z'' = 0.4343 k a_o (z/v) \quad (106)$$

and

$$t'' = 0.4343 k C_o t \quad (107)$$

Equations 104 and 105 provide a means to calculate the concentration of chlorine vapor in the airstream as a function of both axial position and time, provided that the rate parameters can be determined. The rate constant would be determined through experimentation.

5.1 Analytical Development of the Bohart and Adams Breakthrough Relationships

The following development details the analytical methodology taken by Bohart and Adams (ref 7) in arriving at the relationships given by eqs 104 and 105. The development is based on content contained within the appendix of the cited reference.

The following variable transformations are defined:

$$a' = a/a_o \quad (108)$$

$$C_i' = C_i/C_o \quad (109)$$

$$z' = k a_o (z/v) \quad (110)$$

and

$$t' = k C_o t \quad (111)$$

With these variable transformations, the following relationships are developed for $(\partial C_i'/\partial z')$ and $(\partial a'/\partial t')$:

$$\begin{aligned} (\partial C_i'/\partial z') &= (\partial C_i'/\partial C_i) (\partial C_i/\partial z) (\partial z/\partial z') = (1/C_o) (\partial C_i/\partial z) [v/(k a_o)] \\ &= (1/C_o) [(-k a C_i)/v] [v/(k a_o)] = -(a/a_o) (C_i/C_o) \\ &= -a' C_i' \end{aligned} \quad (112)$$

$$\begin{aligned} (\partial a'/\partial t') &= (\partial a'/\partial a) (\partial a/\partial t) (\partial t/\partial t') = (1/a_o) (\partial a/\partial t) [1/(k C_o)] \\ &= (1/a_o) (-k a C_i) [1/(k C_o)] = -(a/a_o) (C_i/C_o) \\ &= -a' C_i' \end{aligned} \quad (113)$$

The following expressions result directly from eqs 112 and 113:

$$[(\partial C_i'/C_i')/\partial z'] = [\partial(\ln C_i')/\partial z'] = -a' \quad (114)$$

and

$$[(\partial a'/a')/\partial t'] = [\partial(\ln a')/\partial t'] = -C_i' \quad (115)$$

The further development of eqs 114 and 115 is based on their integrated forms. Bohart and Adams rationalize the integration of these relationships as follows: At time $t' = 0$ (corresponding to $t = 0$ for nonzero values of k and C_o), the residual loading capacity of the carbon for chlorine is taken to be uniform and constant valued at a_o throughout the entire length of the carbon bed. This uniformity of the residual loading capacity would apply for an adsorbent system that does not have any prior contaminant loading history or operational service. In other words, the adsorbent is fresh and assumed to have uniform loading capabilities throughout the column. The adsorbent possesses maximum loading capability in this condition. Therefore, $a' = 1$ over the entire length of the adsorbent column. The transformation length, z' , as defined by the relationship given by eq 110, is observed to be a function of axial position only (the other parameter values being multiplicative constants). Because a' is assumed to be constant valued, eq 114 can be integrated over the axial length of the carbon bed in accordance with the following development:

$$\int_{C_i'@z'=0}^{C_i'@z'} \partial(\ln C') = - \int_{z'=0}^{z'} a' \partial z' \quad (116)$$

The integral on the left side of the equality in eq 116 is integrated as

$$\ln (C_i'@z') - \ln (C_i'@z'=0) = \ln (C_i/C_o) \Big|_{z'} - \ln (C_i/C_o) \Big|_{z'=0}$$

At position $z = 0$ (corresponding to $z' = 0$), the concentration of chlorine (or component i) in the vapor phase is C_o . Therefore,

$$\ln (C_i/C_o) \Big|_{z'=0} = \ln 1 = 0$$

The integral on the right side of the equality of eq 116 is simply $(-a' z')$ for a constant value of a' . At $t = 0$ (corresponding to $t' = 0$ for nonzero-valued parameters k and C_o), then $a' = 1$. With $a' = 1$, the integrated form of eq 116 is given as

$$C_i' = e^{-z'} \quad (117)$$

At position $z' = 0$ (corresponding to $z = 0$ for nonzero values of k , a_o , and v), the inlet concentration of the chlorine is uniform and constant valued at C_o with time. Therefore, $C_i' = 1$ over any time duration. The transformation time t' , as defined by the relationship given by eq 111, is observed to be a function of time only (the other parameter values being multiplicative constants). Since C_i' is a constant, eq 115 can be integrated over time in accord with the following development;

$$\int_{a'@t'=0}^{a'@t'} \partial(\ln a') = - \int_{t'=0}^{t'} C_i' \partial t' \quad (118)$$

The integral on the left side of the equality in eq 118 is integrated as

$$\ln (a' @ t') - \ln (a' @ t' = 0) = \ln (a/a_o) \Big|_{t'} - \ln (a/a_o) \Big|_{t' = 0}$$

At time $t = 0$ (corresponding to $t' = 0$), the residual capacity of the adsorbent for chlorine is a_o . Therefore

$$\ln (a/a_o) \Big|_{t' = 0} = \ln (a_o/a_o) = \ln (1) = 0$$

The integral on the right side of eq 118 is simply $(C_i' t')$ for a constant value of C_i' . At $z = 0$ (corresponding to $z' = 0$ for nonzero-valued parameters k , a_o , and v), then $C_i' = 1$. With $C_i' = 1$, the integrated form of eq 118 is given as

$$a' = e^{-t'} \quad (119)$$

5.2 Analytical Manipulations with Bohart and Adams Relationships

Through the imposition of boundary conditions, independent relationships for the concentration of chlorine as functions of axial position and time were developed in Section 5.1. These are given by eqs 117 and 119. The aim of this section is to further detail the approach pursued by Bohart and Adams (ref 7) in the development of an analytical expression that couples time and positional dependency to a common expression.

Provided that C_i' does not equal 0, the following expression results directly from eq 112:

$$\{[\partial C_i' / (C_i')^2] / \partial z'\} = -(a' / C_i') \quad (120)$$

Substitution of the relationships developed for C_i' (eq 117) and a' (eq 119) into eq 120 gives the expression

$$\{[\partial C_i' / (C_i')^2] / \partial z'\} = -(1 / e^{t'-z'}) \quad (121)$$

Separation of the variables in eq 121 sets up the following integral expression:

$$\int_{(C_i')_1}^{(C_i')_2} (C_i')^{-2} \partial C_i' = \int_{z'_1}^{z'_2} -(1 / e^{t'-z'}) \partial z' \quad (122)$$

The 1 and 2 subscript designations appearing in the integration limits of eq 122 represent the dimensionless concentration and axial position at specific locations. These designations are defined as follows:

Subscript 1 = parameter value at entrance location or $z' = 0$.

Subscript 2 = parameter value at axial position z' within the carbon bed.

The integral on the left side of the equality given by eq 122 is evaluated as

$$\int_{(C_i')_1}^{(C_i')_2} (C_i')^{-2} \partial C_i' = - (1/C_i') \Bigg|_{(C_i')_1}^{(C_i')_2} = [1/(C_i')_1] - [1/(C_i')_2]$$

The integral on the right side of the equality given by eq 122 is evaluated as

$$\begin{aligned} \int_{z'_1}^{z'_2} - (1/e^{t'-z'}) \partial z' &= - \int_{z'_1}^{z'_2} e^{-(t'-z')} \partial z' = - \int_{z'_1}^{z'_2} e^{(z'-t')} \partial z' \\ &= - \int_{z'_1}^{z'_2} e^{z'} e^{-t'} \partial z' = e^{-t'} \int_{z'_2}^{z'_1} e^{z'} \partial z' \\ &= e^{-t'} (e^{z'_1} - e^{z'_2}) = e^{(z'_1-t')} - e^{(z'_2-t')} \end{aligned}$$

Therefore, eq 122 can be expressed by the integrated form

$$[1/(C_i')_1] - [1/(C_i')_2] = e^{(z'_1-t')} - e^{(z'_2-t')} \quad (123)$$

The parameter values, which are positionally dependent, are determined as follows:

$$(C_i')_1 = (C_i/C_o)_1 = (C_o/C_o) = 1 \text{ at } z'_1 = 0$$

and

$$(C_i')_2 = (C_i/C_o) \text{ at } z'_2 = z'$$

Substitution of these parameter values into eq 123 gives

$$1 - [1/(C_i')] = e^{(0-t')} - e^{(z'-t')} = e^{-t'} - e^{(z'-t')}$$

or

$$[1/(C_i')] = 1 - e^{-t'} + e^{(z'-t')} \quad (124)$$

Equation 124 can be solved explicitly for C_i' , which yields

$$C_i' = e^{t'} / (e^{t'} - 1 + e^{z'}) \quad (125)$$

Recognizing that $e^\theta = 10^{(\theta/\ln 10)}$ on a term-by-term basis, eq 125 can be expressed in terms of common logarithms as

$$C_i' = 10^{(t'/\ln 10)} / [10^{(t'/\ln 10)} - 1 + 10^{(z'/\ln 10)}] \quad (126)$$

Letting $t'' = t'/\ln 10 = 0.4343 t'$ and $z'' = z'/\ln 10 = 0.4343 z'$, eq 126 can be rewritten as

$$C_i' = (C_i/C_o) = 10^{t''} / (10^{t''} - 1 + 10^{z''}) \quad (127)$$

Therefore, eq 127 is the same as eq 104.

The development of an analytical relationship to relate the residual adsorptive capacity of the carbon (a) as a function of time and position is similarly generated. For completeness, the development is as follows.

Provided that the carbon retains residual adsorptive capacity (i.e., $a \neq 0$), the following relationship results directly from eq 113:

$$(\partial a' / \partial t') = -a' C_i'$$

or

$$(1/a'^2) (\partial a' / \partial t') = -C_i' / a' \quad (128)$$

From the relationships developed for C_i' (eq 117) and a' (eq 119), eq 128 can be expressed as

$$(1/a'^2) (\partial a' / \partial t') = -e^{(t'-z')} \quad (129)$$

Separation of variables, and establishing integration limits, eq 129 takes on the integral form

$$\int_{(a')_1}^{(a')_2} (a')^{-2} \partial a' = \int_{t'_1}^{t'_2} -e^{(t'-z')} \partial t' \quad (130)$$

The 1 and 2 subscript designations in the integration limits of eq 130 represent the dimensionless residual chlorine capacity of the carbon at specific times. These designations are defined as follows:

Subscript 1 = parameter value at time $t' = 0$.

Subscript 2 = parameter value at time t' within the carbon bed.

The integral on the left side of the equality of eq 130 is evaluated as

$$\int_{(a')_1}^{(a')_2} (a')^{-2} \partial a' = -(1/a') \left| \begin{matrix} (a')_2 \\ (a')_1 \end{matrix} \right| = [1/(a')_1] - [1/(a')_2]$$

The integral on the right side of the equality of eq 130 is evaluated as

$$\begin{aligned} \int_{t'_1}^{t'_2} -e^{(t'-z')} \partial t' &= -e^{-z'} \int_{t'_1}^{t'_2} e^{t'} \partial t' = -e^{-z'} (e^{t'_2} - e^{t'_1}) \\ &= e^{(t'_1-z')} - e^{(t'_2-z')} \end{aligned}$$

Therefore, eq 130 can be expressed by the integrated form

$$[1/(a')_1] - [1/(a')_2] = e^{(t'_1-z')} - e^{(t'_2-z')} \quad (131)$$

The following parameter values, which are assumed to be spatially independent, are calculated based on the specific times established previously:

$$(a')_1 = 1 \quad \text{at} \quad t'_1 = 0$$

and

$$(a')_2 = a' \quad \text{at} \quad t'_2 = t'$$

Substitution of these parameter values into eq 131 gives the relationship

$$\begin{aligned} 1 - (1/a') &= e^{(0-z')} - e^{(t'-z')} \\ &= e^{-z'} - e^{(t'-z')} \end{aligned}$$

or

$$(1/a') = e^{(t'-z')} + 1 - e^{-z'} \quad (132)$$

Equation 132 can be solved explicitly for a' to yield

$$a' = e^{z'} / (e^{t'} - 1 + e^{z'}) \quad (133)$$

With $e^\theta = 10^{(\theta/\ln 10)}$ on a term-by-term basis, eq 133 can be expressed in terms of common logarithms as

$$a' = 10^{(z'/\ln 10)} / [10^{(t'/\ln 10)} - 1 + 10^{(z'/\ln 10)}] \quad (134)$$

Letting $t'' = t'/\ln 10 = 0.4343 t'$, and $z'' = z'/\ln 10 = 0.4343 z'$, eq 134 can be rewritten as

$$a' = (a/a_o) = 10^{z''} / (10^{t''} - 1 + 10^{z''}) \quad (135)$$

Equation 135 is the same as eq 105.

5.3 Simplifications to the Bohart and Adams Breakthrough Relationships

The breakthrough relationships developed by Bohart and Adams, given by eqs 104 and 105, can be approximated by the following relationships for situations in which z'' and t'' are appreciably large:

$$C_i' = (C_i/C_o) = 1 / [10^{(z''-t'')} + 1] \quad (136)$$

and

$$a' = (a/a_o) = 1 - C_i' \quad (137)$$

The mathematical rationale behind these simplifications is that $10^{z''}$ and $10^{t''}$ would have values appreciably larger than 1. As such, the 1 appearing in the denominators of eqs 104 and 105 could be neglected.

Very small values of both z'' and t'' would infer a location within the carbon adsorbent that is very close to the inlet and a very brief time (based on the definitions given for these parameters). These conditions would generally not allow for the formation of a consistent adsorption wavefront.

5.4 Closing Commentary on the Bohart and Adams Analytical Development

The Bohart and Adams analytical development is based on a first-order adsorption rate expression in which ideal plug flow is assumed. With ideal plug flow, discrete fluid elements are assumed to traverse the reactor length from inlet to outlet, and there is no interaction among the adjacent fluid elements. The effects of axial dispersion are neglected in this idealization. At steady state (steady in that the vapor phase concentration of i remains constant relative to a fixed spatial reference), the concentration of species i is positionally dependent and time invariant. This aspect is analytically reflected in eq 101. Bohart and Adams attempt to couple this ideal plug flow behavior with the idea that the residual capacity of the adsorbent decreases with time, which is reflected by the relationship given by eq 100. A major assumption with their development is that the residual loading capacity of the carbon for the chlorine is perfectly uniform throughout the adsorbent bed. The authors identify this aspect as a limitation with their modeling expressions.

As indicated, the fundamental Bohart-Adams rate relationships are of a form consistent with an ideal design relationship for a PFR. An inherent assumption with the ideal PFR relationship is that a pseudo-steady-state condition exists in that the conversion is spatially dependent (i.e., the degree of conversion is a function of axial location only) and time invariant. An ideal PFR can be likened to a closed batch reactor (closed in the sense that there are no flow streams associated with the reactor vessel) that is conveyed along a tube. The degree of conversion in such a system is dependent upon the space (or duration) time within the tube.

In later efforts at modeling the breakthrough characteristics of carbon adsorbent systems, more complex rate expressions have been assumed. Many of these rate relationships incorporate parameters to differentiate between the various mechanisms that contribute to the removal of components from a contaminated airstream. These removal mechanisms encompass diffusive considerations as well as reactionary rate expressions. The analytics associated with the characterization of breakthrough can become formidable even with simplistic rate mechanisms.

6. THE MECKLENBURG RELATIONSHIP

A conceptual model, attributed to Mecklenburg (circa 1925), is based on the subtraction of a “dead zone thickness” from the actual physical length of an adsorbent column to account for the penetration of contaminants far below the challenge concentration levels. If an adsorbent system is exposed indefinitely to a steady vapor-phase challenge concentration, the effluent concentration will eventually rise to that of the inlet challenge concentration as the adsorbent capacity is diminished with time. The assumptions here are that the contaminant is irreversibly adsorbed onto the carbon substrate, and there is no subsequent off-gassing of the contaminant from the adsorbed state. The intent of this section is to review the basis of the Mecklenburg mass balance.

6.1 Graphical Interpretations for a Strongly Adsorbed Compound

Figure 7 (ref 8) depicts an adsorption wave profile that is characteristic of compounds having a strong affinity for the carbon adsorbent. The plot represents a snapshot of the concentration profile throughout the bed at that moment in time in which a trace or threshold breakthrough concentration of contaminant has reached the effluent end of the adsorbent system. In most cases of interest, this breakthrough concentration is several orders of magnitude less than the influent challenge concentration.

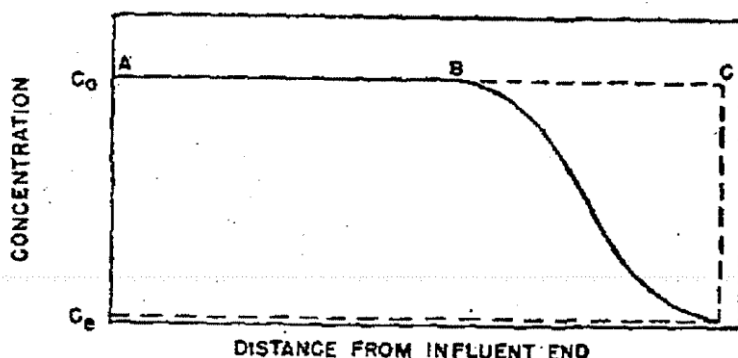


Figure 7. Depiction of adsorption wave profile at breakthrough (from ref 8).

A review of Figure 7 indicates two distinct regions of interest. The first region of interest covers the adsorbent depth encompassed within the region bounded by **A** and **B**. In this region, the localized vapor phase concentration of the adsorbate is equal to C_o (or the challenge concentration). This region represents a saturated loading region in which the adsorbent has reached its maximum loading capacity. Such a maximum (for a physically adsorbed contaminant) would be bounded by equilibrium constraints.

The second region of interest concerns that section of the adsorbent bed encompassed within the region bounded by **B** and **C**. In this region, the adsorbent retains adsorptive capacity because it has not reached a state of saturation, and the concentration of contaminant in the vapor phase decreases with axial position. The width of this region is due to the finite mass-transfer resistances that exist between the bulk vapor phase and the adsorbed state. These resistances affect the rate of adsorption within the system.

With infinitely rapid mass transfer from the vapor phase to an adsorbed state, the downward sloping region of the adsorption wave depicted in Figure 7 would be a vertical line, and the MTZ thickness would be zero. The characteristics and breadth of the decreasing slope that constitutes the MTZ are associated with the finite rate effects associated with the adsorptive process.

The time required for a breakthrough concentration to be observed at the effluent end (i.e., at position $z = L$) of the adsorbent bed is termed as the breakthrough time and is depicted by the symbol t_b . The depth of the adsorbent corresponding to the region of Figure 7 bounded by **B** and **C** is termed the MTZ thickness and is depicted by the symbol M_z . The breadth and characteristics of the MTZ region of the adsorption wave contour are rate dependent.

6.2 Development of the Mecklenburg Breakthrough Relationship

In the development that follows, it is assumed that the removal mechanism is due solely to physical adsorption, and that the adsorptive process is irreversible.

The mass of contaminant that the adsorbent can retain at full saturation is given by the expression

$$(M_i)_{\text{adsorbed @ saturation}} = V_{\text{tot}} \rho_b W_e \quad (138)$$

The expression given by eq 138 represents an equilibrium bounding maximum that is not rate dependent. If the entire volume of adsorbent could be loaded to its saturation capacity, then the mass of adsorbate contained within the system would be described by the relationship given by eq 138 and graphically depicted by the rectangular region bounded by **A-C-C_e-C_o** with reference to Figure 7. The total volume of the adsorbent system includes the volume of the adsorbent as well as the associated void volume. The volume is directly correlated to the depth of the adsorbent in a system having a constant cross-sectional area. With an imposed low-level breakthrough

constraint, the entire volume of the adsorbent cannot be used to a condition of full saturation.

The mass of contaminant that is introduced into the adsorbent system as a vapor can be expressed by

$$(M_i)_{\text{challenge}} = Q C_o t \quad (139)$$

If it is then assumed that there is a zone or region within the carbon adsorbent bed that cannot be fully used for capacity due to a breakthrough constraint, then the total volume of the adsorbent bed must be adjusted (reduced) to account for this. This breakthrough constraint (concentration based) gives rise to an adjustment factor to the total volume appearing in eq 138. Using eq 138 as a basis, a suggested relationship to describe the mass of contaminant retained by the adsorbent at a breakthrough condition is given as

$$(M_i)_{\text{adsorbed @ breakthrough}} = \delta V_{\text{tot}} \rho_b W_e \quad (140)$$

where δ represents that fraction of the total adsorbent system volume that can be used for loading until a breakthrough criteria is reached.

The mass of contaminant that enters the system at that specific time at which a breakthrough criteria is reached at the effluent can be simply expressed through the following modification to eq 139:

$$(M_i)_{\text{challenge @ breakthrough}} = Q C_o t_b \quad (141)$$

Equating the mass of contaminant introduced into the system eq 141 to the mass of contaminant retained by the adsorbent at the breakthrough criteria (eq 140) yields the following relationship:

$$Q C_o t_b = \delta V_{\text{tot}} \rho_b W_e$$

or

$$t_b = [(\rho_b W_e)/(Q C_o)] \delta V_{\text{tot}} \quad (142)$$

Equation 142 represents a very simplified mass balance expression developed through the imposition of a breakthrough criteria. An inherent assumption to this development is that the adsorbent has a characteristic and uniform equilibrium loading capacity throughout the bed.

If the cross-sectional area normal to the principle flow axis is a constant, then $V_{\text{tot}} = A L$, and eq 142 can be expressed as

$$t_b = [(\rho_b W_e)/(Q C_o)] \delta A L \quad (143)$$

A further modification to eq 143 can be made by noting that the volumetric throughput can be related to the cross-sectional flow area and the superficial flow velocity through $Q = A u$. Substitution of this relationship into eq 143 yields the expression

$$t_b = [(\rho_b W_e)/(u C_o)] \delta L \quad (144)$$

The various forms of eq 142 represent variations on a simplified mass balance concept.

It is hypothesized that Mecklenberg related the fraction of the usable bed depth in a manner consistent with the following expression:

$$\delta L = L - M_z \quad (145)$$

where M_z represents that thickness (or segment) of the total bed depth that cannot be fully used for adsorption capacity. Substitution of eq 145 into eq 144 yields

$$t_b = [(\rho_b W_e)/(u C_o)] (L - M_z) \quad (146)$$

Equation 146 is consistent with the analytical approaches that are currently used to estimate the performance characteristics of carbon-based filter systems in military applications against contaminants that are strongly adsorbed onto the adsorbent through a physical adsorption mechanism. Several parameters within eq 146 can be readily evaluated. The difficulty in the application of eq 146 rests with the evaluation of M_z and, to a lesser extent, W_e .

It is surmised that Mecklenburg pursued an analogy similar to this in the mass balance relationships that are attributed to him. These simplified relationships are thought to be consistent with the various forms of eq 142.

7. EFFORTS BY I. M. KLOTZ AND M. DOLE

7.1 Background

Within the open technical literature, numerous articles relate to the adsorption of contaminant compounds on porous solids. This effort will focus on two such efforts because of their relevance to the current review.

Irving M. Klotz (and other investigators) authored several technical articles relating to the analytical aspects of estimating the performance characteristics of activated carbon against vapor-phase contaminants. Over the years, others have also contributed and further developed the analytical approaches that are used. The Klotz (ref 2) and Dole and Klotz (ref 3) efforts relate to the removal of compounds of military significance from a contaminated airstream.

7.2 “The Adsorption Wave” by I. M. Klotz

“The Adsorption Wave” (1946; ref 2) constituted a chapter within a compiled technical report summary generated through the National Defense Research Committee (NDRC) during the 1940s. This early work describes the development of a differential mass balance and several of the rate aspects that factor into the evaluation of the resultant analytical relationships. A modified version of the NDRC chapter by Klotz was also published in the technical journal *Chemical Reviews* (ref 9). The *Chemical Reviews* version was intended for general public release and does not contain the compound specificity that appears in the NDRC version.

As indicated in Sections 2 and 4 of this current review effort, the analytics associated with adsorption are complicated. It is for this reason that rigorous approaches to characterize the performance of activated carbon adsorbent substrates against contaminated vapor streams are often dealt with through simplified analytical expressions. Some analytical modeling approaches are very dependent on actual data to estimate parameter values, whereas other modeling approaches are less dependent on actual data and make use of correlative estimation methods. In the absence of actual data, correlative approaches can provide reasonable tools to estimate filter performance. Although it is useful to appreciate the foundations upon which the analytical models are based, the resultant relationships are often so complex as to render them impractical for estimation purposes by the generic engineering design community.

In “The Adsorption Wave” (ref 2), Klotz provides a relationship based on a specific rate-limiting step that has considerable utility to the design community. The resultant expression requires a minimum of auxiliary data generation and is commonly employed to this day. On the basis of the simplifications that went into the developed expression, there are limitations inherent with its applicability for all situations. These inherent limitations require understanding in the application of the modeling expressions.

7.2.1 Fundamental Analytical Relationships from “The Adsorption Wave”

The Klotz effort begins with the formulation of a mass balance across a volume element of infinitesimal thickness. The analytical development is based on the specification of a parameter η , which represents the amount of toxic gas within the volume element per unit volume of bed. This η parameter is a localized variable for the amount of adsorbate that exists in both the adsorbed state and the vapor phase. In effect, η represents a combination of C_i (i.e., the concentration of adsorbate in the vapor phase) and q_i (i.e., the adsorbate loading on/within the carbon granules).

The mathematical interpretation of η is given as

$$\begin{aligned}\eta &= (\text{moles of toxic gas}) / (\text{volume of bed}) \\ &= M_i / [(MW)_i V_{\text{tot}}]\end{aligned}\tag{147}$$

where V_{tot} represents the combined volumes of the adsorbent and void volumes. V_{tot} does not represent the total volume of the adsorbent column.

The amount and distribution of toxic gas (between the adsorbed solid phase and the vapor phase) is a function of time and position. Relative to a fixed spatial reference, the localized rate of pickup per unit volume of bed can be represented by differentiating eq 147 with respect to time. This gives the relationship

$$(\partial\eta/\partial t) = \left\{ 1/[(MW)_i V_{\text{tot}}] \right\} (\partial M_i/\partial t) \quad (148)$$

In eq 148, it has been assumed that $[\partial(\Delta z)/\partial t]$ is negligible relative to $(\partial M_i/\partial t)$ for a system having a constant cross-sectional flow area.

With the localized rate of change of mass established by eq 148, the development of a mass balance over a differential volume element proceeds as follows.

Consider the adsorption system depicted in Figure 8.

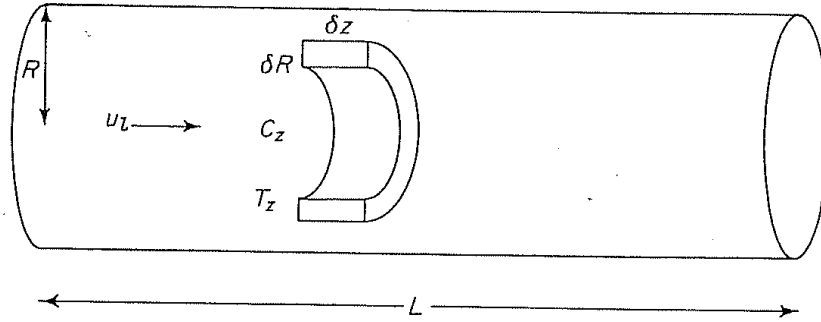


Figure 8. A cylindrical adsorbent system with primary flow in the axial direction (from ref 10).

Figure 8 depicts a cylindrical adsorbent system in which the principle flow is associated with the axial direction. The figure illustrates a sectional view of the differential volume element in a cylindrical configuration and is consistent with Figure 2. The gradients in the angular and radial directions are neglected in the development which follows.

7.2.1.1 Rate of Mass Flow of i into the Volume Element at Axial Position z :

$(\dot{m}_i)_{\text{in}}$

$$(\dot{m}_i)_{\text{in}} = (MW)_i N_i(z, t) (\epsilon A) \quad (149)$$

The molar flux appearing in eq 149 is evaluated at axial position z and time t .

7.2.1.2 Rate of Mass Flow of i Exiting Volume Element at Axial Position
($z + \Delta z$): $(m_i)_{\text{out}}$

$$(m_i)_{\text{out}} = (\text{MW})_i N_i(z + \Delta z, t + \Delta t) (\varepsilon A) \quad (150)$$

As with eq 149, the molar flux of i exiting the differential volume element is evaluated at axial position ($z + \Delta z$) and time ($t + \Delta t$).

7.2.1.3 Rate of Change of Mass of i within the Volume Element: $(\partial M_i / \partial t)$

An expression for the localized rate of change of mass within the volume element can be obtained from the relationship given by eq 148. From eq 148, the following relationship can be written:

$$(\partial M_i / \partial t) = (\text{MW})_i V_{\text{tot}} (\partial \eta / \partial t) \quad (151)$$

7.2.1.4 Analytical Mass Balance Development

In the development that follows, the rate of consumption of species i through a reactionary means is included within the η parameter. As such, the following mass balance expression for i can be written:

$$(\partial M_i / \partial t) = (m_i)_{\text{in}} - (m_i)_{\text{out}} + \overset{0}{\cancel{(m_i)_{\text{gen}}}} \quad (152)$$

where $(m_i)_{\text{gen}} = 0$ because the rate of removal of i through a reactionary pathway is reflected in the localized adsorptive flux [i.e., $(\partial \eta / \partial t)$].

Substituting the relationships given by eqs 149, 150, and 151 into eq 152 yields the following expression:

$$V_{\text{tot}} (\partial \eta / \partial t) = -\varepsilon A [N_i(z + \Delta z, t + \Delta t) - N_i(z, t)] \quad (153)$$

The quantity $[N_i(z + \Delta z, t + \Delta t) - N_i(z, t)]$ represents the total differential of the molar flux of i (see Appendix B). The relationship given by eq 153 can therefore be written as

$$V_{\text{tot}} (\partial \eta / \partial t) = -\varepsilon A dN_i \quad (154)$$

Now, V_{tot} represents the volume occupied by the void spaces and the volume occupied by the adsorbent within the differential volume element. Assuming a constant cross-sectional area normal to the principle flow direction, the relationship $V_{\text{tot}} = A dz$ holds. Substituting this relationship into eq 154 gives the expression

$$(\partial \eta / \partial t) = -\varepsilon (dN_i / dz) \quad (155)$$

Relationships for the molar flux and gradient in the axial direction have been used throughout this review. For an adsorbent-based system, the following relationship (eq 91) is applicable:

$$N_i = v_z C_i - \mathfrak{D}_L (\partial C_i / \partial z)$$

Klotz assumes that the dispersive effects associated with nonideal plug flow are considered to be negligible. To this end, $\mathfrak{D}_L = 0$, and the molar flux can be expressed by

$$N_i = v_z C_i$$

The total derivative of this expression with respect to the axial direction yields

$$(dN_i/dz) = v_z (dC_i/dz) \quad (156)$$

The interstitial velocity is taken to be constant in eq 156.

Substituting the relationship given by eq 156 into eq 155 yields

$$-(1/\mathfrak{E}) (\partial \eta / \partial t) = v_z (dC_i/dz) \quad (157)$$

The concentration gradient of eq 157 represents the total gradient of C_i with respect to axial position. This derivative is dealt with as follows (see Appendix B for information relating to total and partial derivatives).

Because the vapor-phase concentration is a function of axial location and time, the following functionality can be written:

$$C_i = C_i (z, t)$$

The total differential of this relationship can be expressed as

$$dC_i = (\partial C_i / \partial z) dz + (\partial C_i / \partial t) dt \quad (158)$$

or

$$(dC_i/dz) = (\partial C_i / \partial z) + (\partial C_i / \partial t) (dt/dz) \quad (159)$$

Because (dt/dz) is taken to be the reciprocal of the interstitial velocity, eq 159 can be expressed as

$$(dC_i/dz) = (\partial C_i / \partial z) + (1/v_z) (\partial C_i / \partial t) \quad (160)$$

Substituting the relationship given by eq 160 into eq 157 gives

$$-(1/\mathfrak{E}) (\partial \eta / \partial t) = (\partial C_i / \partial t) + v_z (\partial C_i / \partial z) \quad (161)$$

Equation 161 is the same as eq 11 in the Klotz reference paper (ref 2).

It is instructive at this point to compare the Klotz mass balance expression, as given by eq 161, to the relationship that appears in the Ruthven text (ref 6). A form of this Ruthven reference relationship was provided by eq 86.

The intent of the following development is to demonstrate the consistency between the Klotz mass balance and that given in the text by Ruthven. The Ruthven (ref 6) relationship is generically applicable to systems in which axially dispersed plug flow can be assumed.

A relationship between the total volume of the adsorbent bed and the bulk packing density of the adsorbent was reviewed in the development of the relationship leading to eq 61. From eq 61, the following relationship can be written:

$$V_{\text{tot}} = M_{\text{ads}} / \rho_b \quad (162)$$

Substituting the relationship given by eq 162 into eq 147 gives

$$\eta = M_i / [(MW)_i (M_{\text{ads}} / \rho_b)] = (M_i / M_{\text{ads}}) [\rho_b / (MW)_i] \quad (163)$$

Now (M_i / M_{ads}) is the specific loading of species i on the adsorbent expressed on a mass basis, which was previously defined as W_i . Equation 163 can therefore be equivalently expressed as

$$\eta = W_i [\rho_b / (MW)_i] \quad (164)$$

Differentiation of eq 164 with respect to time yields

$$(\partial \eta / \partial t) = [\rho_b / (MW)_i] (\partial W_i / \partial t) \quad (165)$$

A relationship relating the mass based adsorbate loading to a volume-based loading was previously developed as eq 69, which is given as

$$(\partial W_i / \partial t) = [(1 - \epsilon) / \rho_b] (\partial q_i / \partial t)$$

Substituting the relationship given by eq 69 into eq 165 yields

$$(\partial \eta / \partial t) = [(1 - \epsilon) / (MW)_i] (\partial q_i / \partial t) \quad (166)$$

Substituting the relationship given by eq 166 into eq 161 (which represents eq 11 of the Klotz mass balance relationship) gives the following expression:

$$v_z (\partial C_i / \partial z) + (\partial C_i / \partial t) + [1 / (MW)_i] [(1 - \epsilon) / \epsilon] (\partial q_i / \partial t) = 0 \quad (167)$$

Neglecting the effects associated with dispersion ($\mathcal{D}_L = 0$) and assuming that the interstitial velocity in the axial direction is constant (as Klotz does), then eq 167 is observed to be consistent with the Ruthven relationship as given by eq 86.

7.2.2 The Ruthven Relationship

Throughout this review effort, comparisons to a relationship appearing in the Ruthven text reference (ref 6) have been made. Using the approaches contained in Section 4, the development of the Ruthven relationship is briefly summarized as follows.

7.2.2.1 Rate of Mass Flow of i into the Volume Element at Axial Position z : $(\mathcal{M}_i)_{\text{in}}$

$$(\mathcal{M}_i)_{\text{in}} = (\text{MW})_i N_i(z) (\mathcal{E} A) \quad (168)$$

7.2.2.2 Rate of Mass Flow of i Exiting the Volume Element at Axial Position $(z + \Delta z)$: $(\mathcal{M}_i)_{\text{out}}$

$$(\mathcal{M}_i)_{\text{out}} = (\text{MW})_i N_i(z + \Delta z) (\mathcal{E} A) \quad (169)$$

7.2.2.3 Rate of Change of Mass of i within the Volume Element: $(\partial \mathcal{M}_i / \partial t)$

A variation to the approach used to develop eq 76 is needed here because of the difference in the geometry of the system being considered. In this current development, a cylindrical system is again considered; however, the principle flow direction is now taken to be in the axial direction (with eq 76, the primary flow direction was assumed to be radially directed).

In accordance with the development of eq 76, the following relationships describe the localized mass of i within the element depicted in Figure 8 (assuming that the property characteristics are uniform within the differential slice):

$$\begin{aligned} \mathcal{M}_i &= (\mathcal{M}_i)_{\text{adsorbed phase}} + (\mathcal{M}_i)_{\text{vapor phase}} \\ &= V_{\text{tot}} (V_{\text{ads}}/V_{\text{tot}}) q_i + [(\mathcal{M}_i)_{\text{vap}}/V_{\text{void}}] V_{\text{void}} \\ &= [A \Delta z] (1 - \mathcal{E}) q_i + (\text{MW})_i C_i (\mathcal{E} V_{\text{tot}}) \\ &= [A \Delta z] (1 - \mathcal{E}) q_i + (\text{MW})_i C_i \mathcal{E} (A \Delta z) \end{aligned} \quad (170)$$

Differentiating eq 170 with respect to time, assuming that the void fraction and the area normal to the principle flow direction can be taken as constants, and assuming that the terms $[\partial(\Delta z)/\partial t]$ are negligible yields

$$(\partial M_i/\partial t) = [A \Delta z] (1 - \epsilon) (\partial q_i/\partial t) + (MW)_i \epsilon (A \Delta z) (\partial C_i/\partial t) \quad (171)$$

7.2.2.4 Species *i* Mass Balance

The generic mass balance for species *i* is given by eq 152. Substitution of the relationships given by eqs 168, 169, and 171 into eq 152 yields

$$[1/(MW)_i] [(1 - \epsilon)/\epsilon] (\partial q_i/\partial t) + (\partial C_i/\partial t) = -(\partial N_i/\partial z) \quad (172)$$

The axial flux can be expressed in terms of its convective and diffusional components by the following modified form of eq 39 (modified in that an interstitial velocity is used as opposed to a superficial velocity):

$$(\partial N_i/\partial z) = [\partial(v C_i)/\partial z] - D_L (\partial^2 C_i/\partial z^2) \quad (173)$$

Substitution of the relationship given by eq 173 into eq 172 yields

$$-D_L (\partial^2 C_i/\partial z^2) + [\partial(v C_i)/\partial z] + (\partial C_i/\partial t) + [1/(MW)_i] [(1 - \epsilon)/\epsilon] (\partial q_i/\partial t) = 0 \quad (174)$$

Equation 174 is seen to be identical to eq 86, which represents the Ruthven-based reference mass balance relationship.

7.2.3 Aspects Associated with $(\partial \eta/\partial t)$ Appearing in the Klotz Article (Ref 2)

The dynamics associated with the adsorptive loading within the MTZ of an activated carbon column factors considerably into the form of the analytical expressions that would characterize the vapor-phase concentration of the contaminant as a function of time and position. The localized sorptive flux, expressed through $(\partial \eta/\partial t)$ or $(\partial q_i/\partial t)$ (or other equivalent relationships), is very much rate-dependent and will influence the forms of the concentration expressions.

The mechanistic aspects associated with the adsorption process include the following:

- a. The transfer of mass from the bulk fluid phase to the outer surface of the carbon granules. This mechanism is referred to as bulk diffusion. In the bulk vapor phase, the contaminant molecules are largely interacting with diluent molecules when the contaminant concentrations are small. As the contaminant molecules diffuse

through the boundary layer, their interactions among themselves increase as their localized concentrations increase with decreasing distance from the adsorbent surface. The rate of transfer is proportional to a transfer coefficient and a driving force gradient.

- b. The intraparticle transfer of the adsorbed species into the pore structure of the individual carbon granules. This mechanism is called intraparticle or Knudsen diffusion. At this level, the contaminant-contaminant and contaminant-surface interactions occur at a much greater frequency than would have occurred as the contaminant diffused through the boundary layer. The localized concentration of the contaminant increases significantly as the molecules are transported within the porous networks of the carbon. The rate of this transport mechanism would be proportional to a transfer coefficient as well as a driving force.
- c. For situations in which the contaminant removal is through a chemisorption pathway, a reactionary rate expression may very well factor. Such rates are typically proportional to a reaction rate constant as well as concentration(s).
- d. Other potential rate-influencing factors.

It becomes evident that the analytical complexity of the Klotz mass balance expression, as given by eq 161, can become formidable with even simplified forms of $(\partial\eta/\partial t)$. To limit the complexity of the analytic rate relationships, the general approach is to assume that a singular mechanistic pathway governs the overall removal process. This singular mechanistic pathway is referred to as the rate-limiting step.

Compounds having a strong affinity for the surface of the activated carbon substrate tend to exhibit strong physical adsorption characteristics. The adsorption wave contours of this class of materials tend to be consistent with those appearing in Figures 5 and 7. With reasonable flow velocities, the rate-limiting step governing the removal of this class of materials from a contaminated airstream is assumed to be bulk diffusion.

The Klotz article associates a critical bed thickness (termed I_x) to each of the mechanistic pathways associated with a particular removal process. Correlative relationships for the primary mechanistic pathways are provided in the article. These critical bed contributions have an analogy to the heights of transfer units in the chemical engineering practice relating to mass transfer operations. A difficulty in using these expressions rests with parameter quantification.

For cases in which bulk diffusion constitutes the predominant removal mechanism, Klotz suggests the use of a correlation attributed to Gamson, Thodos, and Hougen to calculate the critical bed depth (M_z). The Gamson, Thodos, and Hougen (GTH) correlation presented in the Klotz reference (ref 2) is given as

$$I_t = (2.303/a) (d_p G/\mu)^{0.41} [\mu/(\rho D)]^{0.67} \log (C_o/C_e) \quad (175)$$

in which the dimensionless grouping $(d_p G/\mu)$ is the Reynolds number (Re) and the dimensionless grouping $[\mu/(\rho D)]$ represents the Schmidt number (Sc).

It is indicated that the GTH correlation was derived for cases in which the ratio of (C_o/C_e) is very large and is applicable only in cases of turbulent flow. Klotz presents a plot in which the airflow resistance at various flow rates through carbon columns of varying particle sizes was measured. It was found that there was an approximate transition from laminar to turbulent flow at $Re = 10$ for the charcoals investigated (ref 2). The transition region was identified as that region in which there was a notable change in the slope of the airflow resistance versus flow-rate plot. It is further indicated that although the correlation given by eq 175 is more appropriately applicable to turbulent flow systems, it can also satisfactorily approximate I_t in the laminar flow regimes.

7.2.4 Breakthrough Time Relationship

In situations in which diffusion in air constitutes the predominant rate-controlling step, Klotz combined the simplified mass balance relationship attributed to Mecklenburg (eq 146) with the correlation given by eq 175 to arrive at the following breakthrough time relationship:

$$\begin{aligned} t_b &= [(\rho_b W_e)/(u C_o)] (L - M_z) \\ &= [(\rho_b W_e)/(u C_o)] \left\{ L - \left\{ (1/a) (d_p G/\mu)^{0.41} [\mu/(\rho D)]^{0.67} \ln (C_o/C_e) \right\} \right\} \quad (176) \\ &= [(\rho_b W_e)/(u C_o)] \left\{ L - \left[(1/a) Re^{0.41} Sc^{0.67} \ln (C_o/C_e) \right] \right\} \end{aligned}$$

The relationship given by eq 176 forms the basis of current approaches to estimate the breakthrough times for compounds that are strongly adsorbed. Current relationships incorporate additional parameters aimed at refining the analytical results to actual data; however, the fundamental underlying principles that went into eq 176 are assumed to be valid to this day. The use of this expression requires an understanding of the underlying assumptions that went into its development. These assumptions, which appear throughout this report, are compiled as follows for convenience:

- a. Bulk diffusion is the predominant rate-controlling step relating to the removal of contaminants from the bulk vapor phase to the carbon surface. Intraparticle mass transfer and reactionary processes (if applicable) are assumed to occur on a timescale that is very rapid relative to the rate of bulk phase mass transfer.

- b. The contaminant is strongly adsorbed onto the surface of the adsorbent through an ideal physical adsorption pathway. The adsorption is irreversible.
- c. Propagation of the adsorption wavefront is consistent with the trendlines appearing in Figures 5 and 7. The adsorption waves retain a consistent contour with the progression of time. This is inferring a constant value of M_z (or I_t) with time. The adsorbent bed is assumed to have sufficient depth to permit the establishment of a uniform wave profile.
- d. The ratio of the challenge concentration to the breakthrough concentration is very large. Klotz (ref 2) does not clarify as to what constitutes “very large”.
- e. The inlet challenge concentration is constant, and the equilibrium loading capacity is a constant. This assumption is consistent with that proposed by Bohart and Adams (ref 7) with their residual loading parameter (**a**).
- f. The flow behavior is ideal such that the effects associated with axial dispersion can be neglected.

7.3 Sorption of Chloropicrin and Phosgene on Charcoal from a Flowing Gas Stream by M. Dole and I. M. Klotz (1946; ref 3)

In this work, Dole and Klotz conducted an extensive investigation into determining how various parameters influenced the breakthrough characteristics of chloropicrin (PS) and phosgene (CG) within carbon beds. PS has a moderate vapor pressure (26 torr at 25 °C), and its removal mechanism on activated carbon is attributed to moderate physical adsorption (ref 11). Phosgene has a much higher room-temperature vapor pressure (1425 torr at 25 °C) than PS; its removal mechanism is attributed to a combination of hydrolysis and subsequent reaction on impregnated activated carbons (ref 11).

The parameters investigated by Dole and Klotz included influent concentration and temperature, relative humidity, bed depth, and flow rates. In the analysis that follows, the analytical approaches pursued by Dole and Klotz (ref 3) in quantifying the critical bed-depth thickness (or M_z) are reviewed.

The Dole and Klotz (ref 3) analytical approach can be likened to a further development of the rate expressions suggested by Bohart and Adams, with their early efforts relating to the breakthrough of chlorine through carbon adsorbents. In the Dole and Klotz effort, the rate expressions of Bohart and Adams are combined with the Mecklenburg mass balance concept using modern forms of mass transfer correlative relationships.

A review of the effort of Dole and Klotz (ref 3) is summarized as follows. The Mecklenburg relationship as given by Dole and Klotz is

$$C_o L t_b = A n_o (x - h) \quad (177)$$

where x is the total bed length, L is the volumetric flow rate, C_o is the inlet concentration expressed on a molar basis, and n_o is the equilibrium saturation capacity of the carbon expressed on a moles of i per volume of adsorbent basis. The equilibrium saturation capacity, n_o , is related to W_e by the following correspondence through dimensional considerations:

$$W_e = n_o (MW)_i [(1 - \epsilon)/\rho_b] \quad (178)$$

Substituting the relationship given by eq 178 into eq 177 and using variable designations that have been consistently used throughout this review gives the following expression:

$$(MW)_i C_o Q t_b = A W_e [\rho_b/(1 - \epsilon)] (L - h) \quad (179)$$

7.3.1 Linearity of Life-Thickness Plots

Figure 9 presents a life-thickness plot for phosgene at various flow rates.

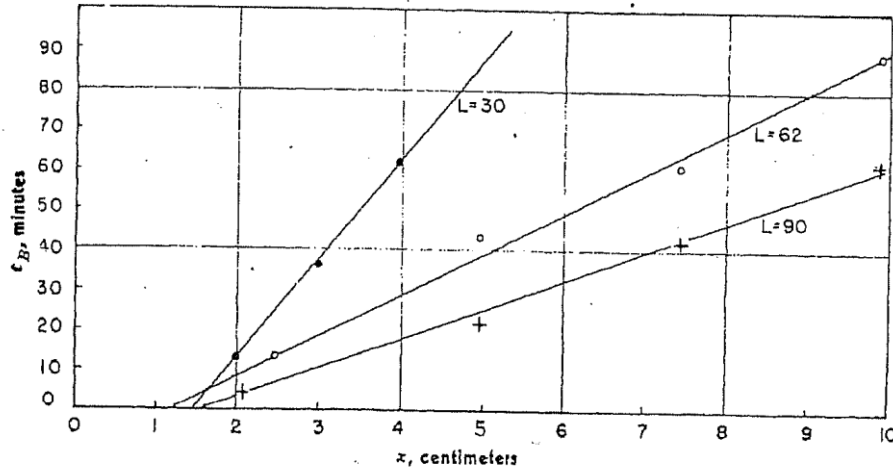


Figure 9. Life-thickness curves for phosgene at various flow rates (from ref 3).

The plot suggests a linear relationship between breakthrough time and bed thickness. On extrapolation to $t_b = 0$, the linear trend lines cross the abscissa at a finite (i.e., nonzero) thickness. This thickness represents the critical bed depth. Dole and Klotz describe this thickness, x_o , as that depth of adsorbent just sufficient to prevent the penetration of gas at a concentration greater than that established for the breakthrough concentration at zero time. An analogy is then made in that this critical bed thickness,

$x_o = z_o$, corresponds to the h parameter given in the Mecklenburg relationships (eqs 177 and 179).

7.3.2 Analytical Basis for the Dole and Klotz Development

The analytical development pursued by Dole and Klotz continues with a relationship appearing in the Bohart and Adams technical paper (ref 7). This relationship (eq 19 of ref 7) is given as

$$(1/C_i') = 1 - e^{-t'} + e^{(z'-t')} \quad (180)$$

It is noted that eq 180 is the same as eq 124, which was considered in Section 5.2 of this review. Substituting the appropriate variable transformations (from Bohart and Adams) into eq 180 yields

$$(C_o/C_i) - 1 = e^{[k a_o (z/v) - k C_o t]} - e^{-k C_o t} \quad (181)$$

Equation 181 can be reexpressed through the following series of expressions:

$$\begin{aligned} (C_o/C_i) - 1 &= [e^{k a_o (z/v)} / e^{k C_o t}] - (1/e^{k C_o t}) \\ &= [e^{k a_o (z/v)} - 1] / e^{k C_o t} \\ &= [e^{k a_o (z/v)} - 1] e^{-k C_o t} \end{aligned} \quad (182)$$

Taking the natural logarithms of each side of eq 182 yields the following series of expressions:

$$\begin{aligned} \ln [(C_o/C_i) - 1] &= \ln \{ [e^{k a_o (z/v)} - 1] e^{-k C_o t} \} \\ &= \ln [e^{k a_o (z/v)} - 1] + \ln e^{-k C_o t} \\ &= \ln [e^{k a_o (z/v)} - 1] - k C_o t \end{aligned} \quad (183)$$

Bohart and Adams describe the variable a_o as an initial uniform volume capacity of the adsorbent for the adsorbing component. In other words, a_o can be likened to an equilibrium saturation capacity (n_o). Equating a_o to n_o , eq 183 can be written as follows:

$$\ln [(C_o/C_i) - 1] = \ln [e^{k n_o (z/v)} - 1] - k C_o t \quad (184)$$

Equation 184 is the same as eq 2 in the Dole and Klotz paper (ref 3).

7.3.3 Critical Bed Depth Proportional to $\ln (C_o/C_b)$

At zero breakthrough time, eq 184 gives

$$(C_o/C_i) - 1 = e^{k_{no} (z_o/v)} - 1$$

or

$$z_o = [v/(k n_o)] \ln (C_o/C_b) \quad (185)$$

Through this analysis, having a basis with the Bohart and Adams development, the critical bed thickness (z_o) is observed to be proportional to $\ln (C_o/C_b)$.

7.3.4 Correlative Mass Transfer Relationships

In this section, mass transfer rates, incorporating a mass transfer coefficient, are used to model the adsorption process through a diffusion-limiting, rate-controlling mechanism. Dole and Klotz make use of a correlative relationship involving the dimensionless Reynolds and Schmidt numbers in their analytical development. The approach is to equate the rate of adsorption onto the surface of the adsorbent within the active MTZ to the rate of introduction of contaminant at the influent. Their analytical development is detailed as follows.

The rate at which i is transferring onto the adsorbent is given by

$$(m_i)_{ads} = (MW)_i k_g a A M_z \Delta p_m \quad (186)$$

where k_g represents a localized mass transfer coefficient expressed on a molar basis. Examination of eq 186 reveals its similarities to modern mass transfer expressions in which the rate of mass transfer is proportional to the product of a transfer coefficient and a gradient, which serves as the driving force. The relationship given by eq 186 corresponds to eq 6 of the Dole and Klotz reference (ref 3). A narrative description of the parameter groupings given by eq 186 is as follows:

- a : The effective area of adsorbent (for mass transfer) per unit volume of adsorbent.
- $A M_z$: The volume within the adsorbent column in which mass transfer occurs. This is also the volume that comprises the MTZ thickness.
- $a A M_z$: The effective area within the MTZ region available for mass transfer. This represents the area available for bulk transport of i from the vapor phase to the exterior surface of the adsorbent granules.
- k_g : The localized gas-phase mass transfer coefficient expressed on a molar basis.
- $(MW)_i k_g$: The localized gas-phase mass transfer coefficient expressed on a mass basis.
- Δp_m : The pressure gradient driving force.

Dole and Klotz give the following correlative relationship for the mass transfer coefficient:

$$k_g = \left\{ [1.82 G / ((MW)_m p_{lm,B})] \right\} [(d_p G) / \mu]^{-0.51} [\mu / (\rho D)]^{-2/3} \quad (187)$$

The correlative relationship given by eq 187 is clearly seen to contain the dimensionless groupings of the Re and Sc. The characteristic length appearing in the Re is the particle diameter of the adsorbent. The analog of eq 187 appearing in the Dole and Klotz reference (ref 3) is eq 7. Equation 187 contains the logarithmic mean partial pressure of the nontransferring component ($p_{lm,b}$). The presence of this term and how it arises in the analytical relationships associated with mass transfer is addressed in Appendix D of this review.

Provided that no contaminant has reached the effluent of the bed, Dole and Klotz maintain that the rate of adsorption of i onto the surface must be equal to the rate at which contaminant is introduced into the adsorbent system at the inlet. The rate of introduction of contaminant i at the inlet on a mass basis can be expressed as

$$(M_i)_{in} = Q C_o (MW)_i \quad (188)$$

Equating the rate at which mass is introduced into the adsorbent column (eq 188) to the rate at which mass is transferred to the external adsorbent surface (eq 186) and solving for the MTZ thickness gives

$$M_z = (Q C_o) / (k_g a A \Delta p_m) \quad (189)$$

Substituting the mole-based mass transfer coefficient, as given by eq 187, into eq 189 gives the following relationship:

$$M_z = [1 / (1.82 a)] \left\{ [(MW)_m Q C_o p_{lm,B}] / (G A \Delta p_m) \right\} Re^{0.51} Sc^{2/3} \quad (190)$$

Because the mass velocity of the airstream goes as $G = u \rho$ and the volumetric flow rate goes as $Q = u A$, eq 190 can be rewritten as

$$M_z = [1 / (1.82 a)] \left\{ [(MW)_m C_o] / \rho \right\} (p_{lm,B} / \Delta p_m) Re^{0.51} Sc^{2/3} \quad (191)$$

The quantity $\left\{ [(MW)_m C_o] / \rho \right\}$ goes as the vapor phase mole fraction of i at the inlet of the adsorbent column through the following development;

$$\begin{aligned} \left\{ [(MW)_m C_o] / \rho \right\} &= C_o / [\rho / (MW)_m] = C_o / C = [(p_i)_o / p] \\ &= (y_i)_o = y_o \end{aligned} \quad (192)$$

Substituting the relationship given by eq 192 into eq 191 yields

$$M_z = [1/(1.82 a)] (y_o p_{lm,B}/\Delta p_m) \text{Re}^{0.51} \text{Sc}^{2/3} \quad (193)$$

Assuming that the vapor phase can be characterized as an ideal mixture, then $y_o = p_o/p$, and eq 193 becomes

$$M_z = [1/(1.82 a)] [(p_o p_{lm,B})/(p \Delta p_m)] \text{Re}^{0.51} \text{Sc}^{2/3} \quad (194)$$

The relationship given by eq 194 is very close to eq 9 of the Dole and Klotz report (ref 3). The relationships differ in the presence of the total pressure term appearing in the denominator (in the Dole and Klotz relationship, this pressure factor is absent).

Dole and Klotz indicate that the following relationship is valid based on engineering experience:

$$[(p_o p_{lm,B})/\Delta p_m] = \ln (C_o/C_b) \quad (195)$$

The relationship given by eq 195 is then substituted into eq 194, which gives the following expression:

$$M_z = [1/(1.82 a)] \text{Re}^{0.51} \text{Sc}^{2/3} \ln (C_o/C_b) \quad (196)$$

It is observed that the relationship given by eq 195 lacks dimensional consistency in that the collection of parameters on the left side of the equality would have the units of a pressure, while the logarithmic ratio on the right side of the equality would be unitless. It is noted that the relationship given by eq 194 retains dimensional consistency. Some rationalizing considerations for the form of the relationship given by eq 195 are postulated in the next section.

7.3.5 Suggested Rationalization for the Validity of the Relationship Given by Equation 194

Dole and Klotz give the following relationship (eq 11 of ref 3) for the mean partial pressure difference of the transferring gas as measured from the main gas stream to the interface:

$$\Delta p_m = (p_o - p_b)/[\ln(p_o/p_b)] \quad (197)$$

Examination of the relationship given by eq 197 infers that it can be likened to a logarithmic mean pressure difference taken across the full axial length of the adsorbent column. It can also be interpreted as the logarithmic mean pressure difference within the fully developed MTZ region of the adsorbent column.

Substituting the relationship given by eq 197 into the pressure ratio term contained in the relationship provided by eq 194 gives

$$[(p_o p_{lm,B})/(p \Delta p_m)] = [p_o/(p_o - p_b)] (p_{lm,B}/p) [\ln(p_o/p_b)] \quad (198)$$

Assuming that the partial pressure of the contaminant in the inlet flow is much greater than the breakthrough partial pressure, such that $p_o \gg p_b$, then the following approximation can be made:

$$[p_o/(p_o - p_b)] \approx (p_o/p_o) = 1 \quad (199)$$

Substituting this approximation into eq 198 yields

$$[(p_o p_{lm,B})/(p \Delta p_m)] \approx (p_{lm,B}/p) [\ln(p_o/p_b)] \quad (200)$$

The logarithmic mean partial pressure of the nontransferring component is given as eq D-21 in Appendix D:

$$p_{lm,B} = (p_{B2} - p_{B1})/[\ln(p_{B2}/p_{B1})]$$

If an ideal binary vapor phase is assumed to be present (where *A* is the transferring component and *B* is the nontransferring component), the following partial pressure relationships can be written:

$$(p_{B2} - p_{B1}) = (p_{A1} - p_{A2})$$

and

$$(p_{B2}/p_{B1}) = (p - p_{A2})/(p - p_{A1})$$

Substitution of these expressions into the relationship given by eq D-21 (in Appendix D) yields the following equivalency for the logarithmic mean partial pressure of the nontransferring component:

$$p_{lm,B} = (p_{A1} - p_{A2})/\left\{\ln[(p - p_{A2})/(p - p_{A1})]\right\} \quad (201)$$

Assuming that the partial pressure in the bulk fluid phase is much greater than the partial pressure of *A* near the surface of the adsorbent such that $p_{A1} \gg p_{A2}$, then eq 201 can be approximated by

$$p_{lm,B} \approx p_{A1}/\left\{\ln[p/(p - p_{A1})]\right\} \quad (202)$$

The relationship given by eq 202 can be reworked through the following expressions:

$$\begin{aligned}
p_{lm,B} &\approx p_{A1} / \left\{ \ln[p/(p - p_{A1})] \right\} = p_{A1} / \left\{ \ln \left\{ 1/[1 - (p_{A1}/p)] \right\} \right\} \\
&= p_{A1} / \left\{ \ln[1/(1 - y_{A1})] \right\} = -p_{A1} / [\ln(1 - y_{A1})]
\end{aligned} \tag{203}$$

The logarithmic term of eq 203 can be expressed as a Taylor-series expansion through the following relationship:

$$\ln(1 - y_{A1}) = -\sum_{n=1}^{\infty} (y_{A1})^n / n \quad \text{for } -1 < y_{A1} < 1 \tag{204}$$

The first several terms of the expansion yield

$$\ln(1 - y_{A1}) \approx -y_{A1} - (y_{A1})^2/2 - (y_{A1})^3/3 - \dots \tag{205}$$

Truncating the series after the first term on the basis that since y_{A1} itself is small, then the subsequent powers of y_{A1} would be negligible, and eq 205 can be approximated as

$$\ln(1 - y_{A1}) \approx -y_{A1} \tag{206}$$

Substitution of the approximation given by eq 206 into eq 203 gives

$$p_{lm,B} \approx p_{A1} / y_{A1} \tag{207}$$

Because $p_{A1} = (p y_{A1})$, eq 207 further simplifies to

$$p_{lm,B} \approx p \tag{208}$$

The relationship given by eq 208 is then substituted into eq 200, which yields

$$[(p_o p_{lm,B}) / (p \Delta p_m)] \approx [\ln(p_o/p_b)] = [\ln(C_o/C_b)] \tag{209}$$

The relationship given by eq 209 is consistent with the final expression as proposed by Dole and Klotz (ref 3) by their eq 10. It is suspected that a pressure term was inadvertently omitted in eq 10 of the Dole and Klotz reference. It is therefore surmised that the relationship given by eq 194 was the intended form of the MTZ thickness as developed by Dole and Klotz.

7.3.6 Relationships for W_e

Several analytical models characterize adsorbent loading as a function of the partial pressure of the contaminant in the vapor phase. These relationships fall under the broad heading of isotherms. Isotherm data for the low-volatility chemical agent compounds of interest typically display a Type 1 Brunauer, Emmett, and Teller (BET)

isotherm, which is generally characterized by a rapid rise in the adsorbent loading at low partial pressures of the adsorbate. This rise in the loading eventually reaches a plateau region at which the adsorbent has reached a saturation capacity. The Type 1 BET isotherm is characterized by a downward concavity on a plot of adsorbent loading versus partial pressure over a very wide range of partial pressures. The generic types of the BET isotherms are illustrated in Figure 10 (ref 6).

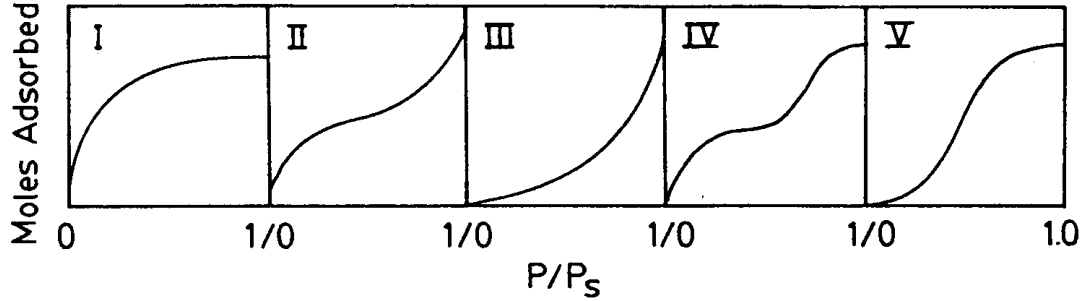


Figure 10. Illustration of BET isotherm types (from ref 6).

Other loading relationships attributed to Langmiur and Dubinin et al. have also been used. The removal of low-volatility compounds by activated carbon-based substrates is generally well characterized by the Dubinin-Radushkevich isotherm relationship.

The equilibrium loading capacity of the adsorbent for the adsorbate under the expected conditions of use (which may well be dynamic) is a key parameter that must be quantified for use in breakthrough estimations. For a given set of conditions, the equilibrium loading capacity places some bounds on the amount of contaminant that can be adsorbed. Being equilibrium-dependent, these loading characteristics are taken to be rate-independent for fixed conditions.

7.3.7 Concluding Comments: Dole and Klotz Analytical Relationships

The relationship given by eq 196 can now be substituted for the parameter h in eq 179 and solved for the breakthrough time, which yields the following expression:

$$t_b = \left\{ (W_e A \rho_b) / [Q C_o (1 - \epsilon) (MW)_i] \right\} \left\{ L - \left\{ [1 / (1.82 a)] \text{Re}^{0.51} \text{Sc}^{2/3} \ln (C_o / C_b) \right\} \right\} \quad (210)$$

The similarities between eq 210 and those expressions that are currently used to estimate the breakthrough times for strongly adsorbed components are noted. The current analytical relationships generally incorporate factors to account for the non-sphericity of the carbon granules and different exponents for the dimensionless Re and Sc numbers; however, the fundamental forms are equivalent.

Expressing the influent challenge concentration on a mass basis such that $\underline{C}_o = C_o (\text{MW})_i$, and substitution of the relationship given for a as developed by eq 59 into eq 210, yields the following equivalent form:

$$t_b = \left\{ (W_e A \rho_b) / [Q \underline{C}_o (1 - \epsilon)] \right\} \left\{ L - \left\{ \left[d_p / [6 (1.82) (1 - \epsilon)] \right] \text{Re}^{0.51} \text{Sc}^{2/3} \ln (C_o / C_b) \right\} \right\} \quad (211)$$

The expression given by eq 211 is even more similar to the current analytical approaches aimed at estimating the breakthrough times of strongly adsorbed compounds onto carbon filters for military applications.

For comparative purposes, eqs 212 and 213 were extracted from page 17 of Peterson and Karwacki (ref 11):

$$t_b = [(W_e A \rho_b) / (Q \underline{C}_o)] (L - M_z) \quad (212)$$

where

$$M_z = \left\{ (\phi_s d_p) / [6 (1 - \epsilon)] \right\} \left[(\phi_s d_p u \rho) / \mu \right]^{0.41} \left[\mu / (\rho D) \right]^{0.67} \ln (C_o / C_b) \quad (213)$$

A comparison of the forms of eqs 212 and 213 with those of eqs 210 and 211 indicates a strong correspondence and a historical lineage of these modern-day relationships to prior analytical efforts.

8. ANALYTICAL EFFORTS BY WHEELER ET AL. AND JONAS ET AL.

8.1 Background Information

Efforts to develop analytical modeling relationships aimed at adsorbent bed optimization were undertaken by the Department of the Army, Edgewood Arsenal through contractual approaches. These efforts were conducted during the 1960s under contract DA 18-035-AMC-279(A) (refs 12 and 15), which was awarded to the AiResearch Manufacturing Company (a division of the Garrett Corporation, Los Angeles, CA) by the U.S. Army Edgewood Arsenal, Chemical Research and Development Laboratories (now known as the U.S. Army ECBC).

An often-cited relationship that apparently resulted from these efforts is the Wheeler relationship, including subsequent modifications to the fundamental relationship. Wheeler (and coauthors) have also published articles in technical trade journals (e.g., ref 14). For the purposes of this review, Wheeler's efforts toward breakthrough relationships formed the focus of the analysis described in the next section.

8.2 Basic Underlying Analytical Relationships

As with previous developments, Wheeler (and others) developed analytical models based on the mass balance approach. It appears that integrated forms of fundamental mass balance expressions formed the basis of the so-called Wheeler (and variant forms) relationships. It is hypothesized that Dr. Leonard Jonas (former employee of an ECBC predecessor organization) consulted with Wheeler on the development of a breakthrough relationship that would have practical applicability to design staff personnel. The source of this hypothesis rests with a reference footnote appearing within a technical article published in the journal *Carbon* by L. A. Jonas and J. A. Rehrmann (ref 13) that reads, “Wheeler, A., private communication.” In their technical article, Jonas and Rehrmann give the following equivalent relationship to characterize the breakthrough concentration for a nonselective catalytic bed poisoning:

$$\ln(C_z/C_o) = [(k_v L)/u] \left\{ t_b / [(\rho_b W_e L)/(\underline{C}_o u)] \right\}^{-1} \quad (214)$$

The original relationship as given in the Jonas and Rehrmann reference used a different nomenclature convention than that appearing in eq 214. The relationship as given by eq 214 reflects the nomenclature convention that has been used consistently throughout this current review effort. This relationship corresponds to eq 1 of the Jonas and Rehrmann reference (ref 13).

Jonas and Rehrmann cite Wheeler and Robell (ref 14) as the source of the relationship given by eq 214.

The following relationship appears as eq 2 in the Jonas and Rehrmann reference (appropriate variable correspondences were made to be consistent with current nomenclature convention):

$$t_b = [(\rho_b W_e)/(\underline{C}_o u)] [L - (u/k_v) \ln(C_o/C_z)] \quad (215)$$

The relationship given by eq 214 can be rearranged to yield eq 215; however, the methodology is not explicitly contained within the Jonas and Rehrmann reference (ref 13). The development of the relationship given by eq 215 is attributed to a private communication with Wheeler. It is noted that eq 215 is of a form that is consistent with those relationships attributed to Wheeler.

8.3 Macroscopic Mass Balance Considerations

Early efforts undertaken by the AiResearch Manufacturing Company under contract to the U.S. Army Edgewood Arsenal during the 1960s provide the basis for how the relationship given by eq 215 was developed. In the development that follows, the underlying principles upon which the Wheeler expressions are based are described in part. This development is based on Wheeler et al. (ref 15).

The total mass of contaminant i that enters the reactor vessel over a time interval t is given by

$$(M_i)_{\text{in}} = (\text{MW})_i C_o Q t \quad (216)$$

The total mass of i that exists in the adsorbed state within the reactor is given by

$$(M_i)_{\text{ads}} = \int_0^L W_i(z, t) \rho_b A dz = \rho_b A \int_0^L W_i(z, t) dz \quad (217)$$

The cross-sectional area and the bulk density have been taken as constants in eq 217. The functional dependence of the specific mass loading on both axial position and time has been explicitly retained in eq 217.

The total mass of i that exits the reactor vessel at axial position $z = L$ is given by

$$(M_i)_{\text{eff}} = \int_0^t C_i(z = L, t) Q (\text{MW})_i dt \quad (218)$$

The variable $C_i(z = L, t)$ is interpreted as the vapor phase concentration of contaminant i evaluated at axial position $z = L$. In the subsequent analytical relationships, the following variable correspondence is used:

$$C_i(z = L, t) = C_i(L) \quad (219)$$

When the variable correspondence given by eq 219 is inserted into eq 218 and the volumetric flow rate is assumed to be constant, eq 218 can be reexpressed by

$$(M_i)_{\text{eff}} = (\text{MW})_i Q \int_0^t C_i(L) dt \quad (220)$$

The macroscopic mass balance over the entire reactor length (L) is given by

$$(M_i)_{\text{in}} = (M_i)_{\text{ads}} + (M_i)_{\text{eff}}$$

Substitution of the relationships given by eqs 216, 217, and 220 into the macroscopic mass balance relationship yields

$$(\text{MW})_i C_o Q t = \rho_b A \int_0^L W_i(z, t) dz + (\text{MW})_i Q \int_0^t C_i(L) dt \quad (221)$$

Wheeler et al. (ref 15) indicate that at very high inlet concentrations, an additional term would have to be incorporated into eq 221 to account for the mass of agent that exists within the vapor phase along the length of the reactor. This additional mass term would have the form

$$(M_i)_{\text{vap}} = (\text{MW})_i A \int_0^L C_i(z) dz \quad (222)$$

Wheeler et al. infer that at reasonably expected inlet concentrations, the bulk of the agent mass will reside on the adsorbent along the reactor length. Given that this approximation is valid, the mass contribution described by eq 222 would be negligible relative to the adsorbed phase mass as given by eq 217.

The saturation loading capacity of the carbon contained within the system is given by

$$L A \rho_b W_e \quad (223)$$

Adding and subtracting the saturation loading capacity of the carbon (the relationship given by eq 223) to the right side of the equality of the relationship given by eq 221 gives

$$\begin{aligned} (\text{MW})_i C_o Q t = \rho_b A \int_0^L W_i(z, t) dz - L A \rho_b W_e \\ + (\text{MW})_i Q \int_0^t C_i(L) dt + L A \rho_b W_e \end{aligned} \quad (224)$$

The relationship given by eq 223 can be equivalently expressed through the following correspondence:

$$L A \rho_b W_e = \rho_b A \int_0^L W_e dz \quad (225)$$

Substitution of the relationship given by eq 225 into eq 224 yields

$$\begin{aligned}
(\text{MW})_i C_o Q t &= \rho_b A \int_0^L W_i(z, t) dz - \rho_b A \int_0^L W_e dz + L A \rho_b W_e \\
&\quad + (\text{MW})_i Q \int_0^t C_i(L) dt \\
&= \rho_b A \int_0^L [W_i(z, t) - W_e] dz + L A \rho_b W_e \\
&\quad + (\text{MW})_i Q \int_0^t C_i(L) dt
\end{aligned} \tag{226}$$

The following mathematical correspondences are noted (where the explicit functional dependence of the localized specific loading has been dropped for convenience):

$$W_i - W_e = -(W_e - W_i) = -W_e [1 - (W_i/W_e)] \tag{227}$$

Substitution of the relationship given by eq 227 into eq 226 and recognizing that W_e is a constant, yields the following expression:

$$(\text{MW})_i C_o Q t = \rho_b A W_e L - \rho_b A W_e \int_0^L [1 - (W_i/W_e)] dz + (\text{MW})_i Q \int_0^t C_i(L) dt \tag{228}$$

Dividing eq 228 by the quantity $[Q C_o (\text{MW})_i]$ yields

$$\begin{aligned}
t &= [(\rho_b A W_e)/(Q C_o (\text{MW})_i)] L \\
&\quad - [(\rho_b A W_e)/(Q C_o (\text{MW})_i)] \int_0^L [1 - (W_i/W_e)] dz \\
&\quad + (1/C_o) \int_0^t C_i(L) dt
\end{aligned} \tag{229}$$

Recognizing that $(1/u) = A/Q$ and that C_o is a constant, eq 229 can be expressed in the following modified form;

$$t = [(\rho_b W_e)/(u C_o (MW)_i)] \left\{ L - \int_0^L [1 - (W_i/W_e)] dz + [(u C_o (MW)_i)/(\rho_b W_e)] \int_0^t [C_i(L)/C_o] dt \right\} \quad (230)$$

The relationship given by eq 230 is eq 12-23 in the Wheeler et al. reference (ref 15). The development of this relationship was based on the assumption that the mass of agent present in the vapor phase along the reactor length was negligible relative to the mass of agent in the adsorbed state. It is observed that many other commonly accepted mass balance relationships account for the presence of the adsorbate in the vapor phase within the interstitial volume of the adsorbent packing.

The Wheeler et al. reference (ref 15) gives the following interpretations to the parameter groupings contained in eq 230:

$$[(\rho_b W_e)/(u C_o (MW)_i)] L$$

represents the time required to saturate the adsorbent column with infinitely rapid adsorption. The relationship

$$[(\rho_b W_e)/(u C_o (MW)_i)] \int_0^L [1 - (W_i/W_e)] dz$$

represents a correction factor to account for that segment of the bed which cannot be fully used; and

$$\int_0^t [C_i(L)/C_o] dt$$

represents the amount of agent exiting the reactor.

For an adsorbent bed having prior contaminant loading, the localized contaminant loading is reduced by the specific loading of the contaminant (W_o). Therefore,

$$(W_i)_{\text{contaminated bed}} = (W_i)_{\text{clean bed}} - W_o \quad (231)$$

Substituting the expression given by eq 231 and the following total differential relationships

$$dz = (\partial C_i / \partial z)^{-1} dC_i \quad \text{and} \quad dt = (\partial C_i / \partial t)^{-1} dC_i$$

into eq 230 gives the following expression for an adsorbent bed having prior contaminant loading:

$$t_b = [(\rho_b W_e)/(u C_o (MW)_i)] \left\{ L - \int_{C_o}^{C_b} [1 - (W_i/W_e)] (\partial C_i / \partial z)^{-1} dC_i - \int_0^L (W_o/W_e) dz \right. \\ \left. + [(u C_o (MW)_i)/(\rho_b W_e)] \int_{C_o}^{C_b} [C_i(L)/C_o] (\partial C_i / \partial t)^{-1} dC_i \right\} \quad (232)$$

Through a series of mathematical manipulations, rationalization arguments, the targeting of resultant relationships to a form consistent with the basic Mecklenburg mass balance, and introduction of an adsorption rate functionality, Wheeler et al. (ref 15) give the following breakthrough relationship for low-break concentrations on an initially clean adsorbent bed:

$$t_b = [(\rho_b W_e)/(u C_o (MW)_i)] \left\{ L - (u/k_v) \int_{C_b}^{C_o} \left\{ [1 - (C_i/C_o)]/[C_i \psi(C_i)] \right\} dC_i \right. \\ \left. + (u/k_v) \int_0^{C_b} \left\{ 1/[C_o \psi(C_i)] \right\} dC_i \right\} \quad (233)$$

Further assumptions with this expression are the direct proportionality between the adsorbent mass loading ratio to the vapor-phase concentration ratio and the incorporation of a steady-state function to characterize the adsorption kinetics. This steady-state functionality, depicted by the symbol $\psi(C_i)$, is dependent on the concentration reduction ratio, defined as $F = C_i/C_o$ such that

$$\psi = \text{fcn}(C_i) = \psi(C_i) = \psi(F) \quad (234)$$

The development of the relationship given by eq 233 (for an initially clean bed) is rather formidable and was not well understood by this author.

Substituting the defined relationship for F into eq 233 yields

$$t_b = [(\rho_b W_e)/(u C_o (MW)_i)] \left\{ L - (u/k_v) \int_{F_b}^1 \left\{ (1 - F)/[F \psi(F)] \right\} dF \right. \\ \left. + (u/k_v) \int_0^{F_b} [1/\psi(F)] dF \right\} \quad (235)$$

Upon comparison of eq 235 to the basic Mecklenburg relationship (eq 146), the depth of the MTZ thickness is given by

$$M_z = (u/k_v) \left\{ \int_{F_b}^1 \left\{ (1-F)/[F \psi(F)] \right\} dF - \int_0^{F_b} [1/\psi(F)] dF \right\} \quad (236)$$

The relationship given by eq 236 is given by eq 12-48 of the Wheeler et al. reference (ref 15).

For the special case in which $\psi(F) = (1 - F)$, eq 236 yields

$$M_z = (u/k_v) \ln[(C_o/C_b) - 1] \quad (237)$$

The relationship given by eq 237 is termed as the “modified Mecklenburg” form of the MTZ thickness. Wheeler et al. indicated that the modified Mecklenburg expression is valid *only* if the velocity of propagation of the adsorption wave is constant from $t = 0$ onward. This is pointed out to be a poor assumption, because the velocity of propagation of the adsorption wavefront is somewhat less than the steady-state propagation associated with a uniformly developed wavefront. The uniformity of the wavefront develops with time and distance into the column. Prior to the establishment of a uniformly characterized adsorption wavefront, the contours of the adsorption wave are dynamic.

Upon consideration of several assumed analytical forms to characterize the adsorption kinetics (see relationship given by eq 234), Wheeler et al. were able to ascertain that the ratio (u/k_v) naturally arose. This occurrence suggested a form of the Mecklenburg-based breakthrough relationship consistent with the following relationship:

$$t_b = [(\rho_b W_e)/(u C_o (MW)_i)] \left\{ L - (u/k_v) \ln[K (C_o/C_b)] \right\} \quad (238)$$

where K is a multiplicative factor that is dependent on the functional form assumed for the concentration reduction ratio (F). The relationship given by eq 238 appears as eq 12-54 of the Wheeler et al. reference (ref 15). The ratio (C_o/C_b) has been assumed to be much larger than 1 in the relationship given by eq 238.

Figure 11 contains a table appearing in the Wheeler et al. reference that denotes various values for the K parameter corresponding to assumed forms of the adsorption rate function. The symbol L_o is the depth of the MTZ, which has been indicated by the symbol M_z throughout this review effort.

$\psi(F)$	L_o	F_{max}	K	F_c
$1 - F$	$\frac{V_L}{k_v} \ln \left(\frac{C_o}{C} - 1 \right)$	0.50	1.0	0.50
$(1 - F)^{1/2}$	$\frac{V_L}{k_v} \ln \left(\frac{1 + \sqrt{1 - C/C_o}}{1 - \sqrt{1 - C/C_o}} e^{-2} \right)$	0.667	$0.542 = 4 e^{-2}$	0.42
$1 - F^{3/2}$	$\frac{V_L}{k_v} \left[\ln \left(\frac{1 + \sqrt{1 - C/C_o}}{1 - \sqrt{1 - C/C_o}} \right) - 2 \left(\frac{1 - \sqrt{1 - C/C_o}}{\sqrt{1 - C/C_o}} \right) \right]$	0.400	4	0.485
$1 - F^2$	$\frac{V_L}{k_v} \ln \frac{\sqrt{1 - F^2}}{2F}$	0.5733	0.50	$0.477 = \sqrt{0.20}$
$1 - F^3$	$\frac{V_L}{k_t} \left[\frac{1}{2} \ln \frac{1 + F + F^2}{3F^2} - \frac{1}{\sqrt{3}} \left(\frac{\pi}{3} - \tan^{-1} \frac{2F + 1}{\sqrt{3}} \right) - \int_0^F \frac{dF}{1 - F^3} \right]$	0.630	$0.425 = \frac{1}{\sqrt{3}} \exp \frac{-\pi}{6\sqrt{3}}$	
$1 - F^\infty$	$\frac{V_L}{k_v} \ln e^{-1} \frac{C_o}{C}$	1.0	$e^{-1} = 0.368$	
$1 - F^{1/2}$	$\frac{V_L}{k_v} \ln \left[\frac{e^2}{F} (1 - \sqrt{F})^2 \right]$	0.444	$e^2 = 7.39$	0.536

Figure 11. Functional forms of $\psi(F)$ and resultant MTZ thicknesses (from ref 15).

The variation in the value of the parameter K with respect to the assumed functionality of $\psi(F)$ is readily apparent in Figure 11. When used in conjunction with the Wheeler et al. relationship given by eq 238, this can cause quite a bit of variance with the estimated breakthrough time. The evaluation of the rate constant k_v would be determined experimentally.

8.4 Jonas and Rehrmann Breakthrough Relationship

In their investigative efforts to characterize the breakthrough of organophosphorous compounds through activated carbon beds, Jonas and Rehrmann (ref 13) used the Wheeler-based relationship as given by eq 238 with $K = 1$. This yields the following relationship:

$$t_b = [(\rho_b W_e)/(u C_o (MW)_i)] \left\{ L - (u/k_v) \ln(C_o/C_b) \right\} \quad (239)$$

From the tabular entries contained in Figure 11, a parameter value of $K = 1$ corresponds to the following functional form for $\psi(F)$:

$$\psi(F) = 1 - F \quad (240)$$

Wheeler et al. (ref 15) indicated that the functional breakthrough relationship given by eq 239 contains some rather significant assumptions, the major one being the assumption of a steady-state propagation velocity of the adsorption wave at time $t = 0$. Wheeler et al. indicated that an initial time interval and adsorbent bed depth are required to establish a consistent wave contour for an initially clean adsorbent column.

8.5 Closing Commentary on the Wheeler-Based Relationships

As indicated earlier in this section, significant portions of the analytical manipulations and rationalizations pursued by Wheeler et al. were not well understood. Although the development of the basic mass balances (given by eqs 230 and 232 are relatively straightforward, much of the later analytical development is of a complex nature.

An assumption relating to the basic Wheeler and Jonas breakthrough relationships is that the amount of contaminant that exists in the vapor phase (i.e., the interstitial volume of the adsorbent packing) is negligible relative to the amount that exists in the adsorbed state. Wheeler et al. qualify this approximation in their development (ref 15). It is noted that other mass balance approaches also include the mass of contaminant that is contained in the interstitial volume.

A potential weakness of the Wheeler et al. and Jonas et al. breakthrough relationships is their reliance on having access to actual data to estimate the rate constant k_v . This data is often not readily available to the typical practicing engineer in making filter performance estimations.

The Klotz et al. mass balance relationships appear to be more user-friendly in that the expressions require the evaluation of specific parameters through readily accepted correlative techniques. The currently used Klotz-based relationships assume that bulk diffusion is the rate-limiting step.

9. CONSIDERATIONS WITH CYANIDE-BASED CONTAMINANTS

Sections 2 through 8 of this review focused on the adsorption of compounds that are assumed to be very favorably removed from a contaminated airstream through an idealized physical adsorption pathway. The notable exceptions were chlorine (ref 7) and phosgene (ref 3), in which hydrolysis and chemisorption mechanistic pathways contribute considerably to the removal of these materials from a contaminated air flow. With compounds having a room temperature vapor pressure of less than 10 torr, the primary removal mechanism is often attributed to physical adsorption. The rate of removal is often assumed to be diffusion-limited in the bulk phase.

The cyanide materials having elevated room-temperature vapor pressures require the presence of specific impregnant materials within the pore structure of the activated carbon provide capacity against this class of compounds. A requisite

characteristic for activated carbons that can be impregnated to increase their capacity against the cyanide-containing compounds is that the basic substrate possess a sufficient macropore volume. This macroporous structure is needed to provide ready access to the vapor contaminants into the porous structure of the carbon and to the intraporous regions that contain the impregnants.

As the analytical expressions for the strongly adsorbed materials are based on diffusive-based rate relationships, these expressions are not appropriate to use with the cyanide-based compounds.

Figure 12 (ref 16) depicts a series of life-thickness curves for Cyanogen Chloride (CK) on a current impregnated carbon substrate. This plot is based on data obtained from the developmental effort for ASZM-TEDA impregnated activated carbon with a particle size range within the 12×30 mesh envelope.

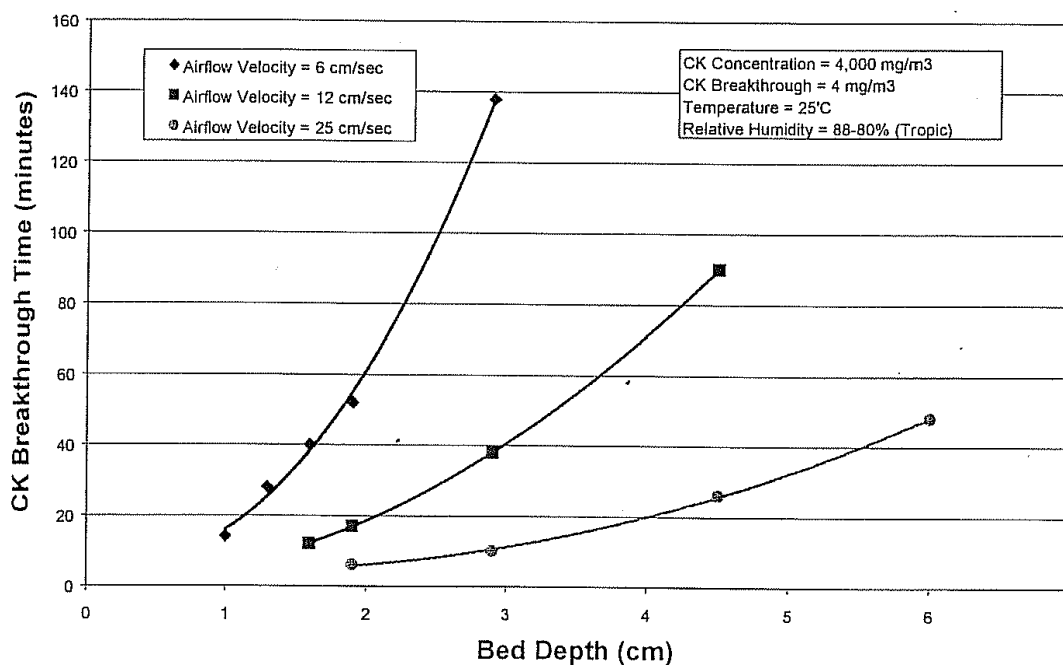


Figure 12. CK life-thickness curves for 12×30 ASZM-TEDA carbon (from ref 16).

Figure 12 is analogous to Figure 9 of this review effort. The fitted trendlines exhibit slight curvature. Linear trendlines could also be fitted (as in the case of Figure 9) that would clearly cross the abscissa at definitive values corresponding to a critical bed depth.

With an elevated room-temperature vapor pressure, CK exhibits greatly reduced physical adsorption capacity as compared to low-volatility organics under near-atmospheric conditions. The addition of impregnant materials (to the activated carbon

substrate) is needed to provide capacity to the carbon against high-volatility and reactive chemical contaminants.

The fundamental mass balance relationships developed in the various sections of this report can be used to characterize the vapor phase concentrations of CK throughout the adsorbent bed as a function of position and time provided that rate parameters associated with the destruction of CK (i.e., the η and R_i terms) are known or can be determined through experimentation. As has been demonstrated, the complexity of the resulting analytical relationships is formidable. The energetic aspects associated with the adsorption and heats of reaction should also be considered for reactionary removal processes (as well as for removal mechanisms that are characterized by ideal physical adsorption).

The rate-limiting step associated with the removal of the cyanide compounds is believed to be due to a combination of initial, limited physical adsorption followed by a sequence of chemical reactionary mechanisms. This is compared to a mass transfer rate-limiting mechanistic sequence. It is generally accepted that the basic activated carbon substrate must process a broad distribution of pore sizes to have sufficient capacity against CK under a range of exposure conditions. The large pores are needed to provide rapid access of the contaminated airstream to the meso- and micropores where the impregnants typically reside. It is within these meso- and micropores that the majority of the porous volume resides.

A simplistic approach at estimating the CK performance of a filter is to relate the actual flow characteristics of the filter to the closest corresponding velocity trend line appearing on a life-thickness plot such as provided in Figure 12. The normalizing parameter is taken to be the residence time. Once a pseudo-bed depth is determined (through the residence-time normalization), a breakthrough time can be estimated through a correlative fit to the data set.

Filter performance estimations against hydrogen cyanide are generally conducted in an analogous manner. The key requirement would be to have actual life-thickness data at the flow conditions that mimic the actual system.

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NOMENCLATURE AND ABBREVIATIONS

α	porosity or fraction of voids per unit gross volume of bed
δ	fraction of the total adsorbent system volume that can be utilized for adsorptive capacity
ε	volume-based void fraction
η	moles of toxic gas on or in the granules contained in a unit volume of bed
θ	circumferential direction
θ (subscript)	circumferentially directed flow
μ	fluid phase viscosity
ρ	density of airstream or density of gas film
ρ_i	density characteristic associated with i
v	analogous to a superficial flow velocity related to the rate of supply (as used in Section 5) of chlorine per length of charcoal saturated per time
φ_s	sphericity factor
ψ	symbol used for collection of parameters = $[(\partial C_i / \partial \theta) (1/r)]$; also, function to characterize the kinetics of adsorption. As used in further developments, the assumed form of this function is taken to be a function the vapor phase concentration reduction ratio (as used in Section 8)
a, a_p	ratio of particle surface area to volume of adsorbent bed
a	residual volume-based chlorine capacity of the charcoal (as used in Section 5)
AB (subscript)	component A with respect to B
ads (subscript)	of or relating to the adsorbent
A_i	surface area associated with characteristic i descriptor
b (subscript)	of or relating to a bulk system characteristic such as a bulk density or when used with a molar concentration, to designate a breakthrough condition
C	total molar concentration
CG	phosgene
C_i	vapor phase molar concentration of component i
$\underline{C}_o$	vapor phase concentration of challenge flow expressed on a mass basis
cyl (subscript)	of or pertaining to a cylinder
d, d_p	particle diameter assumed to be an ideal sphere
$\mathfrak{D}$	binary diffusivity

$\mathcal{D}_i$	generalized dispersion coefficient of component i in a binary system
$\mathcal{D}_{ij}$	dispersion coefficient of component i in the vapor phase associated with direction j
$\mathcal{D}_{AB}$	binary diffusion coefficient of component A in component B
$\mathcal{D}_L$	uniform, nondirectional dispersion coefficient
e (subscript)	effluent value or evaluated at equilibrium condition
F	generic mass transfer coefficient, {moles of i transferred/[area time]}
F	concentration reduction ratio, C_i/C_o (as used in Section 8)
G	mass velocity of airstream, product of a density and velocity
h	height of cylinder or critical bed depth
i (subscript)	designator for component i or generic designator
in (subscript)	associated with a flow or flux entering into volume element
I_x	critical bed thickness contribution due to specific adsorptive mechanistic pathway x
j (subscript)	designator associated with a specific direction in space
J_A	molar flux of component A
K	multiplicative factor that is a function of the concentration ratio F of the Wheeler et al. modeling development (as used in Section 8)
k	rate constant
k_v	first-order rate constant (as used in Section 8)
k_g	gas-phase mass transfer coefficient, {moles of i transferred/[area time (driving force)]}
L	bed depth or length of an adsorbent column also used as a volumetric flow rate
MTZ	mass transfer zone
M_i	mass of component i
M_z	mass transfer zone or critical bed depth/thickness
$(MW)_i$	molecular weight of component i
$(MW)_m$	mean molecular weight of binary vapor-phase system
$\dot{m}_i$	rate of mass flow associated with component i
N_{ij}	molar flux of component i associated with direction j
net (subscript)	net characteristic
n_o	saturation capacity of carbon for contaminant i , expressed in moles of i per volume of adsorbent
o (subscript)	influent concentration or initial condition
out (subscript)	associated with a flow or flux exiting from a volume element

p	total pressure
p_o	partial pressure of gas entering adsorbent system
p_{Ai}	partial pressure of component A at position i
$p_{lm,B}$	log mean partial pressure of nontransferring species in gas film
Δp_m	mean partial pressure difference of transferring compound measured from the bulk vapor phase to a concentration measured at the interface
Q	volumetric flow rate
q_i	mass loading of adsorbate i per volume of adsorbent
r (subscript)	radially directed flow
Re	Reynolds number
R_i	consumption rate of component i on a volumetric basis
r	radius or radial direction
S	arc length ($r \theta$)
Sc	Schmidt number
t	time
t (subscript)	critical bed thickness contribution due to bulk diffusion
tot (subscript)	of or relating to a total system characteristic
total (subscript)	of or relating to a total parameter characteristic
u_j	averaged superficial velocity associated with direction j
V	volume
V_i	volume associated with characteristic i descriptor
v_i	fluid flow velocity associated with direction i
void (subscript)	of or relating to the void space associated with a granular packing of solids
W_i	mass loading of adsorbate i per mass of adsorbent
w	rate of mass transfer
x	characteristic edge dimension of FCC unit cell
x_o	bed depth thickness over which active mass transfer is occurring, critical bed depth, mass transfer zone thickness
x, y, z (subscript)	three mutually perpendicular axis in an orthogonal coordinate system or associated with a directional flow
y_A	vapor phase mole fraction of component A
z	directional axis
z_o	bed depth thickness over which active mass transfer is occurring, critical bed depth, mass transfer zone thickness

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APPENDIX A FLUX GRADIENT IN THE RADIAL DIRECTION

The intent of this appendix is to detail the analytical development of the radial flux gradient given by eq 38. Per the format provided by the eq 11 relationship, the radial flux gradient would be expressed in terms of an arc length (S). This appendix provides the mathematical details in relating the flux gradient expressed in terms of an arc length to an angle (θ).

Dimensional consistency requires that the gradient of the molar flux associated with the radial direction have the units of moles of i /(volume time). Using the form of eq 11, the flux gradient in the radial direction would formally take on the following relationship:

$$(\partial N_{i\theta}/\partial S) = [\partial(u_{\theta} C_i)/\partial S] - \mathfrak{D}_L (\partial^2 C_i/\partial S^2) \quad (\text{A-1})$$

where $\mathfrak{D}_{ij}$ has been assumed to be constant-valued and equal to $\mathfrak{D}_L$.

The arc length is related to its angular and dimensional components through the following expression:

$$S = r \theta \quad (\text{A-2})$$

The total differential of eq A-2 is given by

$$dS = (\partial S/\partial \theta) d\theta + (\partial S/\partial r) dr \quad (\text{A-3})$$

As an expression for the change in S with respect to angular position (θ) is sought at a constant radial position, eq A-3 simplifies to

$$(dS/d\theta) = (\partial S/\partial \theta) \quad (\text{A-4})$$

From the relationships given by eqs A-2 and A-4, the following derivatives can be written for a constant radius:

$$(\partial S/\partial \theta) = r \quad \text{or} \quad (\partial \theta/\partial S) = 1/r \quad (\text{A-5})$$

With the relationship given by eq A-5, the following correspondence holds:

$$[\partial(u_{\theta} C_i)/\partial S] = [\partial(u_{\theta} C_i)/\partial \theta] (\partial \theta/\partial S) = (1/r) [\partial(u_{\theta} C_i)/\partial \theta] \quad (\text{A-6})$$

Similarly, the following correspondence holds:

$$(\partial N_{i\theta}/\partial S) = (\partial N_{i\theta}/\partial \theta) (\partial \theta/\partial S) = (1/r) (\partial N_{i\theta}/\partial \theta) \quad (\text{A-7})$$

With the relation given by eq A-5, the derivative $(\partial^2 C_i / \partial S^2)$ can then be related to the angular position θ through the following development;

$$\begin{aligned} (\partial^2 C_i / \partial S^2) &= [\partial(\partial C_i / \partial S) / \partial S] = \partial[(\partial C_i / \partial \theta) (\partial \theta / \partial S)] / \partial S \\ &= \partial[(\partial C_i / \partial \theta) (1/r)] / \partial S \end{aligned} \quad (\text{A-8})$$

Letting $\psi = [(\partial C_i / \partial \theta) (1/r)]$, eq A-8 can be further developed as

$$\begin{aligned} \partial[(\partial C_i / \partial \theta) (1/r)] / \partial S &= (\partial \psi / \partial S) = (\partial \psi / \partial \theta) (\partial \theta / \partial S) = (\partial \psi / \partial \theta) (1/r) \\ &= (1/r) (\partial \psi / \partial \theta) = (1/r) \left\{ \partial[(\partial C_i / \partial \theta) (1/r)] / \partial \theta \right\} \end{aligned} \quad (\text{A-9})$$

Since the radius is a constant, it can be removed from the derivative of eq A-9, which yields the following series of relationships:

$$\begin{aligned} (\partial^2 C_i / \partial S^2) &= \partial[(\partial C_i / \partial \theta) (1/r)] / \partial \theta = (1/r^2) \left\{ \partial[(\partial C_i / \partial \theta)] / \partial \theta \right\} \\ &= (1/r^2) (\partial^2 C_i / \partial \theta^2) \end{aligned} \quad (\text{A-10})$$

The molar flux gradient in the radial direction can therefore be related to θ through the relationships given by eqs A-6, A-7, and A-10. This correspondence is as follows:

$$\begin{aligned} (\partial N_{i\theta} / \partial S) &= (1/r) (\partial N_{i\theta} / \partial \theta) \\ &= (1/r) [\partial(u_\theta C_i) / \partial \theta] - D_L (1/r^2) (\partial^2 C_i / \partial \theta^2) \end{aligned} \quad (\text{A-11})$$

APPENDIX B

CONTINUITY RELATIONSHIP FOR CYLINDRICAL COORDINATE SYSTEM

This appendix provides the rationale for the relationship given by eq 43. The analytical development contained in this appendix is based on the cylindrical configuration depicted in Figure 2. It is further assumed that the differential volume element is spatially fixed within its coordinate reference frame.

With respect to the z -direction, the rate at which mass enters the differential volume element at position z is given by

$$\rho u_z(z) r \Delta\theta \Delta r \quad (\text{B-1a})$$

The rate at which mass exits the differential volume element in the z -direction at position $(z + \Delta z)$ is given as

$$\rho u_z(z + \Delta z) r \Delta\theta \Delta r \quad (\text{B-1b})$$

With respect to the θ -direction, the rate at which mass enters the differential volume element at position θ is given by

$$\rho u_\theta(\theta) \Delta r \Delta z \quad (\text{B-2a})$$

The rate at which mass exits the differential volume element in the θ -direction at position $(\theta + \Delta\theta)$ is given as

$$\rho u_\theta(\theta + \Delta\theta) \Delta r \Delta z \quad (\text{B-2b})$$

The rate at which mass enters the differential volume element in the r -direction at position r is given by

$$\rho u_r(r) r(r) \Delta\theta \Delta z \quad (\text{B-3a})$$

The rate at which mass exits the differential volume element in the r -direction at radial position $(r + \Delta r)$ is given as

$$\rho u_r(r + \Delta r) r(r + \Delta r) \Delta\theta \Delta z \quad (\text{B-3b})$$

The total mass of material contained within the differential volume element is given by

$$M = \rho \Delta V = \rho r \Delta\theta \Delta r \Delta z \quad (\text{B-4})$$

The rate of change of mass within the differential volume element is given by

$$(dM/dt) = \Delta\theta \Delta r \Delta z [\partial(\rho r)/\partial t] \quad (\text{B-5a})$$

If the mass density within the differential volume element is taken to be a constant (mass conservation), eq B-5a becomes

$$(dM/dt) = \rho \Delta\theta \Delta r \Delta z (\partial r/\partial t) \quad (\text{B-5b})$$

The mass balance relationship written over the differential volume element is expressed as

$$(dM/dt) = \sum (m_i)_{\text{in}} - \sum (m_i)_{\text{out}} \quad (\text{B-6})$$

Substitution of the relationships given by eqs B-1, B-2, B-3, and B-5 into the relationship given by eq B-6 gives the following expression:

$$\begin{aligned} \rho \Delta\theta \Delta r \Delta z (\partial r/\partial t) = & -\rho r \Delta\theta \Delta r [u_z(z + \Delta z) - u_z(z)] \\ & -\rho \Delta r \Delta z [u_\theta(\theta + \Delta\theta) - u_\theta(\theta)] \\ & -\rho \Delta\theta \Delta z [u_r(r + \Delta r) r(r + \Delta r) - u_r(r) r(r)] \end{aligned} \quad (\text{B-7})$$

Division of eq B-7 by the quantity $(\rho \Delta\theta \Delta r \Delta z)$ and taking the limit as $\Delta\theta$, Δr , and Δz collapse to zero gives the following relationship:

$$(\partial r/\partial t) = -r (\partial u_z/\partial z) - (\partial u_\theta/\partial\theta) - [\partial(u_r r)/\partial r] \quad (\text{B-8a})$$

With a fixed spatial reference, $(\partial r/\partial t) = 0$, and eq B-8a simplifies to

$$r (\partial u_z/\partial z) + (\partial u_\theta/\partial\theta) + [\partial(u_r r)/\partial r] = 0 \quad (\text{B-8b})$$

or

$$(\partial u_z/\partial z) + (1/r) (\partial u_\theta/\partial\theta) + (\partial u_r/\partial r) + (u_r/r) = 0 \quad (\text{B-8c})$$

The relationship given by eq B-8c is eq 43.

APPENDIX C ON DIFFERENTIALS, PARTIAL DERIVATIVES, AND TOTAL DERIVATIVES

The differential mass balance developments in this effort rely heavily on the concepts of differentials, partial derivatives, and total derivatives. The intent of this appendix is to clarify their use and interpretation.

Consider the molar flux which has a functional dependence on both time and spatial position. Time and the positional parameters are taken to be independent variables. For a cylindrical coordinate system, the functional form of the molar flux can be represented as follows;

$$N_i = N_i(t, r, \theta, z) \quad (C-1)$$

The molar flux corresponding to an incremental change in time and position can be represented by the following relationship:

$$N_i = N_i(t + \Delta t, r + \Delta r, \theta + \Delta \theta, z + \Delta z) \quad (C-2)$$

The differential or total change of molar flux in making this time and positional transition is the difference between eqs C-2 and C-1. Therefore,

$$\Delta N_i = N_i(t + \Delta t, r + \Delta r, \theta + \Delta \theta, z + \Delta z) - N_i(t, r, \theta, z) \quad (C-3)$$

The relationship given by eq C-3 represents the total differential of the molar flux. It accounts for changes in the flux due to spatial translations in each vector direction as well as time.

An expression that relates the change in the molar flux in terms of its independent variables is then sought. The approach is detailed as follows.

Addition and subtraction of $N_i(t, r + \Delta r, \theta + \Delta \theta, z + \Delta z)$ to the right side of eq C-3 gives the following expression:

$$\begin{aligned} \Delta N_i = \{ & N_i(t + \Delta t, r + \Delta r, \theta + \Delta \theta, z + \Delta z) - N_i(t, r + \Delta r, \theta + \Delta \theta, z + \Delta z) \} \\ & + N_i(t, r + \Delta r, \theta + \Delta \theta, z + \Delta z) - N_i(t, r, \theta, z) \end{aligned} \quad (C-4)$$

Addition and subtraction of $N_i(t, r, \theta + \Delta \theta, z + \Delta z)$ to the right side of eq C-4 gives the following expression:

$$\begin{aligned}
\Delta N_i = & \{N_i(t + \Delta t, r + \Delta r, \theta + \Delta\theta, z + \Delta z) - N_i(t, r + \Delta r, \theta + \Delta\theta, z + \Delta z)\} \\
& + \{N_i(t, r + \Delta r, \theta + \Delta\theta, z + \Delta z) - N_i(t, r, \theta + \Delta\theta, z + \Delta z)\} \\
& + N_i(t, r, \theta + \Delta\theta, z + \Delta z) - N_i(t, r, \theta, z)
\end{aligned} \tag{C-5}$$

Addition and subtraction of $N_i(t, r, \theta, z + \Delta z)$ to the right side of eq C-5 gives the following expression;

$$\begin{aligned}
\Delta N_i = & \{N_i(t + \Delta t, r + \Delta r, \theta + \Delta\theta, z + \Delta z) - N_i(t, r + \Delta r, \theta + \Delta\theta, z + \Delta z)\} \\
& + \{N_i(t, r + \Delta r, \theta + \Delta\theta, z + \Delta z) - N_i(t, r, \theta + \Delta\theta, z + \Delta z)\} \\
& + \{N_i(t, r, \theta + \Delta\theta, z + \Delta z) - N_i(t, r, \theta, z + \Delta z)\} \\
& + \{N_i(t, r, \theta, z + \Delta z) - N_i(t, r, \theta, z)\}
\end{aligned} \tag{C-6}$$

Multiplying the first bracketed expression on the right side of eq C-6 by $(\Delta t/\Delta t)$, the second bracketed expression by $(\Delta r/\Delta r)$, the third bracketed expression by $(\Delta\theta/\Delta\theta)$, and the fourth bracketed expression by $(\Delta z/\Delta z)$, gives the following relationship:

$$\begin{aligned}
\Delta N_i = & \{[N_i(t + \Delta t, r + \Delta r, \theta + \Delta\theta, z + \Delta z) - N_i(t, r + \Delta r, \theta + \Delta\theta, z + \Delta z)]/\Delta t\} \Delta t \\
& + \{[N_i(t, r + \Delta r, \theta + \Delta\theta, z + \Delta z) - N_i(t, r, \theta + \Delta\theta, z + \Delta z)]/\Delta r\} \Delta r \\
& + \{[N_i(t, r, \theta + \Delta\theta, z + \Delta z) - N_i(t, r, \theta, z + \Delta z)]/\Delta\theta\} \Delta\theta \\
& + \{[N_i(t, r, \theta, z + \Delta z) - N_i(t, r, \theta, z)]/\Delta z\} \Delta z
\end{aligned} \tag{C-7}$$

In the limit as the differentials of the independent variables and the dependent variable approach zero, the differentials become total differentials, and the bracketed expressions become partial derivatives. Performing this operation on eq C-7 gives the following:

$$dN_i = (\partial N_i/\partial t) dt + (\partial N_i/\partial r) dr + (\partial N_i/\partial\theta) d\theta + (\partial N_i/\partial z) dz \tag{C-8}$$

Dividing each term of eq C-8 by the total time differential gives

$$(dN_i/dt) = (\partial N_i/\partial t) + (\partial N_i/\partial r) (dr/dt) + (\partial N_i/\partial\theta) (d\theta/dt) + (\partial N_i/\partial z) (dz/dt) \tag{C-9a}$$

The (d/dt) terms represent total derivatives with respect to time. As given by eq C-9a, they correspond to directionally oriented velocities associated with a moving

reference frame. Following the path of a specific volume element, these oriented velocities can be represented as follows:

$$\begin{aligned}v_r &= (dr/dt) \\v_\theta &= (d\theta/dt) \\v_z &= (dz/dt)\end{aligned}\tag{C-10a}$$

Substituting the relationships given by eq C-10 into eq C-9a gives the following relationship:

$$(dN_i/dt) = (\partial N_i/\partial t) + v_r (\partial N_i/\partial r) + v_\theta (\partial N_i/\partial \theta) + v_z (\partial N_i/\partial z) \tag{C-9b}$$

The relationship given by eq C-9b would be applicable if one were interested in the change in molar flux as a given fluid element traversed the adsorbent column. In many situations of practical importance, one of the directional velocities is taken to be dominant relative to the others and it is the principle velocity that is considered. The gradients and velocities associated with the non-principle directions are then assumed to be negligible.

For instances in which one is interested in the molar flux relative to a fixed spatial position, the differential volume element is stationary such that $v_r = v_\theta = v_z = 0$, and eq C-9b gives the following relationship:

$$(dN_i/dt) = (\partial N_i/\partial t) \tag{C-11}$$

The relationship given by eq C-11 would have applicability where one is interested in the rate of change of the molar flux with time with respect to a fixed spatial reference.

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APPENDIX D ASPECTS ASSOCIATED WITH MASS TRANSFER COEFFICIENTS IN BINARY SYSTEMS

(a) Development of Fundamental Steady-State Molar Flux Relationship for a Binary System

The Dole and Klotz developmental efforts introduce a mass transfer coefficient (k_g) and a logarithmic mean partial pressure of the nontransferring component ($p_{lm,b}$) in their analytical relationships. The intent of this appendix is to provide a basis for how these terms arise. The effort that follows is based on a treatment given in a text written by R. E. Treybal, titled *Mass Transfer Operations* (ref 17).

In the analysis that follows, a binary fluid system, comprised of species A and B, is considered. The transfer of mass, relative to a fixed reference plane, will be assumed to occur in a singular direction only. This singular direction is taken to be the z-axis. Figure D-1 gives a diagram of the system that was used in this analysis.

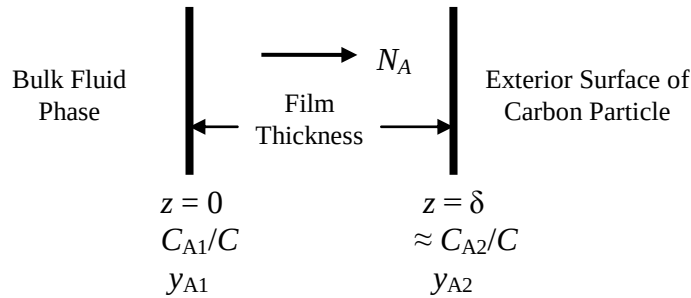


Figure D-1. Depiction of molar flux through a film thickness.

Through Fick's law of diffusion, the molar flux in the z-direction (J_A) is proportional to a diffusion coefficient (or diffusivity), and its concentration gradient. Mathematically, this relationship is expressed as follows;

$$J_A = -D_{AB} (\partial C_A / \partial z) \quad (D-1a)$$

If the total molar concentration (C) is taken as a constant, then eq D-1a can be expressed in terms of its mole fraction equivalent as follows:

$$J_A = -C D_{AB} (\partial y_A / \partial z) \quad (D-1b)$$

The net total molar flux of this binary system relative to a fixed reference plane is given as

$$N = N_A + N_B \quad (D-2)$$

The transfer of A in this binary system is comprised of that portion of the total flux which is comprised of component A and that resulting from its diffusion. Therefore, the transfer of A can be described by the following relationships:

$$\begin{aligned}
 N_A &= N y_A + J_A \\
 &= (N_A + N_B) y_A - \mathfrak{D}_{AB} (\partial C_A / \partial z) \\
 &= (N_A + N_B) (C_A / C) - \mathfrak{D}_{AB} (\partial C_A / \partial z)
 \end{aligned} \tag{D-3}$$

By analogy, a similar expression can be written for component B which yields the following;

$$N_B = (N_A + N_B) (C_B / C) - \mathfrak{D}_{BA} (\partial C_B / \partial z) \tag{D-4}$$

Since the total molar concentration is given by $C = (C_A + C_B)$, eq D-3 and eq D-4 can be added together which gives the following expression;

$$-\mathfrak{D}_{AB} (\partial C_A / \partial z) = \mathfrak{D}_{BA} (\partial C_B / \partial z) \tag{D-5}$$

If the total concentration can be taken as a constant, then $\mathfrak{D}_{AB} = \mathfrak{D}_{BA}$. This argument demonstrates the equivalency between the diffusivities of this binary system provided that the total molar concentration can be taken as a constant.

The following analysis focuses on eq D-3. Separation of eq D-3 yields the following relationship:

$$-[C N_A - (N_A + N_B) C_A]^{-1} \partial C_A = (C \mathfrak{D}_{AB})^{-1} \partial z \tag{D-6}$$

With the total molar concentration (C) and steady-state localized component fluxes (i.e., N_A and N_B as constants), eq D-6 can be integrated between the concentration limits of C_{A1} and C_{A2} , and the position limits z_1 and z_2 , respectively. The integration is carried out as follows:

$$-\int_{C_{A1}}^{C_{A2}} [C N_A - (N_A + N_B) C_A]^{-1} \partial C_A = \int_{z_1}^{z_2} (C \mathfrak{D}_{AB})^{-1} \partial z \tag{D-7}$$

With C and $\mathfrak{D}_{AB}$ as constants, the integral on the right hand side of eq D-7 is readily integrated to yield

$$\int_{z_1}^{z_2} (C \mathfrak{D}_{AB})^{-1} \partial z = (z_2 - z_1) / (C \mathfrak{D}_{AB}) \tag{D-8}$$

The following variable substitutions are made to the integral on the left side of eq D-7:

Letting $u = [C N_A - (N_A + N_B) C_A]$, the following differentials result:

$$\begin{aligned} (\partial u / \partial C_A) &= [\partial(C N_A) / \partial C_A] - \{\partial[(N_A + N_B) C_A] / \partial C_A\} \\ &= -(N_A + N_B) \end{aligned}$$

or

$$\partial C_A = -(N_A + N_B)^{-1} \partial u$$

Changing the limits of integration (to reflect the variable substitution) and making the variable substitutions into the integral on the left side of eq D-7 yields the following expressions:

$$\begin{aligned} - \int_{C_{A1}}^{C_{A2}} [C N_A - (N_A + N_B) C_A]^{-1} \partial C_A &= - \int_{C N_A - (N_A + N_B) C_{A1}}^{C N_A - (N_A + N_B) C_{A2}} u^{-1} [-(N_A + N_B)^{-1}] \partial u \\ &= [1/(N_A + N_B)] \int_{C N_A - (N_A + N_B) C_{A1}}^{C N_A - (N_A + N_B) C_{A2}} u^{-1} \partial u \quad (D-9) \\ &= [1/(N_A + N_B)] \ln \{ [C N_A - (N_A + N_B) C_{A2}] / [C N_A - (N_A + N_B) C_{A1}] \} \end{aligned}$$

Substituting the relationships given by eqs D-8 and D-9 into eq D-7 yields

$$\begin{aligned} [1/(N_A + N_B)] \ln \{ [C N_A - (N_A + N_B) C_{A2}] / [C N_A - (N_A + N_B) C_{A1}] \} \\ = [(z_2 - z_1) / (C \mathfrak{D}_{AB})] \end{aligned} \quad (D-10)$$

Equation D-10 can equivalently be expressed as

$$\begin{aligned} [N_A / (N_A + N_B)] \ln \{ [C N_A - (N_A + N_B) C_{A2}] / [C N_A - (N_A + N_B) C_{A1}] \} \\ = [N_A (z_2 - z_1) / (C \mathfrak{D}_{AB})] \end{aligned} \quad (D-11)$$

Letting $z = z_2 - z_1$, the right side of eq D-11 can be solved for N_A , which yields the following relationship:

$$\begin{aligned} N_A &= [N_A / (N_A + N_B)] [(C \mathfrak{D}_{AB}) / z] \\ &\times \ln \{ [C N_A - (N_A + N_B) C_{A2}] / [C N_A - (N_A + N_B) C_{A1}] \} \end{aligned} \quad (D-12)$$

The argument of the logarithm in eq D-12 can equivalently be expressed through the following relationships:

$$\begin{aligned}
 & [C N_A - (N_A + N_B) C_{A2}] / [C N_A - (N_A + N_B) C_{A1}] \\
 &= (N_A + N_B) \left\{ [(C N_A) / (N_A + N_B)] - C_{A2} \right\} / \left\{ (N_A + N_B) \left\{ [(C N_A) / (N_A + N_B)] - C_{A1} \right\} \right\} \\
 &= C \left\{ [N_A / (N_A + N_B)] - (C_{A2} / C) \right\} / \left\{ C \left\{ [N_A / (N_A + N_B)] - (C_{A1} / C) \right\} \right\} \\
 &= \left\{ [N_A / (N_A + N_B)] - (C_{A2} / C) \right\} / \left\{ [N_A / (N_A + N_B)] - (C_{A1} / C) \right\}
 \end{aligned} \tag{D-13}$$

Substituting the relationship given by eq D-13 into eq D-12 yields

$$\begin{aligned}
 N_A &= [N_A / (N_A + N_B)] [(C \mathfrak{D}_{AB}) / z] \\
 &\times \ln \left\{ \left\{ [N_A / (N_A + N_B)] - (C_{A2} / C) \right\} / \left\{ [N_A / (N_A + N_B)] - (C_{A1} / C) \right\} \right\}
 \end{aligned} \tag{D-14a}$$

With the quantity $[(C \mathfrak{D}_{AB}) / z]$ representing a mass transfer coefficient such as F , this last expression can be expressed as

$$\begin{aligned}
 N_A &= [N_A / (N_A + N_B)] F \\
 &\times \ln \left\{ \left\{ [N_A / (N_A + N_B)] - (C_{A2} / C) \right\} / \left\{ [N_A / (N_A + N_B)] - (C_{A1} / C) \right\} \right\}
 \end{aligned} \tag{D-14b}$$

The development of eq D-14b was based on the assumptions of a constant total molar concentration and steady-state molar fluxes for each of the mobile species.

(b) Background Information on Analytical Basis of Mass Transfer Coefficients

Some background information on the use and concepts associated with mass transfer coefficients is called for at this stage. Much of the information that follows is extracted from *Mass Transfer Operations*, by Robert E. Treybal (ref 17).

Molar fluxes are generally written in the following format:

$$N_A = (\text{mass transfer coefficient}) (\text{driving force}) \tag{D-15a}$$

Combinations of mass transfer coefficients and driving forces can be expressed as follows.

Table D-1. Mass Transfer Coefficients and Corresponding Gradients
(variables used for $N_B = 0$; see Table D-2)

Driving Force Basis (Gradient)	Gas Phase Mass Transfer Coefficient
Pressure (i.e., $p_{A1} - p_{A2}$)	k_G
Mole fraction (i.e., $y_{A1} - y_{A2}$)	k_y
Concentration (i.e., $C_{A1} - C_{A2}$)	k_c
Mass ratio (mass A/mass B)	k_Y

The units on the k -type mass transfer coefficients must be consistent with the units of the driving force gradient. While the molar flux of a component (e.g., N_A) is assigned with the units of [moles transferred/(area time)], dimensional consistency requires some consideration on the specification of the units for the k -type mass transfer coefficient. Table D-2 is based on an extraction from Treybal (ref 17; p 49).

Table D-2. Relations between Mass Transfer Coefficients (ref 17)

Equimolar Counterdiffusion ($N_A = -N_B$)	Diffusion of A through Nondiffusing B ($N_B = 0$)	Units of Mass Transfer Coefficient
Gases	Gases	Gases
$N_A = k_G' \Delta P_A$	$N_A = k_G \Delta P_A$	Moles transferred/[(area) (time) (pressure)]
$N_A = k_y' \Delta y_A$	$N_A = k_y \Delta y_A$	Moles transferred/[(area) (time) (mole fraction)]
$N_A = k_c' \Delta C_A$	$N_A = k_c \Delta C_A$	Moles transferred/[(area) (time) (mol/vol)]
	$W_A = k_Y \Delta Y_A$	Mass transferred/[(area) (time) (mass fraction)]

With this terminology approach, eq D-15a can be expressed in the following analytical form for a binary gas-phase mass transfer system in which component A is diffusing through a mass transfer film thickness and component B is not diffusing through the mass transfer film thickness:

$$N_A = k_G \Delta p_A = k_G (p_{A1} - p_{A2}) \quad (\text{D-15b})$$

where $\Delta p_A = (p_{A1} - p_{A2})$ is a pressure-based driving force, and k_G is a gas-phase mass transfer coefficient.

Mass transfer coefficients are generally correlated through a Reynolds (Re) number and a Schmidt (Sc) number through analytical fits of data. The correlating parameter that contains the mass transfer coefficient is known as the Sherwood (Sh) number. Such correlations generally take on the following form

$$\text{Sh} = f(\text{Re}, \text{Sc}) \quad (\text{D-16})$$

The parameters used in the Sherwood number depend on the basis of the mass transfer coefficients and the driving force. For instance, the mass transfer coefficient (F) as depicted in eq D-14b can be shown to be related to the gas-phase mass transfer coefficient in eq D-15b (for gas-phase mass transfer in which there is the diffusion of component A through nondiffusing component B) through the following expression:

$$F = k_G p_{lm,B} \quad (D-17)$$

where $p_{lm,B}$ is the logarithmic mean partial pressure of component B . Treybal (ref 17) gives the following correspondences among the transfer coefficients for binary diffusion:

$$\begin{aligned} F &= k_G p_{lm,B} = k_y (p_{lm,B} / P_t) = k_c (p_{lm,B} / RT) \\ &= k_y / M_B = k_G' p_t = k_y' = k_c' (p_t / RT) = k_c' c \end{aligned} \quad (D-18)$$

(c) Ideal Physical Adsorption Considered as the Transfer of A through Nontransferring B

Two situations are now considered for the transfer of mass through the film. These are described as follows:

1. Equimolar Counter Diffusion: In this situation, the net molar flux in the z -direction is zero such that $N_A = -N_B$. By the relationship given by eq B-14b, this would require that $[N_A / (N_A + N_B)]$ approach infinity.
2. Transfer of A through Nontransferring B : In this situation, component B is essentially motionless such that $N_B = 0$. Through the relationship given by eq B-14b, this would require that $[N_A / (N_A + N_B)] = 1$.

Assuming the process of ideal physical adsorption to be one in which there is the transfer of a unitary component (i.e., the vapor-phase contaminant) through a medium largely composed of a nontransferring component (i.e., air), then the situation becomes one in which $N_B = 0$ and eq D-14b simplifies to the following relationship:

$$N_A = F \ln \left\{ [1 - (C_{A2}/C)] / [1 - (C_{A1}/C)] \right\} \quad (D-14c)$$

The concentration ratios appearing in eq D-14c are mole fractions and are related to pressures through the following expressions

$$\begin{aligned} y_{A1} &= (C_{A1}/C) = [p_{A1}/(RT)] / [p/(RT)] = p_{A1}/p \\ \text{and} \\ y_{A2} &= (C_{A2}/C) = [p_{A2}/(RT)] / [p/(RT)] = p_{A2}/p \end{aligned}$$

Substituting these relationships into eq D-14c gives

$$N_A = F \ln \left\{ [1 - (p_{A2}/p)] / [1 - (p_{A1}/p)] \right\} \quad (\text{D-14d})$$

Development of the $p_{\text{lm},b}$ factor that appears in the Dole and Klotz reference (ref 3) and is given by eq 201 is based on the following approach.

The molar flux relationships as given by eqs D-14d and D-15b are equated, which gives the following expression:

$$N_A = F \ln \left\{ [1 - (p_{A2}/p)] / [1 - (p_{A1}/p)] \right\} = k_G (p_{A1} - p_{A2}) \quad (\text{D-19})$$

Therefore,

$$F = k_G (p_{A1} - p_{A2}) / \ln \left\{ [1 - (p_{A2}/p)] / [1 - (p_{A1}/p)] \right\} \quad (\text{D-20a})$$

For a binary system, the following partial pressure relationships would hold:

$$(p_{A1} - p_{A2}) = (p_{B2} - p_{B1})$$

and

$$p_{A1} = p - p_{B1}$$

$$p_{A2} = p - p_{B2}$$

Substituting these relationships into eq D-20a gives

$$F = k_G (p_{B2} - p_{B1}) / \ln [p_{B2}/p_{B1}] \quad (\text{D-20b})$$

The definition of the logarithmic mean partial pressure of component B is given as

$$p_{\text{lm},B} = (p_{B2} - p_{B1}) / \ln [p_{B2}/p_{B1}] \quad (\text{D-21})$$

With the definition of the logarithmic mean partial pressure now defined, eq D-20b can be expressed as

$$F = k_G p_{\text{lm},B} \quad (\text{D-20c})$$

Equation D-20c is consistent with the interpretation of F as given by eqs D-17 and D-18.

