CHAPTER 1

RESIDENCE TIME DISTRIBUTION THEORY & PRACTICE

According to Danckwerts (1953), the mean residence time $\bar{\tau}$ of an <u>element of fluid volume</u> within a fully contained, continuous flow reactor with a total fixed volume of V operated at steady state is

(1-1) $$\bar{\tau} \ = \ V/Q$$

in which Q is the steady volumetric flow rate. This relation holds true irrespective of the <u>state of mixing</u>, or <u>type of flow</u> (Denbigh, 1965).[1]

1-1. DANCKWERTS' DERIVATION

Let $\delta V = Q\,d\tau$ represent a fluid element which entered the system τ time ago. Also, let $P(\tau)$ represent the probability that the element <u>remains</u> in the reactor during the period τ. The total volume of the fluid in the reactor must thus be

$$V \ = \ Q \int_{0}^{\infty} P(\tau) \cdot d\tau$$

Now, let $R(\tau)$ represent the probability of a fluid element <u>leaving</u> the system during the period τ so that $P(\tau) + R(\tau) = 1$. The foregoing equation then becomes

$$\frac{V}{Q} \ = \ \int_{0}^{\infty} [1 - R(\tau)]d\tau$$

which upon integration by parts gives

$$\frac{V}{Q} \ = \ [1 - R(\tau = \infty)] \cdot \infty \ - \ [1 - R(\tau = 0)] \cdot 0 \ + \ \int_{R(0)}^{R(\infty)} \tau \cdot dR(\tau)$$

---

[1] A <u>fully contained</u> vessel is one that has no diffusion or dispersion at the entrance or exit of the vessel so that a fluid element once inside the reactor cannot escape back into the input stream, or once removed from the vessel cannot return to the vessel (Seinfeld & Lapidus, 1974).

with boundary conditions of $R(\tau) = 0$ at $\tau = 0$, and 1.0 at $\tau = \infty$ (chance of 100% removal in an infinite time) so that

$$\frac{V}{Q} = \int_0^1 \tau \cdot dR(\tau) = \text{c.g. of } R(\tau) = \bar{\tau} \quad \text{(Eqn.1-1)}$$

The derivative of $R(\tau)$ with τ gives the so-called <u>Residence Time Distribution Function</u> $r(\tau)$ (RTD-function) which in reality is a probability density function (Seinfeld & Lapidus, 1974); i.e.,

(1-2) $$\frac{dR(\tau)}{d\tau} = r(\tau)$$

This derivation generated much comment when first published in 1953 because a tracer particle used to determine the RTD-function experimentally may diffuse at a rate differing from the bulk flow, but it appears that such a limitation probably is not very significant in practice (Spalding, 1958).

1-2. RTD-FUNCTIONS FOR TWO IDEAL REACTORS

Implicit to the following derivations is that $R(\tau)$ applies equally well to N particles introduced individually at different times to a reactor operated at steady state, or N particles introduced all at once to the reactor. This is called <u>ergodicity</u> (Seinfeld & Lapidus, 1974) which can be interpreted to mean that $R(\tau)$ also represents the volume fraction of the fluid leaving the reactor which has resided in the system over a time of τ or less (Kramer & Westerterp, 1963).

The symbol τ has been used here to designate backwards in time, but $R(\tau)$ applies equally well to the future, and so it may also be written as $R(t)$.[2]

The Plug Flow Reactor (PFR): This ideal reactor contains no backmixing whatsoever; hence, every fluid element has the same residence time of $\bar{\tau}$ so that

(1-3) $$R(t) = 0 \text{ when } 0 < t < \bar{\tau}$$
$$R(t) = 1 \text{ when } t \geq \bar{\tau}$$

---

[2] Additionally, nomenclature has changed through the years so that $r(t)$ is now $\mathbf{E}(t)$, $R(t)$ is $\mathbf{F}(t/\tau)$, and $P(t)$ is $\mathbf{I}(t/\tau)$ (Levenspiel, 1962). The earlier notation will continued to be utilized herein, however.

This shows that the RTD-function of this reactor must be infinite at $t = \bar{\tau}$, and zero everywhere else. This particular ideal reactor has also been called piston flow, the non-backmixed reactor, and the ideal tubular reactor.

The Continuous Flow Stirred Tank Reactor (CSTR): The contents of this ideal tank reactor are mixed so intensely that the composition becomes uniform throughout and equal to that in the reactor output. The probability that any fluid element will be removed from the reactor over an instant of time δt must thus be constant; i.e.,

$$(1-4) \qquad R(\delta t) = \frac{Q \cdot \delta t}{V} = \frac{\delta t}{\bar{\tau}}$$

Additionally, the probability of a fluid element remaining in the vessel over the time $t + \delta t$ is $P(t + \delta t) = P(t) \cdot P(\delta t)$ so that

$$[1 - R(t + \delta t)] = [1 - R(t)] \cdot [1 - R(\delta t)]$$

remembering that $P(t) = 1 - R(t)$. Upon taking the product indicated, one obtains

$$R(t + \delta t) - R(t) = R(\delta t) \cdot [1 - R(t)] = \frac{\delta t}{\bar{\tau}} \cdot [1 - R(t)]$$

with the aid of Eqn. 1-4. Letting δt go to the limit of dt, one obtains the differential equation

$$(1-5) \qquad \frac{dR(t)}{dt} + \frac{1}{\bar{\tau}} R(t) = \frac{1}{\bar{\tau}}$$

which has a boundary limit of $R(t=0) = 0$, or

$$(1-6) \qquad R(t) = 1 - \exp{-t/\bar{\tau}}$$

$$(1-7) \qquad r(t) = \frac{dR(t)}{dt} = \frac{1}{\bar{\tau}} \cdot \exp{-t/\bar{\tau}}$$

This ideal reactor has also been called the completely backmixed reactor.

1-3. MATERIALS BALANCES

This approach is commonly used to evaluate the natures of various reactor systems. A general formulation is (Bird, Stewart & Lightfoot, 1960)

(1-8)

| Rate of accumulation of mass of J in the system | = | Rate of mass of J into the system | − | Rate of mass of J out of the system | + | Rate of mass J produced by reaction |

EXERCISE 1-1: Species J dissolved in the bulk flow undergoes a first-order reaction in a CSTR at steady state. What is the concentration of J in the reactor effluent for a steady input concentration of c_i and a first-order rate constant of k?

Being a CSTR, the concentration c within the tank reactor equals that in the effluent and Eqn. 1-8 gives

$$0 = Q \cdot c_i - Q \cdot c - kVc$$

or

(1-9)
$$\frac{c}{c_i} = \frac{1}{1 + k\bar{\tau}}$$

1-4. DETERMINING THE RTD-FUNCTIONS OF REAL REACTORS

Tracer studies are often used to determine experimentally the RTD-functions of real reactors. It can be readily appreciated that the appropriate tracer should be readily soluble in the bulk flow, chemically inert with no sorptive capabilities, and readily analyzed with good accuracy and precision. Two commonly utilized methods of tracer application follow.

The Unit Impulse (Pulse) Input: A total mass m_T of tracer is introduced into the entrance of the reactor in the shortest time practicable. The concentration $c_d(t)$ of the tracer in the effluent is monitored from the moment of addition until it ceases to be detected.

The rate of tracer mass removal from the system is $Qc_d(t)$ so that

(1-10)
$$r(t) = \frac{Q}{m_T} c_d(t)$$

and hence the unit impulse gives directly the RTD-function for any reactor. A major drawback of this approach is that it is impossible to produce physically a unit impulse of infinite magnitude and infinitesimal duration.

The Unit Step Input: A tracer is added at a steady rate to the reactor feed to give a steady input concentration of c_i. The concentration $c_d(t)$ of the tracer in the effluent is then monitored from the instant of tracer addition until it attains a concentration approximating that of c_i.

Now in accord with Denbigh (1965), let t equal the time lapsed from the start of tracer application. The fraction of the volume of the fluid element which entered at that time contributing to the exit stream is $r(t)\delta t$. Similarly, the fraction of the second fluid element which contributes to the exit stream at time $t-\delta t$ is $r(t-\delta t)\delta t$, etc., down to $t-n\delta t = 0$ where $n = t/\delta t$. Consequently,

$$Qc_d(t)\delta t = Qc_i\delta t \ [r(t)\delta t + r(t-\delta t)\delta t +....+ r(t-n\delta t)\delta t]$$

and upon letting $\delta t \to dt$, one obtains

$$(1-11) \qquad \frac{c_d(t)}{c_t} = \int_0^t r(u)du = R(t)$$

<u>The unit step input gives directly the $R(t)$ function for any reactor</u>. A major drawback of this method is that it may prove difficult to determine accurately the small differences between $c_d(t)$ and c_i resulting from the extensive "tailing off" in the RTD-function resulting from the following causes:

Dead Space: A region of a reactor in which fluid elements reside for periods much longer than V/Q. Significant tailing may last from such a space for more than three to four mean residence times (Seinfeld & Lapidus, 1974). Impatience on the part of the experimenter usually causes the study to be terminated too quickly, resulting in computed mean residence times substantially less than the theoretical of V/Q.

Short-circuiting: This occurs when some of the fluid elements slip through the reactor in times much less than V/Q. This must always be balanced, however, by some fluid elements residing in the system for periods much greater than V/Q; hence, it is not always possible to tell if dead spaces or short-circuiting is responsible for the observed tailing of $r(t)$. To make matters worse, some reactors such as fluidized beds possess <u>both</u> significant dead spaces and short-circuiting.

Note that the two simple methods of tracer addition discussed here may not suffice for reactor systems possessing relatively slight dispersion or short mean residence times. In that case a periodically fluctuating input should be considered.

CHAPTER 2

SOLVING COMPOSITE MODELS OF MIXING WITH LAPLACE TRANSFORMS

Composites of ideal reactor elements connected in series and parallel are often used to model the results of tracer tests performed on real reactors. Such composites lend themselves readily to analysis with the Laplace transform (L.T.) technique. Also, the L.T. technique provides a very convenient means of obtaining the moments of RTD-functions (Chapter 3) as well as aid considerably in obtaining the solution of partial differential equations (Chapter 5).

2-1. DEFINITIONS

The L.T. of a real function $f(t)$ is defined as

$$(2-1) \qquad g(s) = \int_0^\infty e^{-st} f(t) dt$$

in which t is a real variable (not necessarily time), s is a complex variable of the form $s_1 + is_2$, and $g(s)$ represents the L.T. of $f(t)$. The limits on the integral depicted must be finite at $t = 0$ as approached from the positive side, and at $t = \infty$; otherwise, $f(t)$ has no L.T. For example, the function $\exp(t^2)$ fails to converge at infinity because $|\exp(t^2)|$ increases more rapidly than $\exp(at)$ at large values of t with a constant. Fortunately, seldom if ever are such uncooperative functions encountered in the physical world (Seinfeld & Lapidus, 1974).

Symbols: A specific property such as concentration $c(t)$ can, of course, be ascribed to the generalized function $f(t)$ appearing in Eqn. 2-1. Common practice is then to replace $f(t)$ by $c(t)$, and $g(s)$ by $C(s)$. This is not feasible, of course, if different properties have already been assigned to the lower and capital cases of the same letter; e.g., $r(t)$ and $R(t)$. In such an event, $\bar{r}(s)$, for example, will be used in lieu of $g(s)$ in Eqn. 2-1.

2-2. LAPLACE TRANSFORM OPERATIONS & PAIRS

Operation 6 of Table I attached shows why the L.T. technique was devised in the first place. To prove, we will first simplify notation by letting $f'(t)$ stand for $df(t)/dt$, $f''(t)$ for $d^2f(t)/dt^2$, etc. Also, we will use $L[f'(t)]$ to designate the L.T. of $f'(t)$. Eqn. 2-1 then gives

$$L[f'(t)] = \int_0^\infty e^{-st} f'(t) dt$$

which upon integration by parts yields Operation 6; i.e.,

$$= s \int_0^\infty e^{-st} f(t)dt + e^{-st} f(t)\,\big|_0^\infty = sg(s) - f(0)$$

Note that one has to know the value of $f(t)$ at $t = 0$ as approached from the positive side in order to satisfy the boundary condition $f(0)$; consequently, it is sometimes written as $f(+0)$.

One can just as well write Operation 6 in the reverse direction to obtain the _inverse_ of the s-domain function; i.e.,

$$L^{-1}[sg(s)] = f'(t) + f(0)$$

as shown by Operation 12 of Table I.

Operation 7 gives the L.T. of a second-order differential; i.e.,

$$L[f''(t)] = s^2 g(s) - sf(+0) - f'(+0)$$

where now two different boundary conditions are stipulated at $t = 0$ as approached from the positive side.

Operation 4 consists of shifting the origin a distance b in the negative direction. This causes $f(t)$ to equal zero at $t < b$, and $f(t-b)$ at $t > b$. Eqn. 2-1 thus becomes

$$L[f(t-b)] = \int_0^b 0 \cdot dt + \int_b^\infty e^{-st} f(t-b)dt$$

$$= e^{-bs} \int_0^\infty e^{-us} f(u)du = e^{-bs} g(s)$$

The foregoing is called the _real-translation_ operation.

Pairing specific functions with their corresponding Laplace transforms are called _Transform Pairs_. They may be used to obtain the inverse of s-domain functions; to wit,

$$L[e^{-at}] = \int_0^\infty \exp{-(s+a)t} \cdot dt = \frac{1}{s+a} \int_0^\infty e^{-j} dj = \frac{1}{s+a}$$
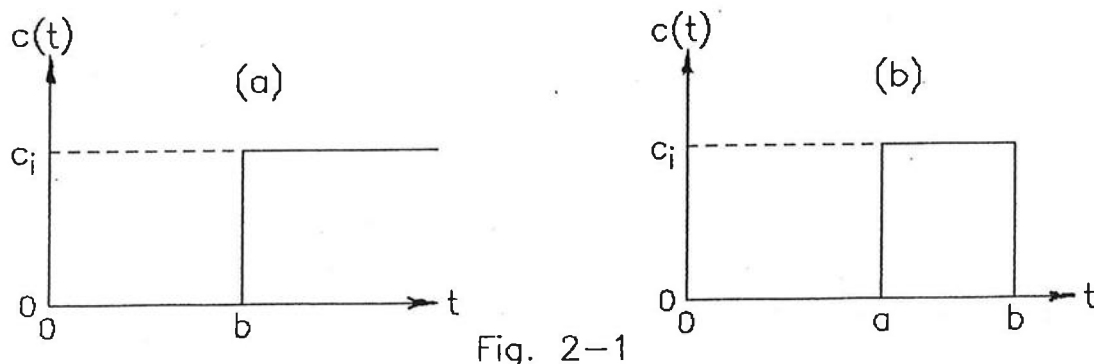
and so

$$L^{-1}\left[\frac{1}{s+a}\right] = e^{-at}$$

in which a is constant (see also Transform Pair 4 of Table II attached to this chapter).

2-3. DERIVATION OF THREE *s*-DOMAIN INPUT FUNCTIONS

Input functions have already been covered in **Section 1-4** of Chapter 1, and their Laplace transforms are listed in Table II as derived below.

Fig. 2-1

Transform Pair 2 of Table II: Commencing at time "*b*" as in Fig. 2-1(a), and then proceeding indefinitely at a constant concentration c_i gives the unit step input function

$$c_i(t)/c_i = 0: \qquad 0 < t < b$$
$$c_i(t)/c_i = 1: \qquad t \geq b$$

Hence, from Eqn. 2-1

$$(2-2) \qquad \frac{C_i(s)}{c_i} = \int_b^\infty e^{-st}dt = \frac{1}{s} \cdot e^{-bs}$$

Transform Pair 3 of Table II: The rectangular pulse input represents a step input at time "*a*" followed by a negative step input of the same magnitude at time "*b*" as shown in Fig. 2-1(b). The L.T. of the unit rectangular pulse input may now be written directly from Eqn. 2-2; i.e.,

$$(2-3) \qquad \frac{C_i(s)}{c_i} = \frac{e^{-as} - e^{-bs}}{s}$$

Transform Pair 1 of Table II: The impulse input equals zero everywhere except at $t = a$.

First let $b = a + \Delta t$ in Eqn. 2-3 and then let the <u>total</u> mass of tracer m_T added at a steady rate over the period Δt be constant so that $c_i = m_T/(Q\Delta t)$. Finally, let $\Delta t \to 0$ to obtain

$$(2-4) \qquad \frac{C_i(s)}{c_i} = \frac{QC_i(s)}{m_T} = e^{-as}\lim_{\Delta t \to 0}\left[\frac{1-e^{-s\cdot\Delta t}}{s\cdot\Delta t}\right] = e^{-as}$$

after one application of L´Hopital´s rule. This input, called the <u>Dirac delta function</u>, is often designated by the symbol $\delta(t-a)$.

We will always apply our inputs in this chapter at time zero $(a = 0)$ so that

(2-5)
$$\frac{C_i(s)}{c_i} = \frac{1}{s} \quad \text{(Unit Step Input)}$$

and

(2-6)
$$\frac{Q}{m_T} C_i(s) = L[\delta(t)] = 1 \quad \text{(Unit Impulse Input)}$$

We also know from the discussion given in Chapter 1 that

(2-7)
$$\overline{R}(s) = \frac{1}{s}\overline{r}(s)$$

2-4. TWO s-DOMAIN TRANSFER FUNCTIONS

CSTR: The concentration $c(t)$ of a conservative substance within a CSTR can be obtained from a materials balance taken about the reactor, or

(2-8)
$$\frac{dc(t)}{dt} + ac(t) = ac_i(t)$$

in which $a = 1/\overline{\tau}$ and $c_i(t)$ = input concentration of the substance.

Employing Operations 1,2, and 6, one obtains the following L.T. of Eqn. 2-8; i.e.,

$$[sC(s) - c(+0)] + aC(s) = aC_i(s)$$

or

(2-9)
$$C(s) = \frac{c(+0) + aC_i(s)}{s+a}$$

where $c(+0)$ is the concentration of the substance within the reactor at time zero. We will always assume herein for modeling purposes that the reactor is free of the substance at time zero $(c(+0) = 0)$; consequently,

(2-10)
$$C(s) = C_d(s) = \left(\frac{a}{s+a}\right)C_i(s) \quad \text{(CSTR)}$$

PFR: Setting "b" equal to τ in Operation 4 gives the L.T. of piston flow directly; i.e.,

(2-11)
$$C_d(s) = \exp(-\tau s) \cdot C_i(s) \quad \text{(PFR)}$$

Note that as in the case of the CSTR, it is assumed that the PFR is free of the conservative substance at time zero.

The Transfer Functions: We know from Chapter 1 that a unit impulse input leads to the RTD-function directly, so that setting $C_i(s) = 1$ in Eqn.'s 2-10 and 2-11 gives

$$(2-12) \qquad \bar{r}(s) = \frac{a}{s+a} \qquad \text{(CSTR)}$$

$$(2-13) \qquad \bar{r}(s) = \exp(-\bar{\tau}s) \qquad \text{(PFR)}$$

Note that $\bar{r}(s)$ is independent of either input or start-up conditions; hence, it is called the __transfer__ or __system__ function in most fields of engineering endeavor.
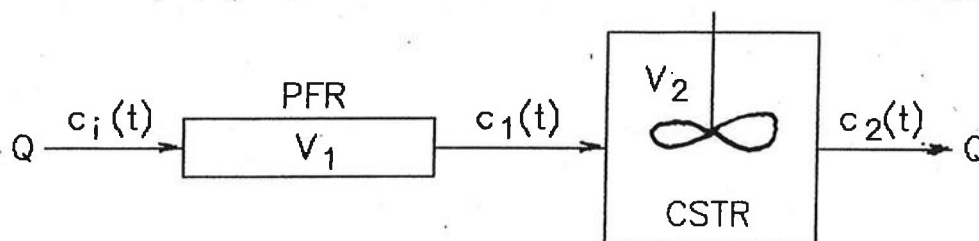
2-5. HOOKUPS IN TANDEM (CASCADES)

Fig. 2-2

A PFR is hooked up in series with a CSTR as shown in Fig. 2-2 above. The solution in the s-domain is (refer to Eqn.'s 2-10 & 2-11)

$$(2-14) \qquad C_2(s) = \frac{a_2}{s+a_2} \cdot C_1(s) = \left(\frac{a_2}{s+a_2}\right) e^{-\tau_1 s} \cdot C_i(s)$$

in which $a_2 = Q/V_2 = 1/\bar{\tau}_2$ and $\tau_1 = V_1/Q$. Letting $C_1(s) = 1$ gives the L.T. of the overall transfer function, or

$$(2-15) \qquad \bar{r}(s) = \exp(-\tau_1 s)\left(\frac{a_2}{s+a_2}\right) = \bar{r}_1(s) \cdot \bar{r}_2(s)$$

as indicated by Eqn.'s 2-12 and 2-13.

Operation 4 and Transform Pair 4 give the inverse of Eqn. 2-15; i.e.,

$$(2-16) \qquad r(t) = 0: \qquad\qquad 0 < t < \tau_1$$

$$r(t) = 1/\bar{\tau}_2 \cdot e^{-(t-\tau_1)/\bar{\tau}_2}: \qquad t \geq \tau_1$$

From the foregoing it is readily apparent after a bit of thought that:

i. The L.T. of the overall transfer function is always

$$(2-17) \qquad \bar{r}(s) = \bar{r}_1(s) \cdot \bar{r}_2(s) \cdot \bar{r}_3(s) \ldots \cdot \bar{r}_n(s) \qquad n = 1,2,3\ldots$$

for n elements in a chain.

ii. The overall transfer function is independent of the order in which the elements are hooked together.

EXERCISE 2-1: A cascade of tank reactors consists of any number
N of identical CSTR's hooked up in series with the total
capacity V being held constant. Determine the RTD-function
for a cascade.

The solution in the s-domain is (refer to Eqn.'s 2-12 and
2-17)

(2-18) $$\bar{r}(s) = \left(\frac{a}{a+s}\right)^N \qquad N = 1,2,3...$$

where $\alpha = N/\bar{\tau}$ and $\bar{\tau} = V/Q$ (a constant). Transform Pair 6 gives
the inverse

(2-19) $$r(t) = a^N \frac{t^{N-1}}{(N-1)!} \cdot e^{-at} = \frac{1}{\bar{\tau}} \cdot \frac{N}{(N-1)!} \cdot \theta^{N-1} \exp -\theta$$

in which $\theta = Nt/\bar{\tau}$ is a dimensionless time.

Dimensionless plots of Eqn. 2-19 are shown in Fig. 2-3 with N
varying from 1 to 40. Clearly, the variance decreases with an
increasing N, and the solution seems to be converging to $t/\bar{\tau} = 1$.
This can be proven mathematically by expanding Eqn. 2-18 into a
binomial series and setting $N = \infty$. The result gives the series
expansion for $\exp(-\bar{\tau}s)$; i.e., plug flow as specified by Eqn.
2-13.

EXERCISE 2-2: Two CSTR's of unequal capacity are hooked up in
series with the total capacity V being held constant. The
portion of V assigned to the smaller reactor is γ. Determine
the RTD-function for this cascade.

The solution in the s-domain is
(2-20) $$\bar{r}(s) = \left(\frac{\alpha}{\alpha+s}\right)\left(\frac{\beta}{\beta+s}\right)$$
in which $\alpha = 1/\gamma\bar{\tau}$, $\beta = 1/(1-\gamma)\bar{\tau}$, and $\bar{\tau} = V/Q$ (a constant).

Transform Pair 8 gives the inverse
(2-21) $$r(t) = \frac{1}{\bar{\tau}(1-2\gamma)}\left[\exp-\left(\frac{\theta}{1-\gamma}\right) - \exp-\left(\frac{\theta}{\gamma}\right)\right] \quad \text{for} \quad 0 < \gamma < 0.5$$
in which $\theta = t/\bar{\tau}$.

EXERCISE 2-3: Determine the RTD-function for a CSTR cascade comprised of two reactors subjected to an instant feedback of βQ as shown in Fig. 2-4 in which $\beta \geq 0$.
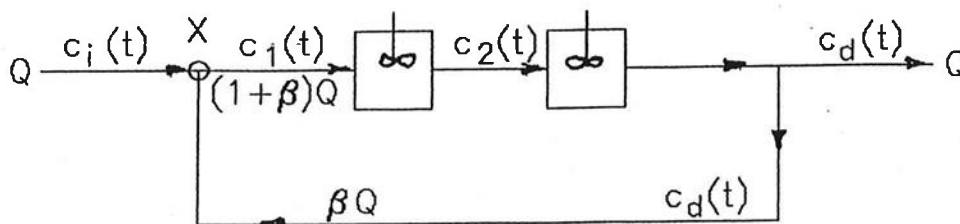

Fig. 2-4

Eqn. 2-10 gives us

$$(2\text{-}22) \qquad C_d(s) = \left(\frac{a}{s+a}\right)C_2(s) = \left(\frac{a}{s+a}\right)^2 C_1(s)$$

in which $a = 2(1+\beta)/\bar{\tau}$. We also know that

$$[(1+\beta)Q] \cdot c_1(t) = Qc_i(t) + (\beta Q) \cdot c_d(t)$$

from taking a materials balance about Junction X; consequently,

$$(2\text{-}23) \qquad C_1(s) = \left(\frac{1}{1+\beta}\right)C_i(s) + \left(\frac{\beta}{1+\beta}\right)C_d(s)$$

in the s-domain. The substitution of the foregoing into Eqn. 2-22 gives

$$\bar{r}(s) = \frac{a^2/(1+\beta)}{s^2 + 2as + a^2/(1+\beta)}$$

after some algebraic manipulation and the application of an unit impulse input.

The second order polynomial in s appearing in the denominator of the foregoing transfer function is not listed in our short table of Transform Pairs. Transform Pair 8 can be used, however, to obtain the inverse to the function after determining the roots r_1 and r_2 of the polynomial; i.e.,

$$(2\text{-}24) \qquad \bar{r}(s) = \frac{a^2/(1+\beta)}{(s-r_1)(s-r_2)} = \frac{a^2/(1+\beta)}{[s+a(1+q)][s+a(1-q)]}$$

in which $q = \sqrt{\beta/(1+\beta)}$. The inverse then becomes

$$(2\text{-}25) \qquad r(t) = \frac{2}{\bar{\tau}q} \cdot e^{-\theta} \cdot \sinh q\theta$$

where $\theta = 2(1+\beta) \cdot (t/\bar{\tau})$.

The procedure shown for obtaining the inverse of a transfer function having a denominator in the form of a polynomial in *s* applies only to polynomials of fourth order or less because this marks the limit at which roots of polynomials can be determined analytically (Burington, R. S., 1949). For higher orders, real values have to be inserted in the equations with roots determined numerically.

2-6. PROCURING THE INVERSE

Up to this point Transform Pairs have been used to obtain the inverses to various *s*-domain functions, but no table can include all possible combinations encountered in practice. Other approaches include the following:

i. The appropriate utilization of certain useful Laplace Operations such as Operations 4 and 14 (the convolution integral) of Table I.

ii. Expansion of the *s*-domain function into a series and then inverting each term of the series.

iii. Employing a standard technique called the method of residues which can be used to obtain the inverse of just about any rational polynomial in *s* of the type covered in this chapter. This approach is described in detail in Appendix A attached hereto. Unfortunately, there seems to exist no standard technique to obtain the inverse of irrational functions in *s*. A few examples of this type will be covered as the need arises in subsequent developments.
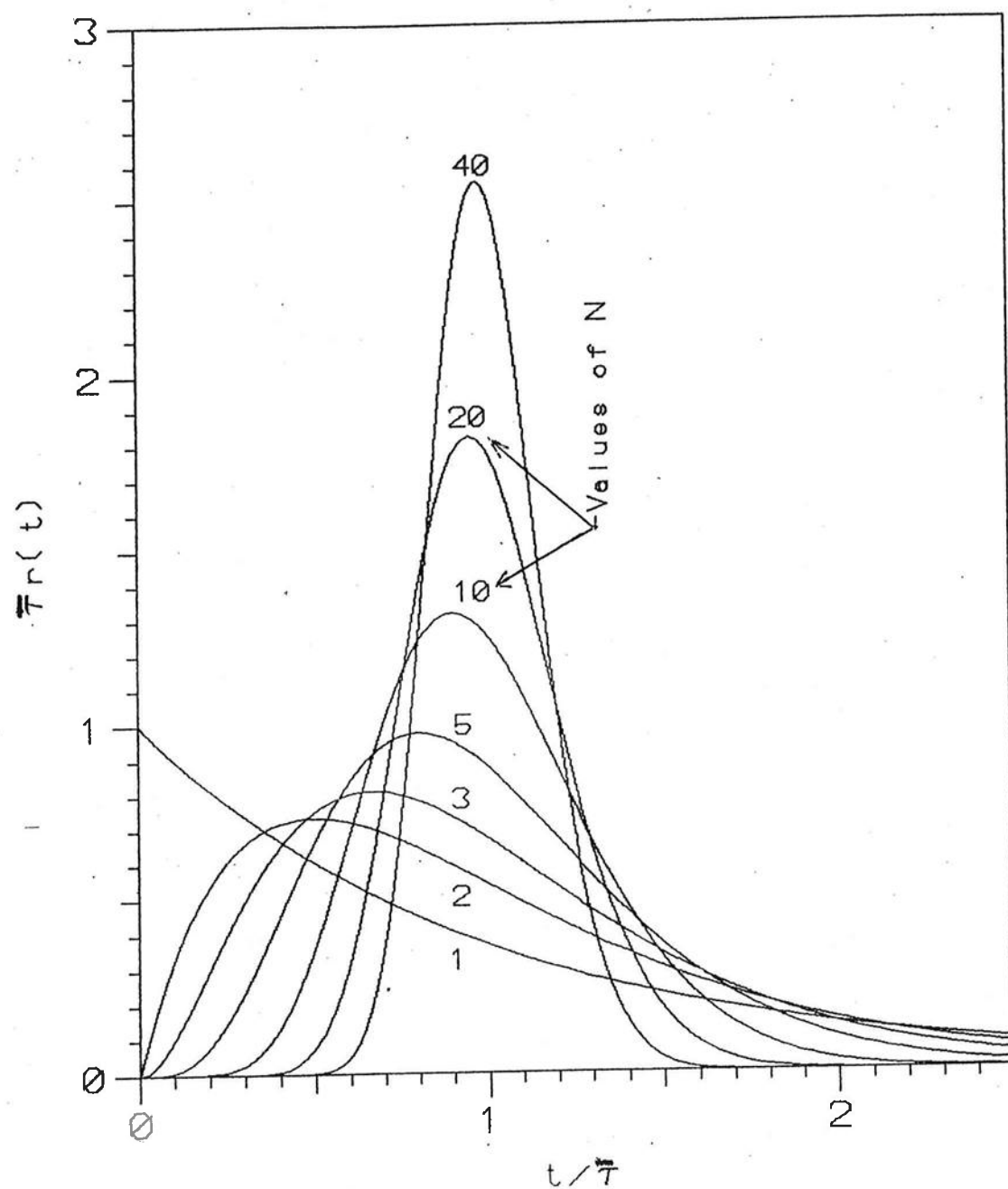
Fig. 2-3.   The RTD-Functions of Various CSTR Cascades

TABLE I.   LAPLACE OPERATIONS*

No.	$f(t)$	$g(s)$
1	$a\,f(t)$	$a\,g(s)$
2	$f_1(t) \pm f_2(t)$	$g_1(s) \pm g_2(s)$
3	$t^n f(t)$	$(-1)^n \dfrac{d^n g(s)}{d s^n}$
4	$0: \quad 0 < t < b/a$ $f(at-b): \quad t > b/a$	$\dfrac{1}{a} e^{-bs/a} g(s/a)$
5	$\dfrac{1}{a} e^{bt/a} f(t/a)$	$g(as-b)$
6	$\dfrac{d f(t)}{d t}$	$s\,g(s) - f(o)$
7	$\dfrac{d^2 f(t)}{d t^2}$	$s^2 g(s) - s f(o) - f'(o)$
8	$\dfrac{\partial}{\partial a} f(t,a)$	$\dfrac{\partial}{\partial a} g(s,a)$
9	$\displaystyle\int_o^t f(u)\,d u$	$\dfrac{1}{s} g(s)$
10	$\displaystyle\lim_{t \to 0} f(t)$	$\displaystyle\lim_{s \to \infty} s\,g(s)$
11	$\displaystyle\lim_{t \to \infty} f(t)$	$\displaystyle\lim_{s \to 0} s\,g(s)$ **

TABLE I.   LAPLACE OPERATIONS*

No.	$f(t)$	$g(s)$
12	$\int_{0}^{\infty} t^{n} f(t)\, dt$	$\lim_{s \to 0} (-1)^{n} \dfrac{d^{n} g(s)}{d s^{n}}$ **
13	$\dfrac{d f(t)}{d t} + f(o)$	$s\, g(s)$
14	$\int_{0}^{t} f_{1}(u) f_{2}(t - u)\, du$	$g_{1}(s) g_{2}(s)$
15	$\dfrac{1}{2 \sqrt{\pi}\, t^{3/2}} \int_{0}^{\infty} u e^{-u^{2}/4t} f(u)\, du$	$g\left(\sqrt{s}\right)$

* Primarily from Roberts, G.H. and Kaufman, H., Table of Laplace Transforms, W.B. Saunders Co., Philadelphia, PA (1966).

** If $s g(s)$ is analytical on the imaginary axis and in the right half-plane.

TABLE II. EXAMPLES OF TRANSFORM PAIRS (Roberts & Kaufman, 1966)

No.	$f(t)$	$g(s)$	Limits
1	$\delta(t-a)$ (Unit Impulse)	e^{-as}	$\Re s > 0$ $a \geq 0$
2	$0: \ 0 < t < b$ $1: \ \ t > b$ (Unit Step)	$\dfrac{1}{s} e^{-bs}$	$\Re s > 0$ $b \geq 0$
3	$0: \ 0 < t < a$ $1: \ a < t < b$ $0: \ \ t > b$ (Unit Pulse)	$\dfrac{e^{-as} - e^{-bs}}{s}$	$\Re s > -\infty$ $0 \leq a < b$
4	e^{-at}	$\dfrac{1}{s+a}$	$\Re s > -\Re a$
5	$\dfrac{1 - e^{-at}}{a}$	$\dfrac{1}{s(s+a)}$	$\Re s > \text{Max} \, 0, -\Re a$
6	$\dfrac{t^{n-1}}{(n-1)!} e^{-at}$	$\dfrac{1}{(s+a)^n}$	$\Re s > -\Re a$
7	$\sin \alpha t$	$\dfrac{\alpha}{s^2 + \alpha^2}$	$\Re s > \Im \alpha$
8	$\dfrac{e^{-\alpha t} - e^{-\beta t}}{\beta - \alpha}$	$\dfrac{1}{(s+\alpha)(s+\beta)}$	$\Re s > \text{Max} - \Re \alpha, -\Re \beta$
9	$\dfrac{1}{\sqrt{\pi t}}$	$\dfrac{1}{\sqrt{s}}$	$\Re s > 0$
10	t^n	$n! \, s^{-n-1}$	$\Re s > 0$

CHAPTER 3

MOMENTS OF TRANSFER FUNCTIONS

Moments of transfer functions serve to check the quality of tracer work as well as to facilitate selection of the best deterministic model of mixing.

3-1. DEFINITIONS

Zero Moment: This is defined as

$$(3-1) \qquad \int_0^\infty r(t)dt \;=\; R(t)]_0^\infty \;=\; 1$$

(see Chapter 1).

First Moment: The first moment of the transfer function about the origin at $t = 0$ is

$$(3-2) \qquad \int_0^\infty t \cdot r(t)dt \;=\; \int_0^1 t \cdot dR(t) \;=\; \bar{\tau}$$

which must also equal V/Q if the reactor is fully contained.

The first moment of the distribution about $\bar{\tau}$ is

$$(3-3) \qquad \int_0^\infty (t-\bar{\tau})r(t)dt \;=\; \int_0^\infty t \cdot r(t)dt \;-\; \bar{\tau} \;=\; 0$$

This proves that the moment of the $r(t)$ function to the left of $\bar{\tau}$ must always equal that to the right.

Variance: Designated by σ^2, this represents the second moment of the distribution taken about $\bar{\tau}$, or

$$\sigma^2 \;=\; \int_0^\infty (t-\bar{\tau})^2 r(t)dt \;=\; \int_0^\infty t^2 r(t)dt \;-\; 2\bar{\tau}\int_0^\infty t \cdot r(t)dt \;+\; \bar{\tau}^2 \int_0^\infty r(t)dt$$

which simplifies to

$$(3-4) \qquad \sigma^2 \;=\; \int_0^\infty t^2 r(t)dt \;-\; \bar{\tau}^2$$

with the use of Eqn.'s 3-1 and 3-2.

3-2. DETERMINATION

The moments of a postulated RTD-function can, of course, be computed directly by performing the integrations specified in the foregoing section. A much simpler approach consists of determining them from the *s*-domain solution without procuring the inverse. The proof follows.

According to Operation 3 of Table I:

$$L^{-1}\left[(-1)^n \frac{d^n g(s)}{ds^n}\right] = t^n f(t)$$

in which n is the n'th derivative of Eqn. 2-1 as follows:

$$g(s) = \int_0^\infty e^{-st} f(t) dt$$

$$-\frac{dg(s)}{ds} = \int_0^\infty e^{-st} t f(t) dt$$

$$\frac{d^2 g(s)}{ds^2} = \int_0^\infty e^{-st} t^2 f(t) dt$$

$$\vdots$$

$$(-1)^n \frac{d^n g(s)}{ds^n} = \int_0^\infty e^{-st} t^n f(t) dt$$

Additionally, Operation 9 shows us that

$$L^{-1}\left[\frac{1}{s}(-1)^n \frac{d^n g(s)}{ds^n}\right] = \int_0^t u^n f(u) du$$

We must now resort to Operation 11 to extend the upper limit on the integral in the real domain to infinity; i.e.,

$$\lim_{s \to 0}\left[\frac{s}{s}(-1)^n \frac{d^n g(s)}{ds^n}\right] = \lim_{t \to \infty}\left[\int_0^t u^n f(u) du\right]$$

or

(3-5)
$$(-1)^n \frac{d^n \bar{r}(s)}{ds^n}\Big|_{s=0} = \int_0^\infty t^n r(t) dt$$

as applied specifically to the transfer function. Note that n also represents the n'th moment of the transfer function about the origin at $t = 0$.

EXERCISE 3-1: Use Eqn. 3-5 to determine the moments and variance of the transfer function derived in Chapter 2 for the CSTR cascade model. The L.T. of this function was determined to be;

(2-18)
$$\bar{r}(s) = \left(\frac{a}{a+s}\right)^N \quad \text{where} \quad a = \frac{N}{\tau} \quad \& \quad N = 1,2,3\ldots$$

It is readily apparent that the foregoing equation equals unity irrespective of N if s is set equal to zero, thus fulfilling the requirement for a zero moment of a transfer function.

Eqn. 3-5 gives a first moment ($n = 1$) of

$$-\frac{d\bar{r}(s)}{ds}\Big|_{s=0} = \frac{Na^N}{(a+s)^{N+1}}\Big|_{s=0} = \frac{N}{a} = \frac{V}{Q}$$

when taken about the origin at $t = 0$.

Likewise, the second moment taken about the origin at $t = 0$ is

$$\frac{d^2\bar{r}(s)}{ds^2}\Big|_{s=0} = \frac{N(N+1)a^N}{(a+s)^{N+2}}\Big|_{s=0} = \frac{N(N+1)\cdot\bar{\tau}^2}{N^2} = \bar{\tau}^2 + \frac{\bar{\tau}^2}{N}$$

which gives a variance of (Eqn. 3-4)

$$(3-6) \qquad \sigma^2 = \frac{d^2\bar{r}(s)}{ds^2}\Big|_{s=0} - \bar{\tau}^2 = \frac{\bar{\tau}^2}{N}$$

Note that the variance decreases from a maximum of $\bar{\tau}^2$ for $N = 1$ (a single CSTR) to zero at $N = \infty$ (piston flow).

EXERCISE 3-2: Repeat Exercise 3-1 for the transfer function derived in Chapter 2 for the problem of a cascade of two tank reactors with instant feedback. The L.T. of the function was found in that exercise to be

$$\bar{r}(s) = \frac{c}{s^2+2as+c} \quad \text{where} \quad a = \frac{2(1+\beta)}{\bar{\tau}}, \quad c = \frac{a^2}{1+\beta} \quad \& \quad \beta \geq 0.$$

It is readily apparent that the foregoing equation equals unity irrespective of β if s is set equal to zero. This therefore fulfills the requirement for the zero moment of a transfer function.

Eqn. 3-5 gives a first moment of

$$-\frac{d\bar{r}(s)}{ds}\Big|_{s=0} = -\frac{2c(a+s)}{(s^2+2as+c)^2}\Big|_{s=0} = \frac{2a}{c} = \bar{\tau} = \frac{V}{Q}$$

when taken about the origin at $t = 0$. Note that the mean residence time is independent of β.

Likewise, the second moment taken about the origin is

$$\frac{d^2\bar{r}(s)}{ds^2}\Big|_{s=0} = \frac{6c\left[s^2+2as+\frac{1}{3}(4a^2-c)\right]}{(s^2+2as+c)^3}\Big|_{s=0} = \frac{2(4a^2-c)}{c^2} = 2\bar{\tau}^2 - \frac{\bar{\tau}^2}{2(1+\beta)}$$

which gives a variance of (Eqn. 3-4)

$$(3-6) \qquad \sigma^2 = \frac{d^2\bar{r}(s)}{ds^2}\Big|_{s=0} - \bar{\tau}^2 = \left(\frac{1+2\beta}{1+\beta}\right)\frac{\bar{\tau}^2}{2}$$

Note that the variance of this model with feedback increases from a minimum of two equal-sized CSTR's in series with no feedback ($\beta = 0$) to that of a single CSTR with infinite feedback ($\beta = \infty$).

CHAPTER 4
REACTIONS WITH BACKMIXING

4-1. DEFINITIONS

The chemical reaction rate k reflects the chemical kinetics of a reaction system which is completely mixed down to a microscopic scale if all of the reactants are present within the same carrier fluid (homogeneous reactions); or if the rates are not influenced by physical transport (diffusion and mass transfer) of the reactants toward a reaction site, or of products away from it, if these sites exist on particulates suspended in the carrier fluid (heterogeneous reactions) (Kramer & Westerterp, 1963). The actual conversion rate within a real reactor should thus be less than the chemical reaction rate if the foregoing specifications are not met.

The chemical reaction rate for a single reaction between A and B is

(4-1)
$$r_A = -kc_A^{\alpha}c_B^{\beta}$$

in which c_A and c_B are the concentrations of reactants A and B respectively, k is the reaction velocity constant, and r_A represents the rate of chemical reaction for species A. It is then said that the reaction is of order α with respect to A, order β with respect to B, and order $\alpha+\beta$ for the total. It should be pointed out here that the values of these orders do not necessarily have to be integers because certain kinds of catalyzed reactions can yield fractional orders (Kramer & Westerterp, 1963).

Unlike chemical engineering, most reactions encountered in water and wastewater treatment are very dilute and thus do not affect the carrier fluid density significantly. We may thus state that the relative degree of conversion ζ is

(4-2)
$$\zeta = 1 - \frac{c_J}{c_{Jo}}$$

in which c_J is the concentration of the limiting reactant J, and c_{Jo} its concentration at the time of reaction initiation.

4-2. BACKMIXING EFFECTS

Backmixing (dispersion) may affect the degree of conversion adversely as shown in developments given by Kramer & Westerterp (1963) which are summarized below.

Suppose we have the n'th order reaction
$$r_A = -kc_A^n$$
in two separate streams of equal volume V but with differing reactant concentrations c'_A and c''_A. If the two streams fail to mix on a microscale then the conversion rate will be
$$Vk[(c'_A)^n + (c''_A)^n] = 2Vk\langle c_a^n \rangle$$

If, on the other hand, the streams mix do mix completely on a microscale then the concentration is $(c'_A + c''_A)/2$ for each volume with an overall conversion rate of $2Vk\langle c_A\rangle^n$. These two rates equal each other only when $n = 1$ (first order reaction); otherwise the "segregated" condition will give a greater conversion than that of "maximum mixedness" if $n > 1$, and vice versa if $n < 1$.

The Completely Segregated Condition: Suppose the RTD-function is known for a reactor system, and the nature of the reaction is such as to remain completely segregated, then the portion of reactant A remaining in a fluid element which entered the system τ time ago is $c_A(\tau)/c_{Ao}$ as in the case of a batch operation. The portion of the outlet stream which contains elements of residence time τ is $r(\tau)d\tau$. Different streams having different residence times τ are combined at the outlet, however, so the average portion of the reactant remaining in the outlet stream is

(4-3)
$$\left\langle \frac{c_{Ad}}{c_{Al}} \right\rangle = \int_{\tau=0}^{\tau=\infty} \left[\frac{c_A(\tau)}{c_{Ao}} \right]_{Batch} r(\tau) \cdot d\tau$$

or

$$\langle \zeta_A \rangle = \int_{\tau=0}^{\tau=\infty} [\zeta_A]_{Batch} \, r(\tau) \cdot d\tau$$

Kramer's Example: Kramer & Westerterp (1963) used the following example to help clarify the foregoing.

Assume we have a PFR and CSTR connected in series as shown in Fig. 2-2 of Chapter 2 with the RTD-function given by Eqn. 2-16. (A reversal in the flow direction of Q is permissible.) Assume also that we have a second order chemical reaction rate ($r_A = -kc_A{}^2$).

<u>Maximum Mixedness:</u> It may be easily shown by materials balances (see Eqn. 1-8, Chapter 1) that the steady state conversion of reactant A in the CSTR portion of the cascade is

$$c_{A2} = -\frac{c_{A1}}{2kc_{A1}\bar{\tau}_2} \cdot \left(1 - \sqrt{1 + 4kc_{A1}\bar{\tau}_2}\right) \quad \text{in which} \quad \bar{\tau} = \frac{V_2}{Q};$$

whereas that in the PFR portion of the cascade will be the same as in a batch reactor (no dispersion) so that

$$c_{A2} = \frac{c_{A1}}{1 + kc_{A1}\tau_1} \quad \text{in which} \quad \tau_1 = \frac{V_1}{Q}.$$

i. The flow Q is in the direction shown in Fig. 2-2. The appropriate simultaneous solution of the two foregoing equations gives the solution

$$\zeta_A = 1 + \frac{1}{2kc_{Ao}\bar{\tau}_2} \cdot \left(1 - \sqrt{1 + 4\frac{kc_{Ao}\bar{\tau}_2}{1 + kc_{Ao}\tau_1}}\right)$$

ii. The flow is reversed in Fig. 2-2 so that reaction mixture passes first through the CSTR and then the PFR. The solution now becomes

$$\xi_A = 1 + \frac{1 - \sqrt{1 + 4kc_{Ao}\bar{\tau}_2}}{2kc_{Ao}\bar{\tau}_2 - kc_{Ao}\tau_1\left(1 - \sqrt{1 + 4kc_{Ao}\bar{\tau}_2}\right)}$$

Complete Segregation: Eqn. 2-16 is discontinuous so that Eqn. 4-3 now becomes

$$\xi_A = \int_{\tau_1}^{\infty} \left(1 - \frac{1}{1 + kc_{Ao}\tau}\right) \times \frac{1}{\bar{\tau}_2} e^{-(\tau - \tau_1)/\bar{\tau}_2} d\tau$$

with the solution

$$\xi_A = 1 - \frac{e^z}{kc_{Ao}\bar{\tau}_2} E_1(z) \quad \text{where} \quad z = \frac{\tau_1}{\bar{\tau}_2} + \frac{1}{kc_{Ao}\bar{\tau}_2} \geq 0$$

and

$$E_1(z) = \int_z^{\infty} \frac{e^{-t}}{t} dt = -0.5772156649 - \ln z - \sum_1^{\infty} \frac{(-1)^n z^n}{nn!}$$

These solutions give three different degrees of conversion for the same set of parameters. For example, if $kc_{Ao}\tau_1 = 2$ and $\bar{\tau}_2/\tau_1 = 4$ then

Maximum Mixedness: Case *i.* $\quad \xi_A = 0.849$

Case *ii.* $\quad \xi_A = 0.814$

Complete Segregation: $\quad \xi_A = 0.864$

The completely segregated reaction gives the greatest amount of conversion because the reaction order is greater than unity. For maximum mixedness, reactor arrangement *i* yields the greater conversion because it maintains the higher concentration of the two arrangements evaluated, and a second order reaction is strongly concentration dependent.

Kramer's example shows that reactor performance is dependent – except for the special case of a first order reaction – on the extent of mixing of the fluid elements of different concentration inside it as well as if the mixing occurs early or late in the reactor relative to the mean time of passage. This kind of information is not supplied by the RTD-function and so the degree of conversion can only be evaluated within limits. In order to obtain the exact answer, one would have to model the exact movement and mixing of fluid elements through the reactor system, a difficult task under the best of circumstances.

4-3. FIRST ORDER REACTIONS

Suppose we have a first order reaction ($r_A = -kc_A$) so that

$$\left[\frac{c_A(t)}{c_{Ao}}\right]_{Batch} = e^{-kt}$$

We know that the conversion effected by a first order reaction can be determined by the completely segregated equation as well as materials balances; thus from Eqn. 4-3

$$(4-4) \qquad \left\langle \frac{c_{Ad}}{c_{At}} \right\rangle = \int_{\tau=0}^{\tau\to\infty} e^{-k\tau} r(\tau) \cdot d\tau$$

This formulation is identical to that used to determine the L.T. of the RTD-function of a reactor if the reaction velocity constant k is replaced by the complex variable s; consequently, the substitution of k for s in the expression for $\bar{r}(s)$ gives automatically the steady state conversion effected by a first order reaction within the reactor system.

EXERCISE 4-1: Determine the steady state ratio of the effluent to feed concentration for a first order reaction occurring within the following types of reactors: *i*). a PFR and CSTR in tandem; *ii*). a CSTR cascade; and *iii*). a cascade of two reactors with feedback.

i.   Eqn. 2-15 of Chapter 2 gives the following L.T. of the RTD-function;

$$\bar{r}(s) = \exp -\tau_1 s \left(\frac{1}{1 + \bar{\tau}_2 s} \right)$$

Consequently,

$$\left\langle \frac{c_{A2}}{c_{At}} \right\rangle = \exp -k\tau_1 \left(\frac{1}{1 + k\bar{\tau}_2} \right)$$

ii.   From Eqn. 2-18,

$$\bar{r}(s) = \left(1 + \frac{s\bar{\tau}}{N} \right)^{-N} \qquad \text{hence} \qquad \left\langle \frac{c_{Ad}}{c_{At}} \right\rangle = \left(1 + \frac{k\bar{\tau}}{N} \right)^{-N}.$$

iii.   From the expression leading directly to Eqn. 2-24 in Chapter 2,

$$\bar{r}(s) = \frac{a^2}{(1+\beta)(s^2 + 2as) + a^2} \qquad \text{where} \qquad a = \frac{2(1+\beta)}{\bar{\tau}} \qquad \text{and}$$

β is the ratio of the feedback to input flow.   Hence,

$$\left\langle \frac{c_{Ad}}{c_{At}} \right\rangle = \frac{1}{k\bar{\tau}[1 + k\bar{\tau}/4(1+\beta)] + 1}$$

CHAPTER 5
PERMEATION OF SOLIDS

5-1. BARRER'S EQUATION

Let a ribbon of plastic be exposed at a constant temperature to a constant vapor pressure p of a volatile organic chemical (VOC) (see Fig. 5-1 below). The gain in weight with time of the ribbon is often determined by a microbalance and evaluated with the aid of Barrer's equation (Barrer, 1951).
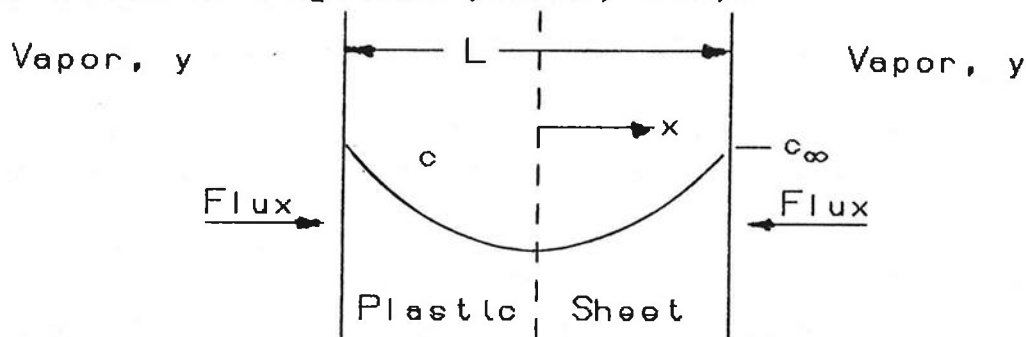

Fig. 5-1

Derivation: The total rate of mass flux of a VOC into the plastic is

$$\text{Flux} = \frac{dm}{dt} = (2A_s)D_M \cdot \frac{dc}{dx}\Big|_{x=L/2}$$

in which c is its concentration within the polymer, m is the total mass of the VOC permeated into the polymer sample, $L/2$ is the half-thickness of the ribbon, A_s is the area of one side of the ribbon, D_M is the Fickian <u>coefficient of molecular diffusion</u> of the chemical through the polymer, and the concentration gradient specified is that at the gas-solid interface. The concentration of the VOC in the plastic at the gas-solid interface c_∞ is determined by the <u>partition equation</u>

(5-1) $$c_\infty = K \cdot y$$

in which y is its concentration in the gas phase ($y = p/RT$) and K a coefficient.

Now

$$\frac{d(m/m_\infty)}{dt} = \frac{df_s}{dt} = \frac{2D_M}{c_\infty L} \cdot \frac{dc}{dx}\Big|_{x=L/2}$$

because the total mass of VOC gained at full saturation m_∞ is $c_\infty A_s L$. The overall fraction of polymer saturation is $f_s = m/m_\infty$, and the foregoing simplifies to

$$\frac{df_s}{d\theta} - \frac{1}{c_-} \cdot \frac{dc}{dz}\Big|_{z=1} \quad \text{in which} \quad \theta = \frac{D_M t}{(L/2)^2} \quad \& \quad z = \frac{x}{L/2}$$

in dimensionless coordinates. Operation 6, Table I may now be used to obtain the L.T. of the foregoing expression; i.e.,

$$sF_s(s) - f_s(0) = \frac{1}{c_-} \cdot \frac{dC(s)}{dz}\Big|_{z=1} .$$

Next, we must solve the partial differential equation

(5-2)
$$\frac{\partial c}{\partial \theta} = \frac{\partial^2 c}{\partial z^2}$$

based on the following boundary conditions (BC) in order to determine the concentration gradient at the gas-solid interface.

i. The polymer sample is free of the VOC at time zero so that c and $f_s = 0$.

ii. The concentration c_- of the VOC in the plastic at the gas-solid interface is always proportional to y as shown by Eqn. 5-1.

iii. Concentration symmetry across the plastic slab center dictates that $dc/dz = 0$ at $z = 0$.

iv. The concentration of the VOC vapor in the microbalance is increased from zero to y instantaneous at time zero (a step input).

BC #i then gives

(5-3)
$$F_s(s) = \frac{1}{c_-} \cdot \frac{1}{s} \cdot \frac{dC(s)}{dz}\Big|_{z=1}$$

for Barrer's equation as well as the following L.T. of Eqn. 5-2 with respect to time;

$$\frac{d^2 C(s)}{dz^2} - sC(s) = 0.$$

Taking the L.T. again with respect to z gives

$$C(u,s) = \frac{u \cdot C(0,s) + dC(s)/dz\big|_{z=0}}{u^2 - s}$$

in which u is used instead of s to designate the complex variable in z, and $C(0,s)$ represents the L.T. with time of the concentration at $z = 0$. (Note that whilst dependent on time, $C(0,s)$ is independent of z.)

BC #iii stipulates a zero concentration gradient at $z = 0$ which reduces the foregoing to

(5-4)
$$C(u,s) = C(0,s) \cdot \frac{u}{(u - \sqrt{s})(u + \sqrt{s})} .$$

This function possesses two simple poles at $u = \pm\sqrt{s}$; hence, either Eqn. A-3 or A-4 of Appendix A can be used to obtain the following inverse of u;

(5-5)
$$C(s) = C(0,s) \cdot \frac{(e^{+\sqrt{s}z} + e^{-\sqrt{s}z})}{2} = C(0,s) \cdot \cosh\sqrt{s}\,z.$$

BC #iv and Transform Pair No. 2 of Table II combined with setting $z = 1$ in Eqn. 5-5 gives

$$C(1,s) = C(0,s) \cdot \cosh\sqrt{s} = \frac{c_\infty}{s}$$

so that

(5-6)
$$\frac{C(s)}{c_\infty} = \frac{1}{s} \cdot \frac{\cosh\sqrt{s}\,z}{\cosh\sqrt{s}}.$$

This is the s-domain solution for concentration within the plastic sheet.

Taking the derivative of Eqn. 5-6 with respect to z, setting $z = 1$ and then substituting the result back into Eqn. 5-3 gives the following s-domain solution for Barrer's equation;

(5-7)
$$F_s(s) = \frac{1}{s^{3/2}} \cdot \frac{\sinh\sqrt{s}}{\cosh\sqrt{s}}.$$

Inverses: Eqn.s 5-6 and 5-7 are irrational as written. Sometimes, however, one is lucky enough to be able to expand such functions into an infinite series which then can be inverted term by term. For example, writing Eqn. 5-7 in its exponential form gives

$$F_s(s) = \frac{e^{\sqrt{s}} - e^{-\sqrt{s}}}{s^{3/2}(e^{\sqrt{s}} + e^{-\sqrt{s}})} = \frac{(1 - e^{-2\sqrt{s}})^2}{s^{3/2}(1 - e^{-4\sqrt{s}})}$$

or

$$F_s(s) = \frac{1}{s^{3/2}} + 2\sum_{n=1}^{\infty} \frac{(-1)^n e^{-2n\sqrt{s}}}{s^{3/2}}$$

upon expansion into an infinite series with the aid of the binomial series (Burington, 1949). An extensive table of Transform Pairs such as that of Roberts & Kaufman (1966) shows that

$$L^{-1}\left[\frac{1}{s^{3/2}}\right] = 2\sqrt{\frac{\theta}{\pi}}$$

and

$$L^{-1}\left[\frac{e^{-2n\sqrt{s}}}{s^{3/2}}\right] = 2\sqrt{\frac{\theta}{\pi}} \cdot e^{-n^2/\theta} - 2n \cdot \text{erfc}\frac{n}{\sqrt{\theta}}$$

in which erfc x is the complimentary error function of x (refer to Abramowitz & Stegun, 1966). Summing up each term in the series then gives one form of Barrer's equation; i.e.,

$$(5-8) \qquad f_s = 2\sqrt{\frac{\theta}{\pi}} + 4\sqrt{\frac{\theta}{\pi}} \cdot \sum_{n=1}^{\infty} (-1)^n e^{-n^2/\theta} - 4\sum_{n=1}^{\infty} (-1)^n n \cdot \mathrm{erfc}\frac{n}{\sqrt{\theta}}.$$

Another solution to Eqn. 5-7 can be obtained by expanding the periodic functions of $\sqrt{s}$ into infinite products to obtain

$$F_s(s) = \frac{\sqrt{s} \prod_{n=1}^{\infty} [1 + s/(n^2\pi^2)]}{s^{3/2} \prod_{n=1}^{\infty} \{1 + 4s/[(2n-1)^2\pi^2]\}}.$$

This proves that Eqn. 5-7 is actually rational and possesses a simple pole at $s = 0$ as well as an infinite number of simple poles s_n at $-\alpha_n^2 = -(2n-1)^2\pi^2/4$. (Remember that these poles also are the zeros to $\cosh\sqrt{s}$.)

The residue at $s = 0$ is (Eqn. A-3 of Appendix A)

$$\mathrm{res}\ g(0) = \lim_{s\to 0} \frac{(s-0)}{s} \cdot \frac{\prod_{n=1}^{\infty}[1 + s/(n^2\pi^2)]}{\prod_{n=1}^{\infty}\{1 + 4s/[(2n-1)^2\pi^2]\}} \cdot e^{+s\theta} = 1$$

Also from Eqn. A-4,

$$\mathrm{res}\ g(s_n) = \frac{P(s)}{Q'(s)}e^{+s\theta}\Big|_{s=s_n} = \frac{2\sinh\sqrt{s}}{3\sqrt{s}\cosh\sqrt{s} + s\cdot\sinh\sqrt{s}} \cdot e^{+s\theta}\Big|_{s=s_n}$$

$$= \frac{2\sinh\sqrt{s}}{s\cdot\sinh\sqrt{s}} \cdot e^{+s\theta}\Big|_{s=s_n} = -\frac{2}{\alpha_n^2}\cdot e^{-\alpha_n^2\theta}.$$

The sum of all residues then gives another version of Barrer's equation;

$$(5-9) \qquad f_s = 1 - 2\sum_{n=1}^{\infty}\frac{1}{\alpha_n^2}\cdot\exp-\alpha_n^2\theta \quad \text{in} \quad \text{which} \quad \alpha_n = (2n-1)\pi/2.$$

Eqn. 5-9 is shown plotted against $\sqrt{\theta}$ in Fig. 5-2, with the portion less than a f_s of about 0.55 yielding a straight line in accord with the first term of Eqn. 5-8; hence,

$$(5-10) \qquad f_s = \sqrt{\frac{4}{\pi}}\cdot\sqrt{\theta} \quad \text{when} \quad f_s < 0.55.$$

Just the first term of the series given by Eqn. 5-9 also suffices for a $f_s > 0.55$, or

$$(5-11) \qquad f_s \approx 1 - \frac{8}{\pi^2}\cdot\exp\frac{-\pi^2\theta}{4} \quad \text{when} \quad f_s > 0.55.$$

EXERCISE 5-1: Invert Eqn. 5-6 via the infinite products approach.

Expanding the periodic functions in $\sqrt{s}$ into infinite products quickly shows that Eqn. 5-6 and 5-7 possess identical rational poles – one at $s = 0$ and an infinite number s_n at $-\alpha_n^2 = -(2n-1)^2\pi^2/4$. Additionally, the residues at $s = 0$ equal plus unity in both cases.

The n'th residue for Eqn. 5-6 is (Eqn. A-4 of Appendix A)

$$\text{res } g(s_n) = \frac{2\cosh\sqrt{s}\,z}{2\cosh\sqrt{s} + \sqrt{s}\cdot\sinh\sqrt{s}}e^{+s\theta}\Big|_{s=s_n} = \frac{2\cosh i\alpha_n z}{i\alpha_n\cdot\sinh i\alpha_n}e^{-\alpha_n^2\theta}$$

$$= -\frac{2\cos\alpha_n z}{\alpha_n\sin\alpha_n}e^{-\alpha_n^2\theta} = 2(-1)^n\cdot\frac{\cos\alpha_n z}{\alpha_n}\cdot e^{-\alpha_n^2\theta}$$

thanks to the fact that $\sin\alpha_n = -(-1)^n$. The sum of all residues then yields the inverse

$$(5\text{-}12) \qquad \frac{c}{c_\infty} = 1 + 2\cdot\sum_{n=1}^{\infty}\frac{(-1)^n}{\alpha_n}\cdot\cos\alpha_n z\cdot\exp-\alpha_n^2\theta$$

in which $\theta = D_M t/(L/2)^2$ and $\alpha_n = (2n-1)\pi/2$. Plots of this function are shown in Fig. 5-3.

Note: Developments paralleling those presented here are spelled out in Appendix B for a slender rod, and for a sphere.

5-2. MODIFICATION OF BARRER'S EQUATION

Bontoux (1990) investigated the permeation of pipe grade polybutylene by several volatile chemicals using the microbalance technique. Instrumentation available at the time made it impossible, however, to deliver the VOC vapor to the microbalance chamber rapidly enough to duplicate a step input at time zero. Rather, the input forcing function varied with time in the manner shown Fig. 5-4, which necessitated a modification of Barrer's equation. in
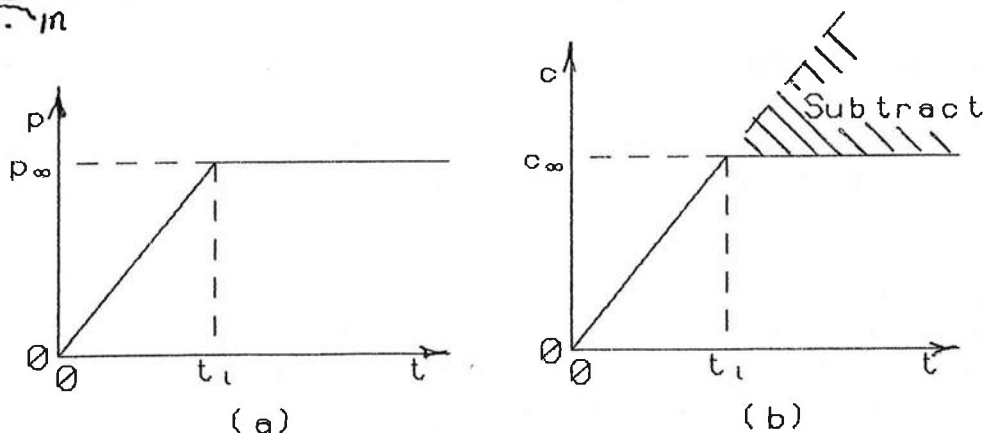

Fig. 5-4

The derivation presented herein duplicates in all respects that of **Section 5-1** except, of course, for BC #*iv* which defines the input function. The revised discontinuous input necessitates a two-stage approach.

I. $0 < \theta < \theta_l$: The derivation of f_s within this region is identical to that of **Section 5-1** up through Eqn. 5-5. The forcing function is now

$$c|_{x=1} \; = \; \frac{c_\infty}{t_l} \cdot t \; = \; \frac{c_\infty}{\theta_l} \cdot \theta$$

which has a L.T. of (see Transform Pair No. 10, Table II)

$$C(1,s) \; = \; \frac{1}{s^2} \cdot \frac{c_\infty}{\theta_l} \; = \; C(0,s) \cdot \cosh \sqrt{s}.$$

Eqn. 5-5 now becomes

(5-13)
$$C(s) \; = \; \frac{c_\infty}{\theta_l} \cdot \frac{1}{s^2} \cdot \frac{\cosh \sqrt{s}\, z}{\cosh \sqrt{s}}.$$

Also, performing the same mathematical manipulations as utilized in the previous section, the f_s function becomes

(5-14)
$$F_s(s) \; = \; \frac{1}{\theta_l s^{5/2}} \cdot \frac{\sinh \sqrt{s}}{\cosh \sqrt{s}}.$$

Inverses: As shown by Operation No. 9, Table I, the integration over time of Equations 5-8 or 5-9 will give the inverse of Eqn. 5-14 after dividing by the constant θ_l. Thus, for Eqn. 5-8 (first term only)

(5-15)
$$f_s \; \simeq \; \frac{2}{\sqrt{\pi}\,\theta_l} \cdot \int_0^\theta u^{1/2} du \; = \; \frac{4}{3\sqrt{\pi}} \cdot \frac{\theta^{3/2}}{\theta_l} \quad \text{when} \quad \theta \leq \theta_l.$$

Utilizing the same approach, Eqn. 5-9 gives

(5-16)
$$f_s \; = \; \frac{\theta}{\theta_l} \; - \; \frac{2}{\theta_l} \cdot \sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} (1 - \exp -\alpha_n^2 \theta) \quad \text{in which} \quad \theta = \frac{4 D_M}{L^2} t,$$

$\theta_l = \frac{4 D_M}{L^2} t_l$, and $\alpha_n = (2n-1)\pi/2$.

Comparison of Eqn. 5-15 with 5-16 at $\theta = \theta_l$ shows that the former is accurate to within 1% at a f_s of 0.52 or less.

II. $\theta > \theta_l$: Fig. 5-4 (b) shows that in this region all that one has to do to obtain the inverse of Eqn. 5-14 is to extend the inverse solution for the first-stage indefinitely, and then subtract the same function from itself after a time delay of $\theta - \theta_l$; i.e., Eqn. 5-15 gives

(5-17)
$$f_s \cong \frac{4}{3\sqrt{\pi}} \cdot \frac{1}{\theta_l} \cdot [\theta^{3/2} - (\theta - \theta_l)^{3/2}]$$

and Eqn. 5-16

(5-18)
$$f_s = 1 - \frac{2}{\theta_l} \cdot \sum_{n=1}^{\infty} \frac{1}{\alpha_n^4} \cdot [\exp -\alpha_n^2(\theta - \theta_l) - \exp -\alpha_n^2 \theta]$$

after the rearrangement of some terms. Eqn. 5-17 should not, of course, be trusted much above half-saturation.

The solutions given by the foregoing expressions for $\theta_l = 0.09$ and 0.25 are compared with Barrer's Eqn. 5-9 in Fig. 5-5. Note that the time lag θ_l increases the time to half-saturation significantly.

EXERCISE 5-2: Bontoux (1990) used a microbalance to determine the increase in weight of a piece of polybutylene water pipe exposed to the vapor exerted by the pure liquid of *n*-nonane (activity = 1.0) at 20°C. The results shown plotted against the square root of time in Fig. 5-6 reflect the effects of the time t_1 required to develop fully the vapor pressure within the microbalance chamber.

Match the observed data with the modified Barrer's equation.

Bontoux (1990) devised a two point scheme to determine the unknowns consisting of the time to half-saturation $\sqrt{t_{1/2}}$ and the maximum vertical distance Δf_s between line (a) of Fig. 5-6 and the sag in the plotted data (10.3 h$^{1/2}$ and 0.11, respectively). Its derivation is too lengthy to be repeated here, but it yielded a value of 0.0516 for θ_l as well as

$$\sqrt{\theta_{1/2}} = 0.472 = \frac{2}{L}\sqrt{D_M}\sqrt{t_{1/2}} = \frac{2}{L}\sqrt{D_M} \cdot 10.3$$

so that

$$\frac{2}{L}\sqrt{D_M} = 0.0458 h^{-1/2} \quad \text{and} \quad \sqrt{\theta} = 0.0458\sqrt{t}$$

with t in hours. The observed data may now be compared directly with the modified Barrer's equation as shown in Fig. 5-7.

There exist discrepancies. The polybutylene specimen gained weight too rapidly at $f_s > 0.6$ which in turn was followed by a period of quasi equilibrium and then a slow additional uptake to a final true equilibrium. This **anomalous** type of diffusion behavior is typical for non-glassy polymers such as polybutylene exposed to high external VOC activities (Crank & Park, 1975).

Bontoux (1990) found that the anomalous responses disappeared in the polybutylene at VOC activities of 0.6 to 0.8 or less, depending on the chemical, but that the apparent diffusion coefficient D_M decreased with the external *n*-nonane concentration in accord with the exponential expression

(5-19)
$$D_M(m^2/day) = 2.0 \times 10^{-9} \cdot e^{5.7a} \quad \text{at} \quad 20°C$$

in which *a* is the activity of the *n*-nonane surrounding the poly-
butylene. Thus, $D_M = 6 \times 10^{-7}$ m²/day at a *n*-nonane activity of
unity. Note, however, that the VOC will continue to permeate
through the polymer even at very low activities.

5-3. DESORPTION

Little, Hodgson & Gadgil (1994) investigated the desorption
of volatile organic compounds from new floor coverings such as
vinyl tiling and plastic backed carpets into a ventilated air
chamber as shown in Fig. 5-8. The permeation characteristics of
a VOC within the floor covering were determined by monitoring its
concentration *y* in the air.
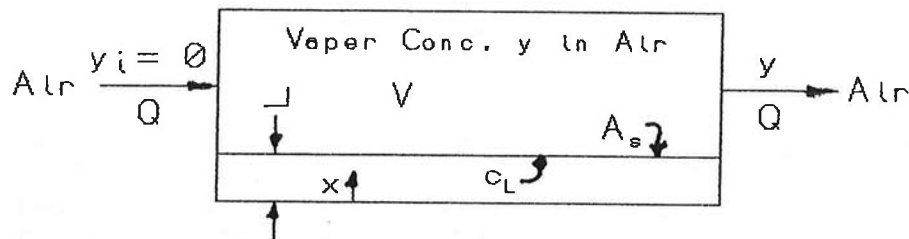
Fig. 5-8

Two assumptions made by the investigators were that the gas
phase is completely backmixed within the chamber (i.e., a CSTR),
and that there exists no significant gas phase resistance to mass
transfer so that the partition equation

(5-20)
$$c_L = K \cdot y$$

is always valid. They also postulated the following boundary
conditions (BC):

i. The initial concentration of a VOC within the plastic layer
of the floor covering is distributed uniformly throughout so
that $c = c_0$ at $t = 0$.

ii. The bottom of the chamber is impervious to a VOC so that
$$\frac{dc}{dx}\Big|_{x=0} = 0.$$

iii. The air within the chamber contains no VOC at time zero so
that $y = 0$ at $t = 0$.

iv. The air entering the chamber is always fresh so that $y_i = 0$.

The Solid Phase: The permeation of the VOC through the plastic
was evaluated with a partial differential equation equivalent to

(5-21)
$$\frac{\partial c}{\partial \theta} = \frac{\partial^2 c}{\partial z^2} \quad \text{in which} \quad \theta = \frac{D_M t}{L^2} \quad \& \quad z = \frac{x}{L}$$

which in turn yields a L.T. with respect to time of

$$\frac{d^2 C(s)}{dz^2} = s \cdot C(s) - c_a$$

after observing BC #i. Taking the L.T. again with respect to distance together with BC #ii gives

$$C(u,s) = C(0,s)\frac{u}{u^2-s} - \frac{c_a}{u(u^2-s)}$$

which has the inverse

(5-22)
$$C(s) = \frac{c_a}{s} - c_a \cdot \cosh\sqrt{s}\,z + C(0,s) \cdot \cosh\sqrt{s}\,z$$

in which $C(0,s)$ designates the L.T. with time of the concentration at $z = 0$. This unknown can be transferred to $z = 1$ by setting $z = 1$ so that

$$C(0,s) = \frac{C_L(s)}{\cosh\sqrt{s}} + c_a - \frac{c_a}{s \cdot \cosh\sqrt{s}}$$

followed by substitution back into Eqn. 5-22. Finally, taking the derivative with z and setting $z = 1$ gives

(5-23)
$$\frac{dC(s)}{dz}\Big|_{z=1} = -\frac{c_a}{\sqrt{s}} \cdot \frac{\sinh\sqrt{s}}{\cosh\sqrt{s}} + K \cdot Y(s)C_L(s)\frac{\sqrt{s}\sinh\sqrt{s}}{\cosh\sqrt{s}}.$$

after combining with the L.T. of Eqn. 5-20; i.e.,

$$C_L(s) = K \cdot Y(s).$$

The overall loss of the VOC from the plastic layer is of practical significance. This can be determined employing the same methods as used previously in this chapter so that

$$\frac{d(m_e/m_a)}{d\theta} = \frac{df_e}{d\theta} = -\frac{1}{c_a}\frac{dc}{dz}\Big|_{z=1}$$

in which m_e is now the mass of the VOC released from the layer, $m_o = c_o A_e L$, and $f_e = m_e/m_o$ is the fraction of the VOC desorbed. As a result of BC #i, $f_e = 0$ at time zero, and the L.T. of the foregoing equation with respect to time gives

(5-24)
$$F_e(s) = -\frac{1}{c_a} \cdot \frac{1}{s} \cdot \frac{dC(s)}{dz}\Big|_{z=1}.$$

The Gas Phase: One can now use Eqn. 1-8 of Chapter 1 to obtain a materials balance about the air chamber assuming that it is completely backmixed. The result after consideration of BC #iv gives

$$\frac{dy}{dt} = -\frac{Q}{V}y - \frac{D_u A_s}{V}\frac{dc}{dx}\Big|_{x=L}$$

in which V is the air chamber volume, Q is the volumetric airflow rate, and A_e the surface area of the plastic layer exposed to the air. (A minus sign was attached to the concentration gradient term at $x = L$ because we are considering here the opposing gas phase). Expressing the foregoing expression in terms of a dimensionless time and distance, one obtains

$$k\frac{dy}{d\theta} = -h \cdot y - \frac{1}{K}\frac{dc}{dz}\Big|_{z=1}$$

in which $h = \dfrac{Q \cdot L}{A_s D_M K}$ and $k = \dfrac{V}{LA_s K}$.

Finally, taking the L.T. of the foregoing with respect to time and utilizing BC #*iii*, one obtains

(5-25)
$$\frac{dC(s)}{dz}\Big|_{z=1} = -K \cdot Y(s) \cdot (h + ks).$$

The s-Domain Solutions: Solving Eqn.s 5-23 and 5-25 simultaneously for $Y(s)$ gives

(5-26)
$$Y(s) = \frac{c_o}{K} \cdot \frac{1}{\sqrt{s}} \cdot \frac{\sinh\sqrt{s}}{(h+ks)\cosh\sqrt{s} + \sqrt{s}\sinh\sqrt{s}}.$$

Solving the same two equations simultaneously for the concentration gradient at the gas-water interface gives

$$\frac{dC(s)}{dz}\Big|_{z=1} = -\frac{c_o}{\sqrt{s}} \cdot \frac{(h+ks)\sinh\sqrt{s}}{(h+ks)\cosh\sqrt{s} + \sqrt{s}\sinh\sqrt{s}}$$

which upon substitution into Eqn. 5-24 yields

(5-27)
$$F_o(s) = \frac{1}{s^{3/2}} \cdot \frac{(h+ks)\sinh\sqrt{s}}{(h+ks)\cosh\sqrt{s} + \sqrt{s}\sinh\sqrt{s}}.$$

Inverses: The expansion of Eqn. 5-26 into infinite products gives

$$Y(s) = \frac{c_o}{K} \cdot \frac{\prod_1^\infty [1 + s/(n^2\pi^2)]}{(h+ks)\prod_1^\infty \{1 + 4s/[(2n-1)^2\pi^2]\} + s\prod_1^\infty [1 + s/(n^2\pi^2)]}$$

which shows that this function is rational, and that it has no pole at $s = 0$. It does possess an infinite number of simple negative poles which cannot be formulated directly in the manner employed for the previous cases covered in this chapter. We will, however, use the same general approach to convert them to positive poles; i.e., for the n´th pole let $s_n = -\alpha_n^2$ so that $\sqrt{s_n} = i\alpha_n$.

The infinite number of simple poles can be evaluated by setting the denominator of Eqn. 5-26 equal to zero, or

$$(h - k\alpha_n^2)\cosh i\alpha_n + i\alpha_n \sinh i\alpha_n = 0$$

which gives

$$\alpha_n \frac{i\sinh i\alpha_n}{\cosh i\alpha_n} = -\alpha_n \frac{\sin\alpha_n}{\cos\alpha_n} = -(h - k\alpha_n^2)$$

so that

(5-28)
$$\alpha_n \tan\alpha_n = h - k\alpha_n^2$$

Note that iterative numerical procedures are required to derive α_n even when h and k are known.

The n'th residue of Eqn. 5-26 can be now obtained with Eqn. A-4 of Appendix A, or

$$\text{res }(s_n) = 2\frac{c_o}{K} \cdot \frac{i\alpha_n \sinh i\alpha_n \cdot e^{-\alpha_n^2\theta}}{(h - 3k\alpha_n^2 - \alpha_n^2)\cosh i\alpha_n + (2 + h - k\alpha_n^2)i\alpha_n \sinh i\alpha_n}$$

$$= 2\frac{c_o}{K} \cdot \frac{\alpha_n \tan\alpha_n \cdot e^{-\alpha_n^2\theta}}{(2 + h - k\alpha_n^2)\alpha_n \tan\alpha_n - (h - 3k\alpha_n^2 - \alpha_n^2)}.$$

Eqn. 5-28 can now be used to simplify further the residue. The final solution for the sum of all residues is

(5-29)
$$y = \frac{2c_o}{K}\sum_{n=1}^{\infty} \frac{(h - k\alpha_n^2) \cdot e^{-\alpha_n^2\theta}}{(h - k\alpha_n^2)^2 + (1 + k)\alpha_n^2 + h} \quad \text{where} \quad \theta = \frac{D_M}{L^2}t$$

which parallels that given by Little, Hodgson & Gadgil (1994).

The identical procedure may be used to obtain the inverse to Eqn. 5-27 except it does possess a simple pole at $s = 0$ which can be easily shown to have a residue of plus unity. All of the remaining poles are identical to those obtained for Eqn. 5-26. The final solution is

(5-30)
$$f_\bullet = 1 - 2\sum_{n=1}^{\infty} \frac{(h - k\alpha_n^2)^2 \cdot e^{-\alpha_n^2\theta}}{\alpha_n^2[(h - k\alpha_n^2)^2 + (1 + k)\alpha_n^2 + h]}.$$

EXERCISE 5-3: Use the following data reported by Little, Hodgson & Gadgil (1994) for the desorption of ethylbenzene from a newly manufactured carpet to derive plots of Eqn.s 5-29 and 5-30.

$V = 20m^3$; $A_\Theta = 8.8m^2$; $Q = 20m^3/hr$; thickness of carpet's plastic backing $L = 1.25mm$; $c_o = 560mg/m^3$ of ethylbenzene; $D_M = 4.3 \times 10^{-12}$ m^2/s; and $K = 2400$. These data give values of 76 and 0.76 for h and k, respectively.

The concentration y in $\mu g/m^3$ of the ethylbenzene in air as predicted by Eqn. 5-29 is plotted against the square root of time t in hours in Fig. 5-9. Concentrations prior to the peak at about one hour are not shown because more than 50 terms were required to obtain convergence.

The results obtained from Eqn. 5-30 are shown in Fig. 5-10. The rate of convergence of this equation is superior to Eqn. 5-29. The surprising thing, however, is that the plot looks very much like Barrer's equation for a slab despite the variable concentration y in the air; i.e., the fraction f_e of ethylbenzene desorbed from the carpet was directly proportional to the square root of t when $f_e < 0.55$.
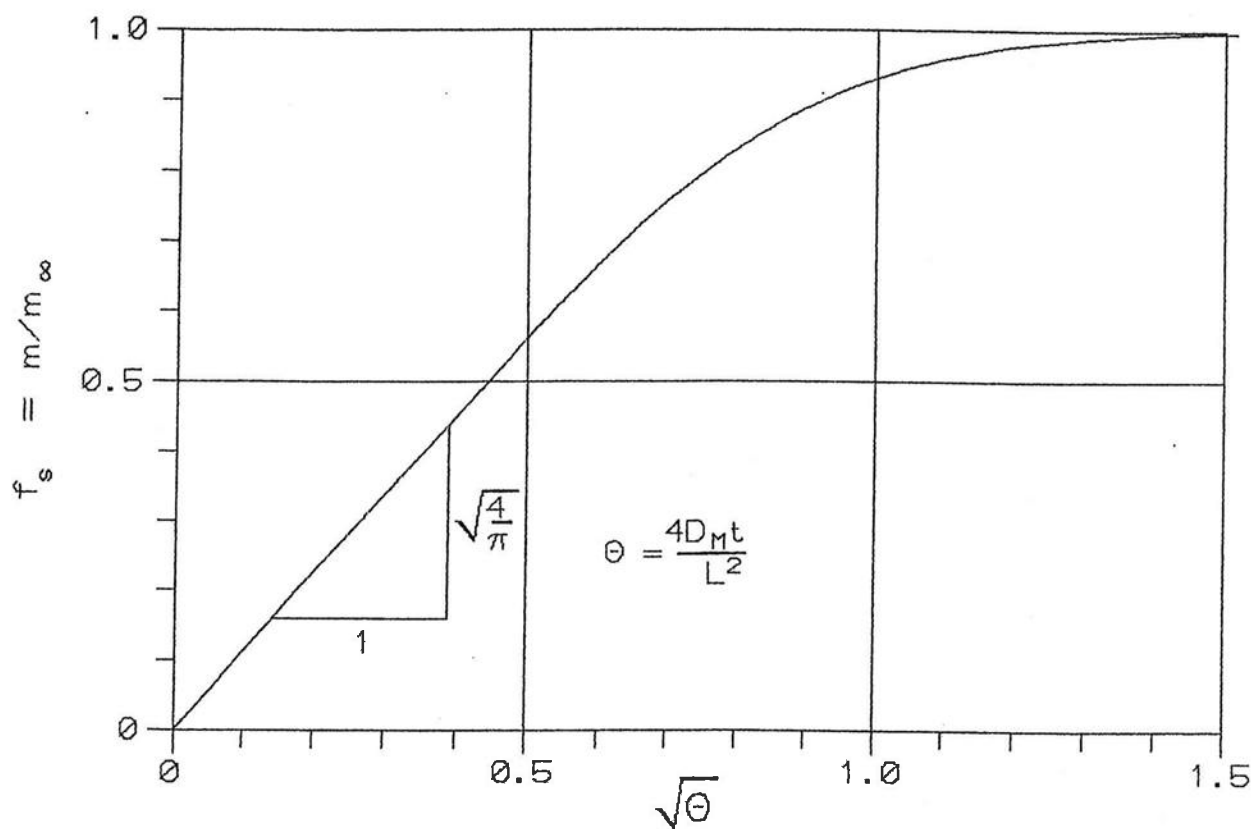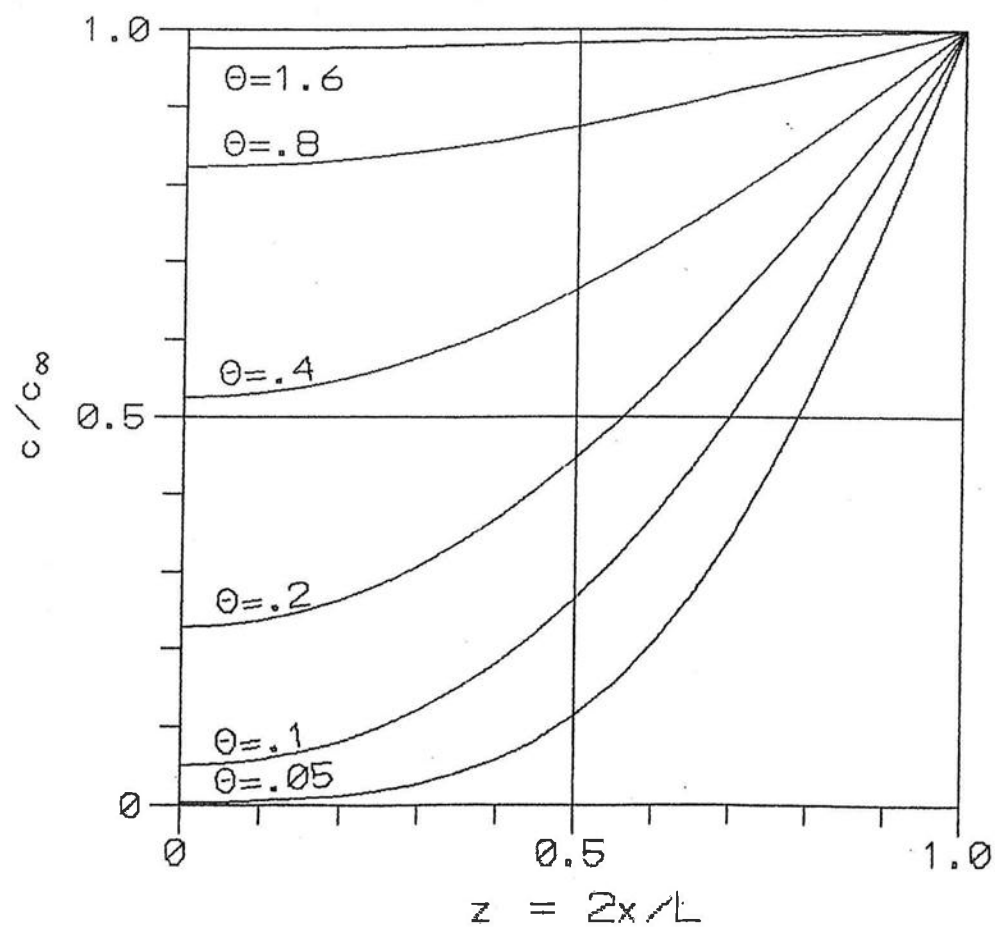
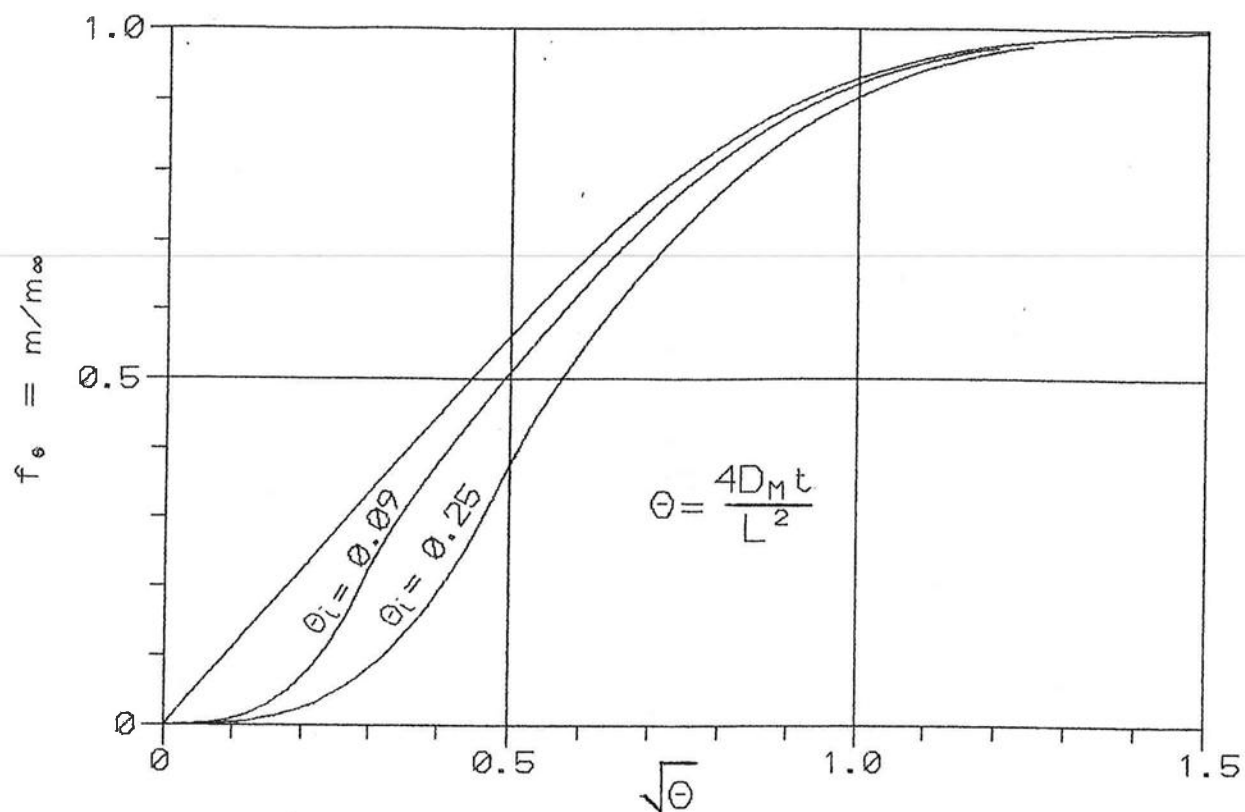Fig 5-2.   Plot of Barrer's Equation for a Thin Slab

Figure shows a plot with vertical axis $f_s = m/m_\infty$ from 0 to 1.0, horizontal axis $\sqrt{\Theta}$ from 0 to 1.5. Slope triangle labeled $\sqrt{\dfrac{4}{\pi}}$ over 1. Equation:

$$\Theta = \frac{4D_M t}{L^2}$$

Fig 5-3.   Permeation into a Thin Slab

Figure shows vertical axis c/c_∞ from 0 to 1.0, horizontal axis $z = 2x/L$ from 0 to 1.0, with curves labeled $\Theta=1.6$, $\Theta=.8$, $\Theta=.4$, $\Theta=.2$, $\Theta=.1$, $\Theta=.05$.

The figure shows $f_\Theta = m/m_\infty$ on the vertical axis (from 0 to 1.0) plotted against $\sqrt{\Theta}$ on the horizontal axis (from 0 to 1.5). Two curves are labeled $\Theta_i = 0.09$ and $\Theta_i = 0.25$.

$$\Theta = \frac{4 D_M t}{L^2}$$

Fig. 5-5.   Barrer's Equation Modified for Non-Ideal Input of VOC Vapor to the Microbalance Chamber.

initial sample weight = 13.14g   maximum weight gain = 1.48g
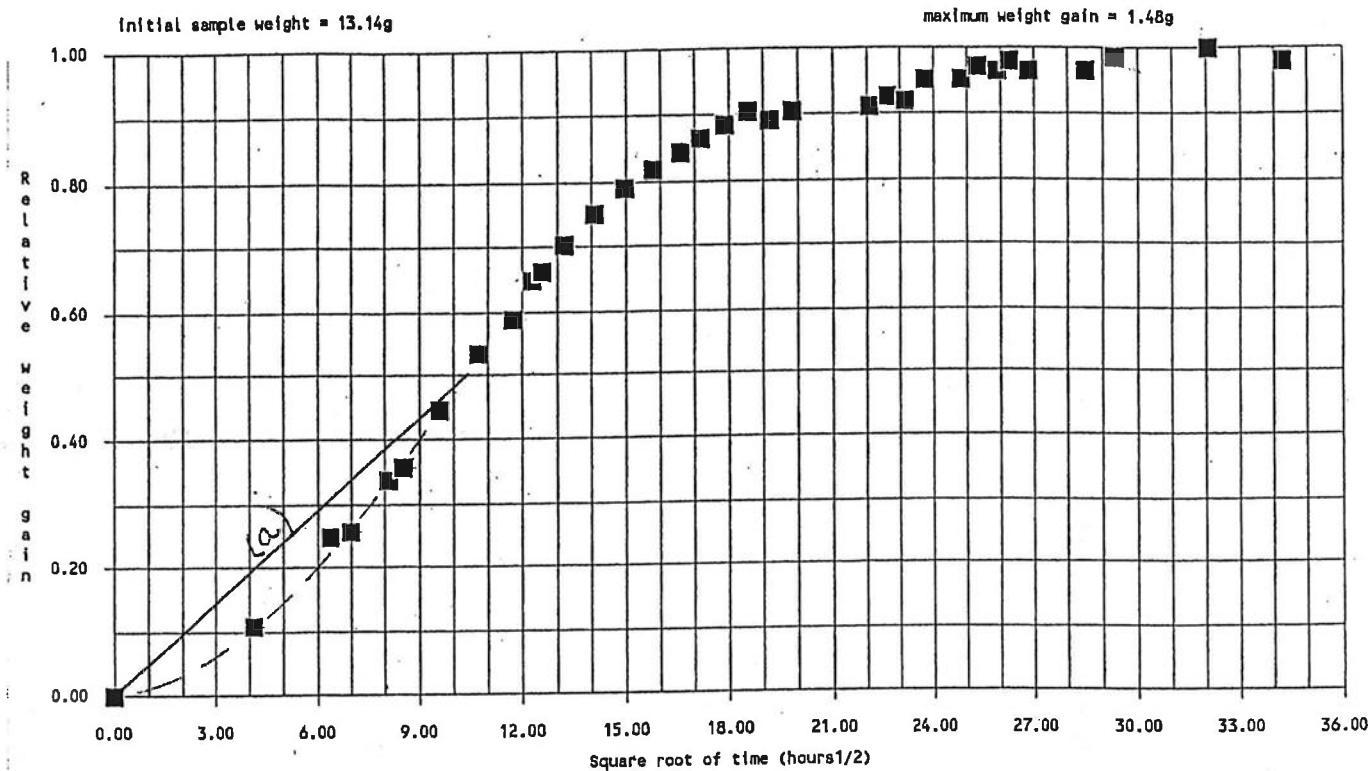
Fig. 5-6. Observed Gain in Weight of a Polybutylene Specimen Exposed to the Vapor of *n*-Nonane at Unit Activity (Bontoux, 1990).
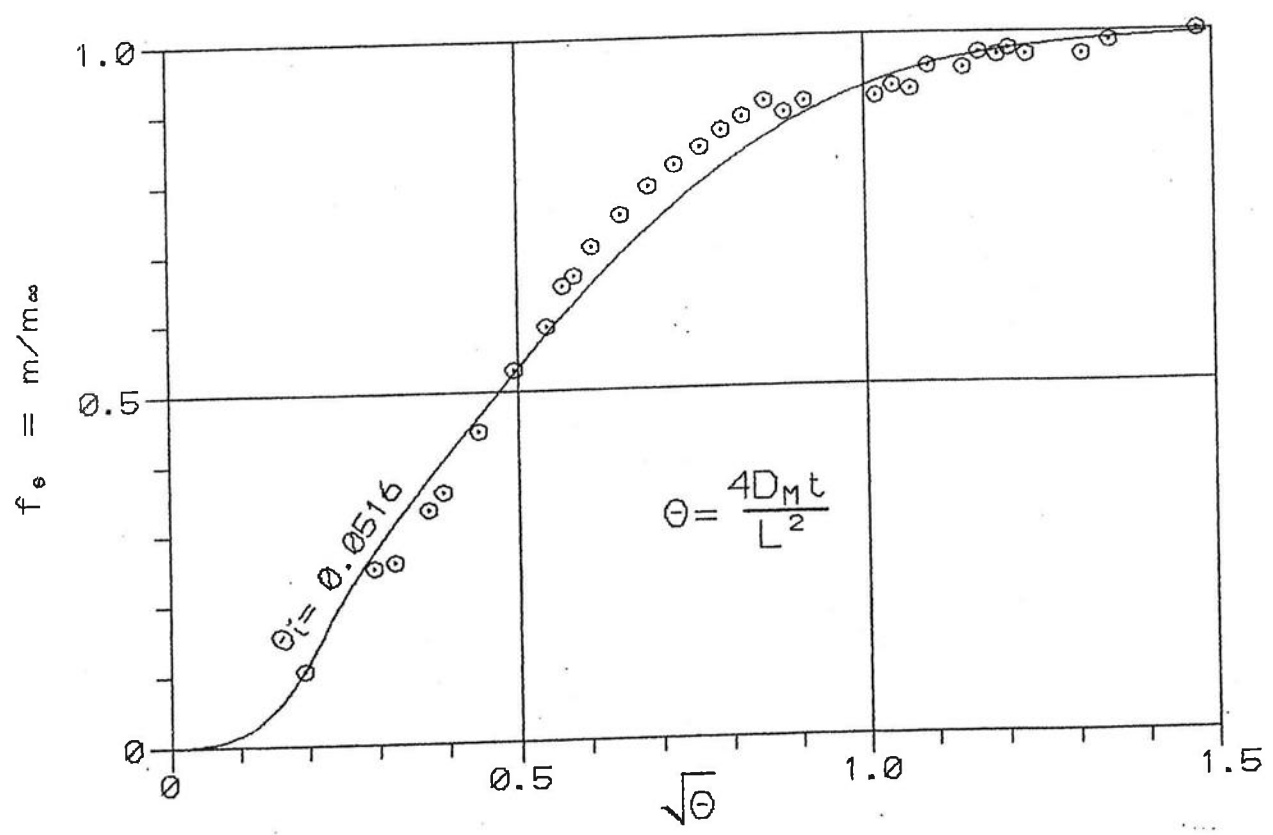
Fig. 5-7. Comparison of Bontoux's Observed Unit Activity *n*-Nonane Data with Modified Barrer's Equation.

42
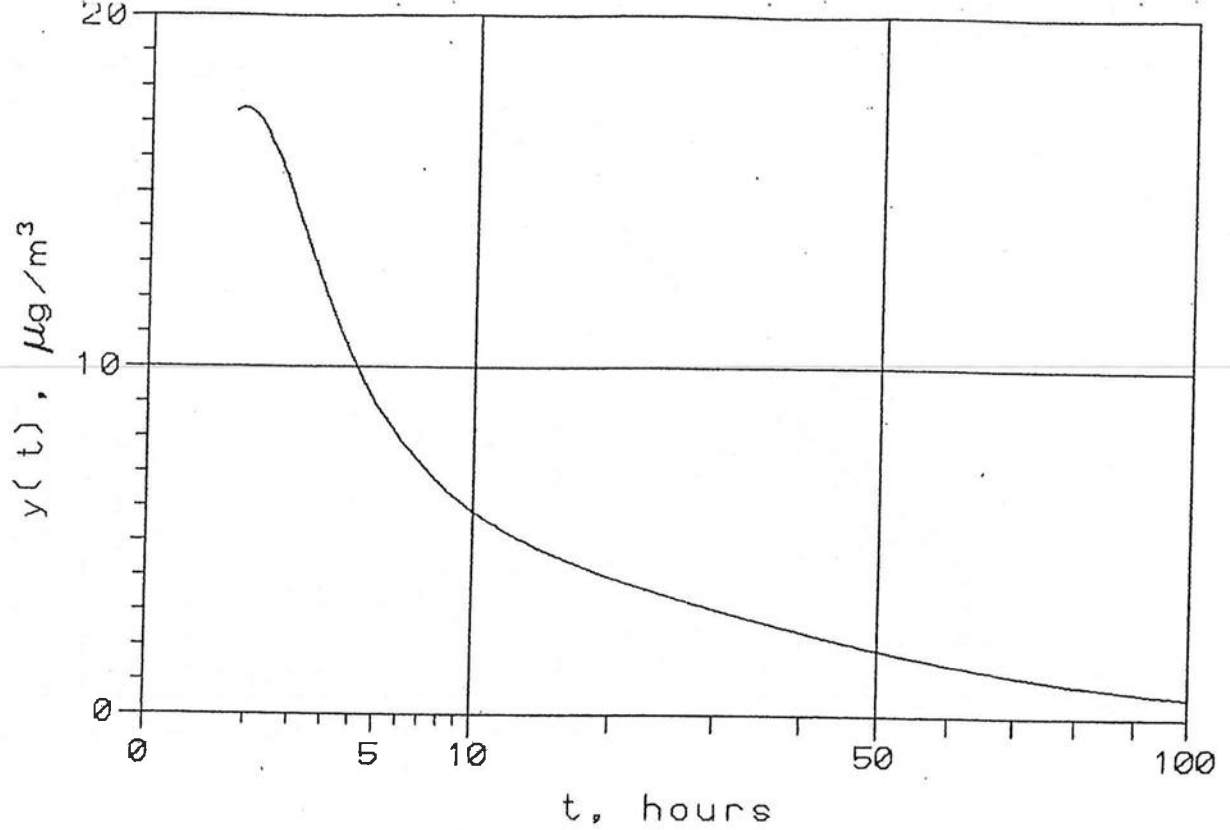
Fig. 5-9. Concentration of Ethylbenzene in the Ventilated Air
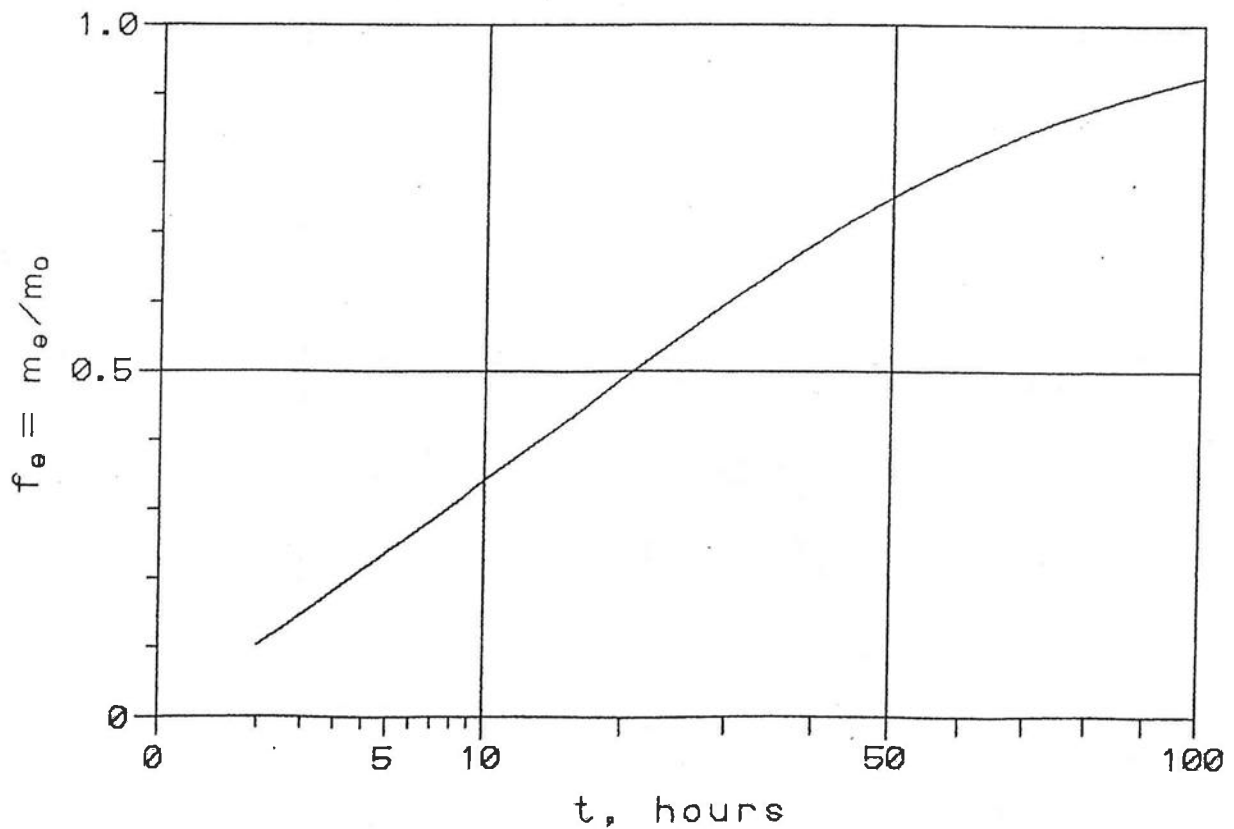Over a Newly Installed Carpet (see Exercise 5-3 for Details).

Fig. 5-10. Loss of Weight of Ethylbenzene from the Newly
Installed Carpet (see Exercise 5-3 for Details).

CHAPTER 6

DISPERSION IN PIPES & TUBES

The axially-dispersed plug flow equation

$$(6-1) \qquad \frac{\partial <c>}{\partial t} = E_L \frac{\partial^2 <c>}{\partial x^2} - <v> \frac{\partial <c>}{\partial x}$$

is commonly used to describe turbulent dispersion within straight pipes and tubes in which $<c>$ represents concentration averaged over the cross-sectional area A_x of the tube at a distance x from some origin, t is time, and E_L is known as the coefficient of longitudinal dispersion. Additionally, $<v>= Q/A_x$ in which $<v>$ represents the average flow velocity within the tube and Q is the volumetric flow rate (steady) through the tube.

6-1. TUBES OF INFINITE LENGTH

Assume that the tracer extends uniformly at a concentration of c_o for $x < 0$ to and at minus infinity at $t = 0$, and a zero concentration for $x > 0$ to and at plus infinity. The concentration $<c>$ after a given time t is (Kramers & Westerterp, 1963)[1]

$$(6-2)$$

$$\frac{<c>}{c_o} = \frac{1}{2}\left[1 - \frac{2}{\sqrt{\pi}} \int_0^t \exp(-u^2)du\right] = \frac{1}{2}[1 - \text{erf}(\zeta)] \quad \text{where} \quad \zeta = \frac{x - <v>t}{\sqrt{4E_L t}}.$$

Setting $x = L$ at some fixed point of interest in the tube (a sample collection point, say, or the distance to the end of a tube discharging freely into the atmosphere), one obtains

$$R(t) = \frac{1}{2}\left[1 - \text{erf}\left(\sqrt{\frac{N'}{2}} \cdot \frac{1 - t/\bar{t}}{\sqrt{t/\bar{t}}}\right)\right]$$

in which $R(t)$ represents the integral of the $r(t)$ function (refer to Eqn. 1-2 of Chapter 1), $\bar{t} = L/<v>$, and $N' = <v>L/2E_L$. Consequently,

$$\frac{dR(t)}{dt} = r(t) = -\frac{1}{2}\frac{d\text{erf}(\zeta)}{d\zeta}\Big|_{x=L} \cdot \frac{d\zeta}{dt}\Big|_{x=L}$$

or

---

[1] Laplace Transforms, as defined herein, cannot be used to solve completely unbounded problems. Special transforms do exist for such a purpose but they seldom are used.

$$(6-3) \qquad \bar{i}r(t) = \frac{1}{2}\sqrt{\frac{N'}{2\pi}}\sqrt{\frac{\bar{t}}{t}}\cdot\left(\frac{1+t/\bar{t}}{t/\bar{t}}\right)\cdot\exp\left[-\frac{N'}{2}\cdot\frac{(1-t/\bar{t})^2}{t/\bar{t}}\right]$$

in which $\bar{t} = L/\langle v \rangle$ & $N' = \langle v \rangle L/(2E_L)$.

Moments of the $r(t)$ function: According to Levenspiel (1962), this RTD-function has a first moment about the origin of

$$(6-4) \qquad \bar{\tau} = \bar{t}\cdot\left(1+\frac{1}{N'}\right)$$

and a variance of

$$(6-5) \qquad \sigma^2 = \bar{t}^2\left(\frac{1}{N'}+\frac{2}{N'^2}\right)$$

in which $\bar{t} = L/\langle v \rangle$. Note that for the first time we have encountered a reactor problem where the mean residence time $\bar{\tau}$ does not equal $V/Q = L/\langle v \rangle$. Why not?

Plots of Eqn. 6-3 are presented in Fig. 6-1 (attached to the end of this chapter) for values of N' ranging from 1/2 to 32.

6-2. PARTIALLY BOUNDED TUBULAR REACTORS
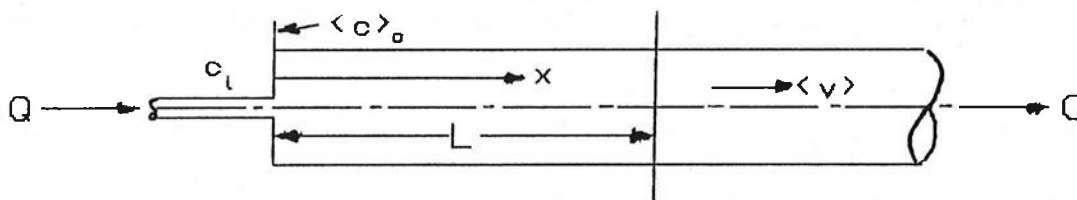
A sketch of this reactor follows:

Fig. 6-2

The Laplace Transform technique may now be used to derive the $r(t)$ function for this reactor because it is bounded at both x & $t = 0$. The boundary conditions (BCs) are:

i. No tracer exists within the reactor at $t = 0$ so that $\langle c \rangle = 0$ throughout.

ii. $\langle v \rangle c_i = \langle v \rangle\langle c \rangle_0 - E_L\frac{\partial\langle c \rangle}{\partial x}\Big|_{x=0}$ at $x = 0$.

iii. $\langle c \rangle$ must remain finite as $x \to \infty$.

The L.T. of Eqn. 6-1 with respect to time gives

$$sC(s) = E_L\frac{d^2C(s)}{dx^2} - \langle v \rangle\frac{dC(s)}{dx}$$

after making allowance for BC #i. (Note that $C(s)$ is used herein to designate the L.T. of $\langle c \rangle$ with respect to time.) Allowing u to represent the complex variable of x, taking the L.T. of the foregoing again with respect to distance as well as BC #ii gives

$$C(u,s) \cdot (s - E_L u^2 + <v>u) = C_0(s)(-E_L u + <v>) - E_L \frac{dC(s)}{dx}\Big|_{x=0}$$

and

$$-E_L \frac{dC(s)}{dx}\Big|_{x=0} = <v>C_\iota(s) - <v>C_0(s)$$

which upon solving simultaneously yields

$$C(u,s) = \left[uC_0(s) - \frac{<v>}{E_L}C_\iota(s)\right] \cdot \left[u^2 - \frac{<v>}{E_L}u - \frac{1}{E_L}s\right]^{-1}$$

$$= \left[uC_0(s) - \frac{<v>}{E_L}C_\iota(s)\right]/[(u+\alpha)(u+\beta)]$$

in which $\alpha = -\frac{<v>}{2E_L}(1+q)$, $\beta = -\frac{<v>}{2E_L}(1-q)$ & $q = \sqrt{1 + \frac{4E_L}{<v>^2}s}$.

Inverses: Procuring first the inverse with respect to distance, one may see that the foregoing function has two simple poles at $-\alpha$ and $-\beta$. It may thus be inverted by the Method of Residues (Appendix A) to obtain

$$(6-6) \qquad C(s) = \frac{(1+q)C_0(s) - 2C_\iota(s)}{2q} \cdot \exp\frac{<v>}{2E_L}(1+q)x$$

$$- \frac{(1-q)C_0(s) - 2C_\iota(s)}{2q} \cdot \exp\frac{<v>}{2E_L}(1-q)x.$$

Keeping in mind that $q \geq 1$, it may be seen that BC #*iii* will be fulfilled only if

$$(1+q)C_0(s) = 2C_\iota(s).$$

Additionally, the L.T. with respect to time of the input function $C_\iota(s)$ must equal unity to obtain the $r(t)$ function, and x is set equal to L to remind one that $r(t)$ is determined over time at some fixed point of reference. Eqn. 6-6 then becomes

$$(6-7) \qquad \bar{r}(s) = \frac{2}{1+q} \cdot \exp[N'(1-q)] \quad \text{in which} \quad N' = \frac{<v>L}{2E_L}.$$

Operation 5 of Table I may now be used to simplify the foregoing significantly prior to obtaining its inverse with respect to time, or

$$r(t) = \frac{<v>}{L}N' \cdot \exp\left[N'\left(1 - \frac{<v>t}{2L}\right)\right] \cdot L^{-1}\left[\frac{1}{1+\sqrt{s}} \cdot \exp -N'\sqrt{s}\right].$$

(Note that s is now dimensionless because it represents the L.T. of the dimensionless time $<v>^2 t/(4E_L)$.) The completed solution can be obtained from Transform Pairs tabulated by Abramowitz & Stegun (1966) as well as others to obtain the ultimate solution

$$(6-8) \quad \bar{\tau} \cdot r(t) = \sqrt{\frac{2N'}{\pi\theta}} \cdot \exp\left[-\frac{N'}{2}\frac{(1-\theta)^2}{\theta}\right] - N'e^{2N'} \cdot \mathrm{erfc}\left[\sqrt{\frac{N'}{2}} \cdot \frac{(\theta+1)}{\sqrt{\theta}}\right]$$

in which $\bar{t} = L/\langle v\rangle$, $\theta = t/\bar{t}$ and $N' = \langle v\rangle L/(2E_L)$.

Moments of the r(t) Function: These can be obtained directly from Eqn. 6-7 following the instructions given in Chapter 3. For example, setting $s = 0$ in the equation makes $q = 1$, which in turn yields a zero moment of unity as proscribed for a $r(t)$ function.

Eqn. 6-7 also gives a first moment about the origin of

$$(6-9) \quad \bar{\tau} = \bar{t} \cdot \left(1 + \frac{1}{2N'}\right)$$

and a variance of

$$(6-10) \quad \sigma^2 = \bar{t}^2\left(\frac{1}{N'} + \frac{3}{4N'^2}\right)$$

in which $\bar{t} = L/\langle v\rangle$.

Plots of Eqn. 6-8 are presented in Fig. 6-3 for the same values of N' as used in Fig. 6-1.

6-3. COMPLETELY BOUNDED TUBULAR REACTORS

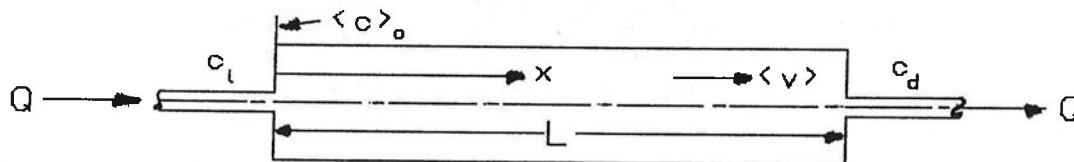A sketch of a fully bounded reactor of overall length L follows:

Fig. 6-4

Two of the three boundary conditions for this reactor are identical to BCs *i* & *ii* of the partially bound reactor evaluated in Section 6-2. The BC appropriate for the exit at $x = L$ generated much speculation in the 1950s with the one postulated by Dankwerts in 1953 eventually being accepted; to wit

iii. $\dfrac{d\langle c\rangle}{dx} = 0$ at $x = L$

which ensures that no sudden discontinuity in concentration occurs at the exit of the reactor.

The derivation follows in all respects that made previously for the partially bound reactor up through Eqn. 6-6, repeated here for convenience.

$$(6-6) \quad C(s) = \frac{(1+q)C_0(s) - 2C_i(s)}{2q} \cdot \exp\frac{\langle v\rangle}{2E_L}(1+q)x$$
$$- \frac{(1-q)C_0(s) - 2C_i(s)}{2q} \cdot \exp\frac{\langle v\rangle}{2E_L}(1-q)x.$$

Taking the derivative of Eqn. 6-6 with respect to x, and then setting the result equal to zero at $x = L$ as specified by BC #*iii* above gives

$$C_0(s) = 2C_i(s) \cdot \frac{(1+q) \cdot e^{N'q} - (1-q) \cdot e^{-N'q}}{(1+q)^2 e^{N'q} - (1-q)^2 e^{-N'q}}$$

which upon substitution back into the equation yields

(6-11)

$$\frac{C(s)}{C_i(s)} = 2e^{N'x/L} \cdot \frac{(1+q) \cdot \exp[N'q(1-x/L)] - (1-q) \cdot \exp[-N'q(1-x/L)]}{(1+q)^2 \exp N'q - (1-q)^2 \exp{-N'q}}$$

in which $q = \sqrt{1 + \frac{2L}{\langle v \rangle N'} s}$ & $N' = \frac{\langle v \rangle L}{2E_L}$.

Assuming that we are concerned only with the $r(t)$ function at the exit of the reactor, $C_i(s)$ is set equal to unity and x equal to L in Eqn. 6-11 to obtain

(6-12)
$$\bar{r}(s) = \frac{4q}{(1+q)^2 \cdot \exp{-N'(1-q)} - (1-q)^2 \cdot \exp{-N'(1+q)}}$$
$$= \frac{2q \cdot \exp N'}{(1+q^2) \cdot \sinh N'q + 2q \cdot \cosh N'q}.$$

Moments of the r(t) function: Following the instructions given in Chapter 3, it can be shown that the moments of Eqn. 6-12 in real time are

(6-13)
$$\bar{\tau} = L/\langle v \rangle = V/Q$$

for the first moment taken about the origin, and

(6-14)
$$\sigma^2 = \bar{\tau}^2 \left[\frac{1}{N'} - \frac{1}{2N'^2}(1 - e^{-2N'}) \right]$$

for the variance.

An Inverse of Eqn. 6-12: Operation 5 of Table I gives
(6-15)

$$\bar{\tau} \cdot r(t) = N' \exp N' \left(1 - \frac{t}{2\bar{\tau}}\right) L^{-1} \left[\frac{\sqrt{s}}{(1+s)\sinh N'\sqrt{s} + 2\sqrt{s}\cosh N'\sqrt{s}} \right]$$

in which s now represents the L.T. of the dimensionless quotient $N't/(2\bar{\tau})$. Note that the portion of the foregoing equation remaining to be inverted resembles Eqn. 5-27 of Section 5-3 (Chapter 5), and so can be inverted using the same techniques.

Expanding the periodic functions of the portion remaining to be inverted into infinite products shows that it possesses no pole at $s = 0$, and an infinite number of simple negative poles.

Following our established convention, let $s_n = -\alpha_n^2$ so that $\sqrt{s_n} = i\alpha_n$. The zeros equation, obtained by setting the denominator of the s-domain function equal to zero, thus becomes

$$(6-16) \qquad \tan N'\alpha_n = \frac{2\alpha_n}{\alpha_n^2 - 1}$$

in which α_n is now always positive.

Eqn. A-4 of Appendix A can now be used to determine the n'th residue

$$\text{res } g(s_n) = \left. \frac{2s \cdot e^{sN't/2\bar{\tau}}}{[N'(1+s)+2]\cosh N'\sqrt{s} + 2\sqrt{s}(1+N')\sinh N'\sqrt{s}} \right|_{s=-\alpha_n^2}$$

$$= \frac{-2\alpha_n^2 \cdot e^{-\alpha_n^2 N'\theta/2}/\cos N'\alpha_n}{N'(1-\alpha_n^2)+2 - 2\alpha_n(1+N')\tan N'\alpha_n}$$

in which $\theta = t/\bar{\tau}$. The substitution of the zeros obtained from Eqn. 6-16 into the foregoing plus summing up all residues and including the additional terms already inverted, one obtains

$$(6-17) \qquad \bar{\tau} \cdot r(t) = N'e^{N'} \sum_{n=1}^{\infty} \frac{2\alpha_n^2(\alpha_n^2-1) \cdot \sec N'\alpha_n \cdot \exp[-N'(\alpha_n^2+1)\theta/2]}{N'(\alpha_n^2+1)^2 + 2(\alpha_n^2+1)}.$$

Unfortunately, the secant appearing in the numerator of the foregoing equation generates an alternating plus-minus series. This creates no difficulty when the convergence is quick at a N' of about eight or less as indicated in Fig. 6-5, but it does as the number of terms required for convergence increases at a N' much in excess of eight because the greater the number of terms, the greater the need for accuracy in the lead-off terms. Eventually, this need exceeds the abilities of most personal computers or hand-held calculators. This is the reason why only the portion of the $r(t)$ in excess of $\theta = 1$ is shown in Fig. 6-5 at $N' = 32$.

Commentary: It is readily apparent from the equations given for the moments of the $r(t)$ functions that

$$\bar{\tau} \to \frac{L}{<v>} = V/Q \quad \& \quad \sigma^2 \to \frac{\bar{\tau}^2}{N'}$$

as $N' \to \infty$ $(F_L \to 0)$. This is supported by the curves presented in Figs. 6-2, 6-4, & 6-5, with all three dispersion models discussed herein seemingly yielding nearly identical $r(t)$ functions at $N' = 32$.

Expansion of the exponential term of Eqn. 6-14 for the completely bounded tubular reactor into an infinite series gives

$$\sigma^2 = \bar{\tau}^2 \left(1 - \frac{4N'}{3!} + \frac{8N'^2}{4!} - \cdots \right).$$

It is now apparent that as $N' \rightarrow 0$ ($E_L \rightarrow \infty$) that $\sigma^2 \rightarrow \bar{\tau}^2$, or the variance of a single ideal CSTR. If, on the other hand, $E_L = 0$ so that N' is infinite, then Eqn. 6-14 gives a variance of zero; i.e., ideal plug flow. The Dankwerts' boundary conditions thus lead to a continuous transformation from a single CSTR to plug flow.

First-Order Reactions: It was demonstrated in Chapter 4 that the fraction remaining of a substance undergoing a first-order reaction in a reactor operated to steady state can be determined by substituting the first-order rate constant k for s in the L.T. of the reactor's $r(t)$ function. Eqn. 6-7 thus gives

$$(6\text{-}18) \qquad \frac{<c>}{c_t} = \frac{2}{1+q} \cdot \exp[N'(1-q)]$$

for a partially bounded tubular reactor, and Eqn. 6-12 shows that

$$(6\text{-}19) \qquad \frac{c_d}{c_t} = \frac{4q}{(1+q)^2 \exp{-N'(1-q)} \; - \; (1-q)^2 \exp{-N'(1+q)}}$$

for a fully bounded reactor in which

$$N' = \frac{<v>L}{2E_L} \quad \text{and} \quad q = \sqrt{1 + \frac{4E_L}{<v>^2}k} = \sqrt{1 + \frac{2}{N'}(k\bar{t})}$$

where $\bar{t} = L/<v>$.

6-4.   OBSERVATIONS OF LONGITUDINAL DISPERSION

A dimensionless Peclet Number Pe_L is commonly used to report the results of dispersion measurements made in long pipelines approximating the infinite tube of Section 6-1 herein; i.e.,

$$Pe_L = \frac{<v>d_t}{E_L}$$

in which d_t is the inside tube diameter. The observed Pe_L numbers are then correlated against the observed Reynolds Number

$$Re = \frac{<v>d_t}{v}$$

as in Fig. 6-6 in which v is the kinematic viscosity of the fluid. If the flow is laminar then the Schmidt Number

$$Sc = \frac{v}{D_M}$$

must also be known in which D_M is the *coefficient of molecular diffusion* of the solute in the solvent, or the self-diffusion coefficient of the solvent itself. Note that an equation relating the Peclet Number to the Reynolds and Schmidt Numbers in the laminar flow regime is also given on Fig. 6-6. Finally, the Pe_L is related to the dispersion number N' by the following:

$$(6-20) \qquad N' = \frac{<v>L}{2E_L} = \frac{Pe_L}{2}\left(\frac{L}{d_t}\right).$$

Fig. 6-6 shows that the longitudinal dispersion coefficient E_L increases as the Reynolds Number decreases from fully developed turbulent flow to laminar flow. The radial velocity gradient is the primary cause of the increase in dispersion, and only the relatively slow process of molecular diffusion can generate flux in the radial direction in laminar flow; hence, the inclusion of D_M in the dispersion correlations shown in the figure. The radial flux resulting from the turbulent eddies is much greater in turbulent flow, and the mean radial velocity gradient is reduced considerably.

The inclusion of elbows in a tubular reactor increases the apparent longitudinal turbulence. According to one 1969 study reported briefly by Sherwood, Pigford & Wilke (1975), series of 90° elbows in a $1^1/_4$-in line increased E_L by 8 to 61%.

EXERCISE 6-1: Water @ 20°C flows through a 20-cm I.D. straight tube. Determine the E_L and N' of tagged water molecules 5 meters from the inlet at mean flow velocities of 10 cm/s and 0.5 cm/s.

ν = 1 centipoise @ 20°C.

$D_M \cong 2.2 \times 10^{-5}$ cm²/s for the self-diffusion coefficient of water @ 20°C (Sherwood, Pigford & Wilke, 1975).

For $<v>$ = 10 cm/s: Re = $10 \times 20/0.01 = 2 \times 10^4$ (turbulent flow). From Fig. 6-6 $Pe_L^{-1} = 0.42$. Thus, $E_L = (<v>d_t)Pe_L^{-1} = 10 \times 20 \times 0.42 = 84$ cm²/s & $N' = (Pe_L/2)(L/d_t) = (1/2)(1/.42)(500/20) = 30$.

For $<v>$ = 0.5 cm/s: Re = $0.5 \times 20/0.01 = 1000$ (laminar flow). Now Sc = $0.01/2.2 \times 10^{-5} = 455$ and from the equation given on Fig. 6-6, $Pe_L^{-1} = (1000 \times 455)^{-1} + (1000 \times 455/192) = 2370$. Thus, $E_L = 0.5 \times 20 \times 2370 = 23,700$ cm²/s & $N' = (1/2)(1/2370)(500/20) = 0.0053$.
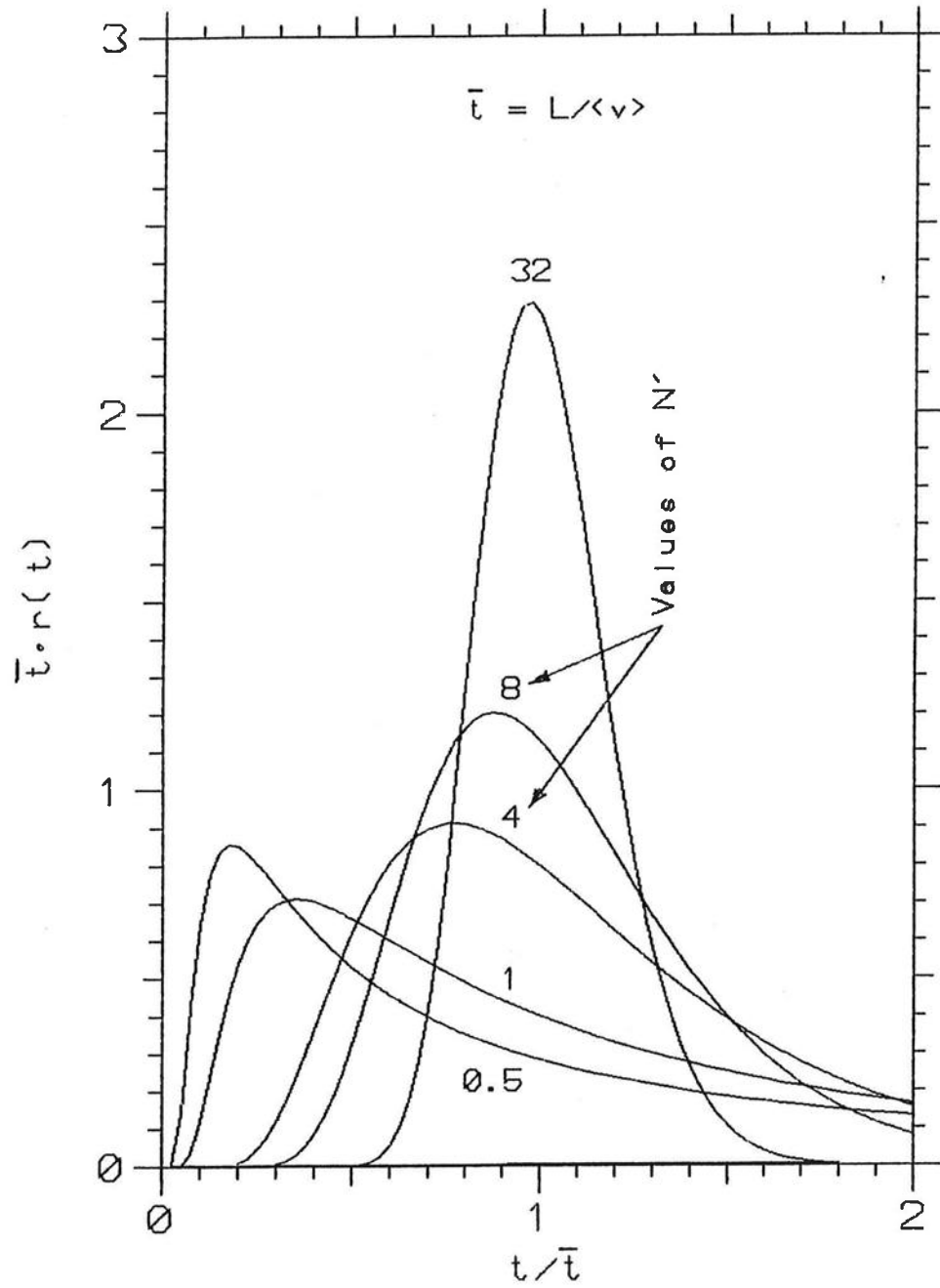
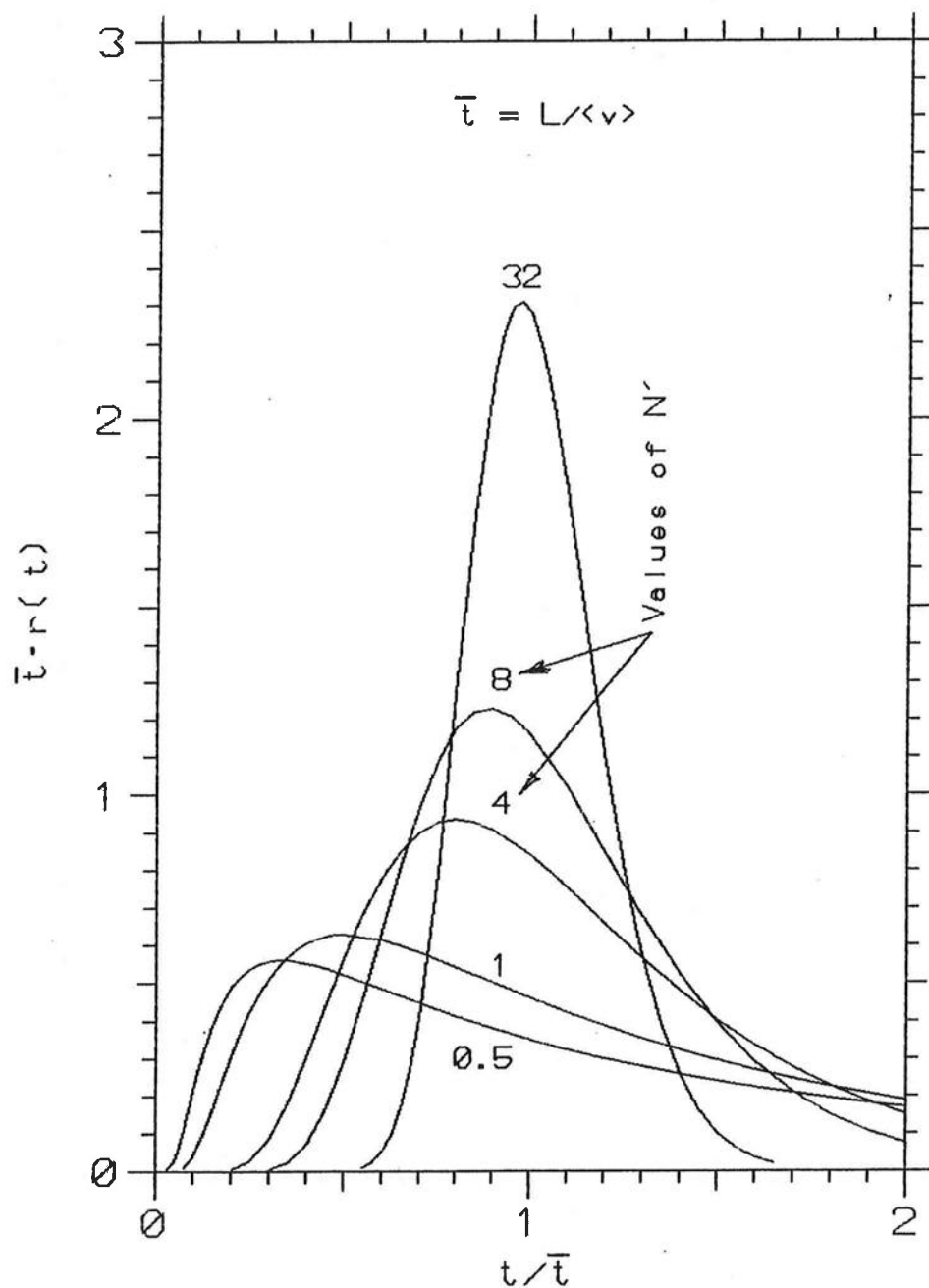Fig. 6-1. RTD-Functions for an Unbounded Infinite Pipe or Tube (Eqn. 6-3).

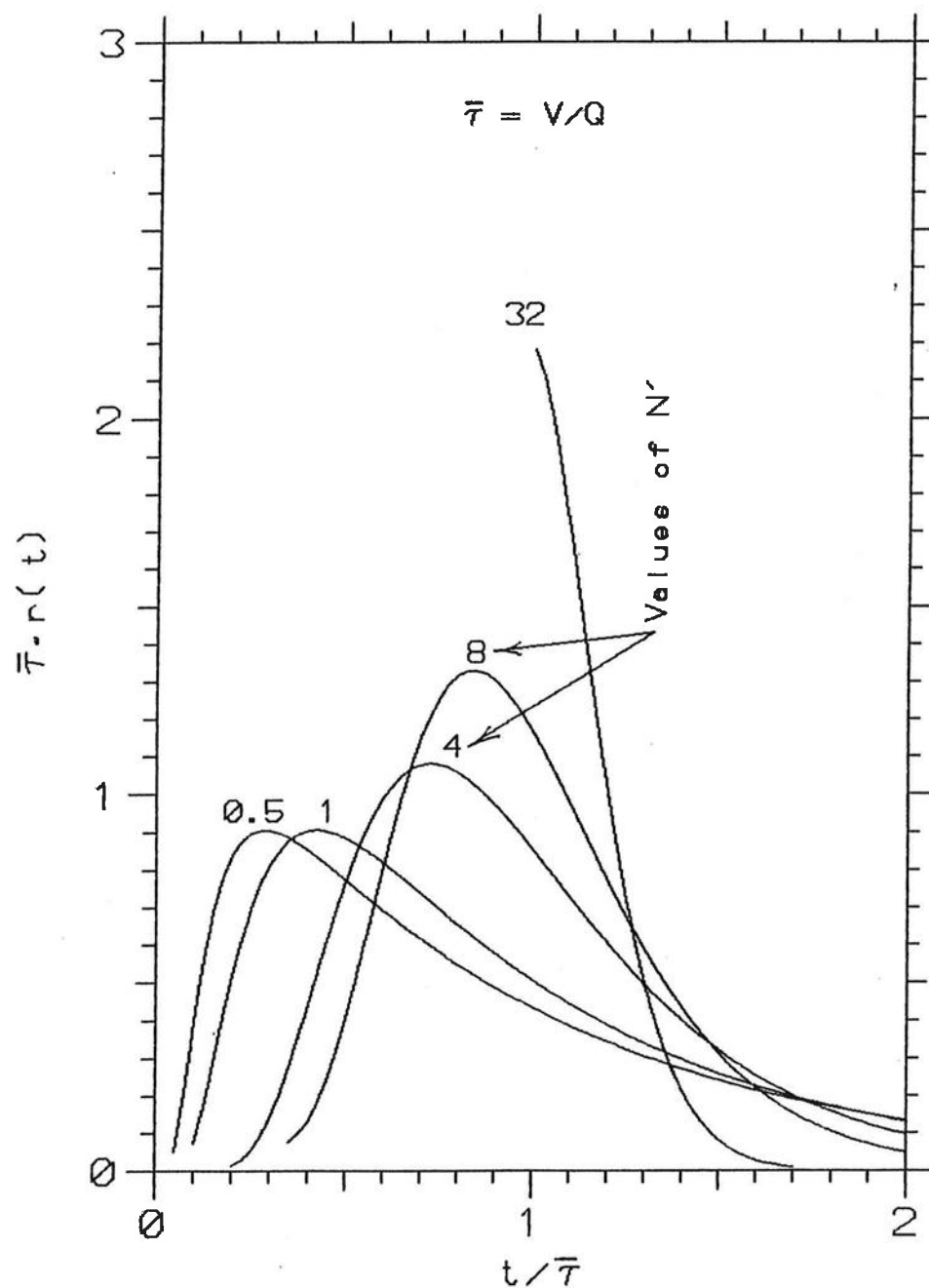Fig. 6-3. RTD-Functions for a Pipe or Tube Bounded at the Intake Only (Eqn. 6-8).

Fig. 6-5. RTD-Functions for a Completely Bounded Tubular Reactor (Eqn. 6-17).
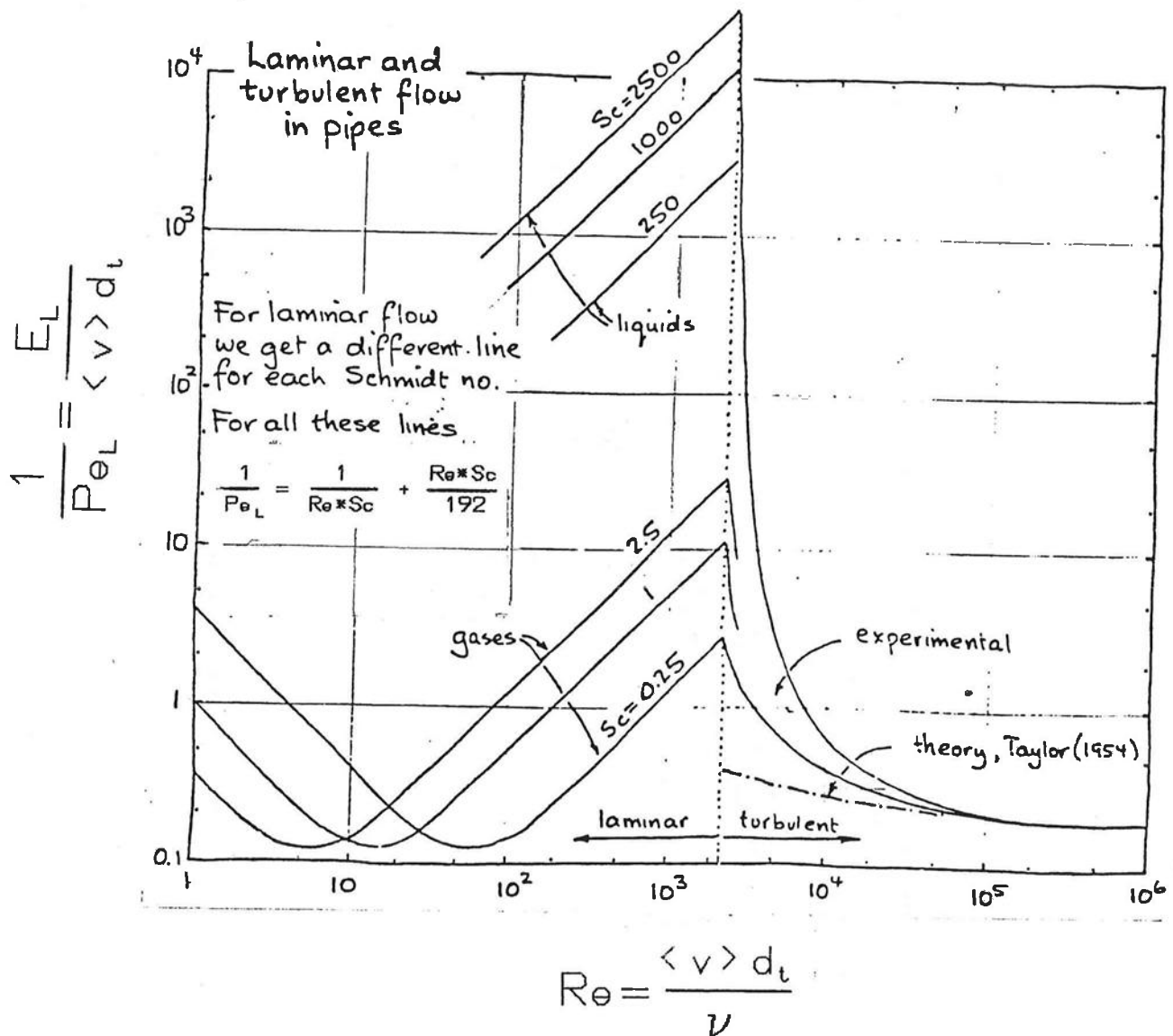
The figure shows a log-log plot with vertical axis $\dfrac{1}{Pe_L} = \dfrac{E_L}{\langle v \rangle \, d_t}$ ranging from 0.1 to 10^4, and horizontal axis $Re = \dfrac{\langle v \rangle \, d_t}{\nu}$ ranging from 1 to 10^6.

Labels on the figure:

Laminar and turbulent flow in pipes

$Sc = 2500$, 1000, 250 — liquids

For laminar flow we get a different line for each Schmidt no. For all these lines

$$\frac{1}{Pe_L} = \frac{1}{Re * Sc} + \frac{Re * Sc}{192}$$

2.5, 1, $Sc = 0.25$ — gases

experimental

theory, Taylor (1954)

laminar ← | → turbulent

Fig. 6-6. Correlations Used to Predict the Coefficient of Longitudinal Dispersion in Long Pipes & Tubes (from Levenspiel, 1979).

CHAPTER 7

FIXED-BED REACTORS

Ion exchange and activated carbon absorption are two examples of processes performed in fine particle fixed-bed reactor columns of the following style.
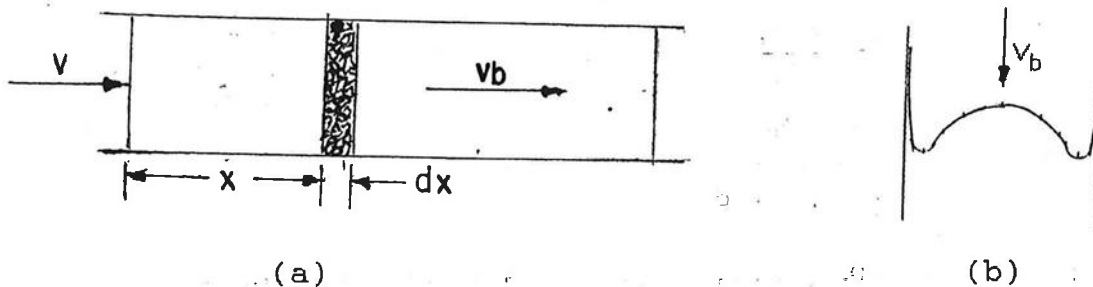

(a)   (b)

Fig. 7-1

The average interstitial velocity v_b of the fluid flowing through the particle bed of the column is

$$(7-1) \qquad v_b = \frac{Q}{\epsilon A_x} = \frac{v}{\epsilon}$$

in which Q is the total rate of fluid flow through the bed (steady), A_x is the cross-sectional area of the column, v is the approach velocity, and ϵ is the fractional void space within the fixed-bed.

The interstitial velocity will actually vary across the column as shown in Fig. 7-1(b). It will peak at about one particle diameter from the column wall (the wall effect), and it will exceed that at the center of the column by 100% or more if the column to bed particle diameter ratio is considerably less than 30, or by less than 20% if the ratio exceeds 30 (Denbigh, 1965).

Apparent dispersion of the fluid elements within the bed results from the obstruction to flow of the bed particles as well as the wall effect. The apparent dispersion in the longitudinal direction always exceeds that across the column (Denbigh, 1965: Kramer & Westerterp, 1963), and observed values of the longitudinal dispersion coefficient E_L are presented in Fig. 7-2 for columns packed randomly with uniform spheres.

7-1. MASS TRANSPORT EQUATION

The axially dispersed plug flow equation (refer to Eqn. 6-1 of Chapter 6) is commonly used to depict mass transfer in the fluid phase. The nomenclature of Eqn. 6-1 must be revised, however, to fit the case of a fixed-bed reactor, or

(7-2)
$$\frac{\partial c}{\partial t} = E_L \frac{\partial^2 c}{\partial x^2} - v_b \frac{\partial c}{\partial x}.$$

The number of transfer units N' as defined for Eqn. 6-3 must also be modified along with the Reynolds and longitudinal Peclet Numbers so that

$$N' = \frac{v_b L}{E_L}$$

$$Pe_L = \frac{v_b d_p}{E_L} \quad \& \quad Re_b = \frac{v d_p}{\nu}$$

in which L now designates the total bed depth, d_p is the particle diameter, and ν is the kinematic viscosity. (Note that the author of Fig. 6-2 uses the approach velocity v rather than v_b for Re_b).

Solving the N' and Pe_L equations for E_L and equating gives

$$2N' = \left(\frac{L}{d_p}\right) Pe_L.$$

Also, Fig. 6-2 shows that the Pe_L for liquids increases from about 0.5 at $Re_b < 20$ to 2 at $Re_b > 1000$ so that the foregoing becomes

(7-3)
$$\frac{1}{4}\left(\frac{L}{d_p}\right) \leq N' \leq \frac{L}{d_p}.$$

The diameters of ion-exchange resin beads commonly are in the order of 0.4 mm. This gives a L/d_p ratio of about 318 for a bed depth of only 5 inches, and a N' ranging from about 80 to 318 transfer units in accord with Eqn. 7-3. We know from the work done in Chapter 6 on flows in tubes that such large values of N' will yield very little dispersion (e.g., Fig. 6-1 etc.); consequently, the dispersion term of Eqn. 7-2 is usually ignored when dealing with fine-particle fixed-bed reactors.

One must now balance the transfer of mass occurring between the fluid and solid phases, or

$$(A_x \delta x)\epsilon r_b = -(A_x \delta x)\rho_b \frac{dq}{dt}$$

so that

$$r_b = -\frac{\rho_b}{\epsilon}\frac{dq}{dt}$$

in which ρ_b is the bulk density of the bed solids (mass of solids per unit of overall column volume), q is the moles of c that have reacted with the bed solids per unit mass of the solids, and r_b is the reaction rate relative to the fluid phase (moles of c per unit of fluid volume per unit time). Using the foregoing to augment Eqn. 7-2 while eliminating the dispersion term gives

$$\epsilon \frac{\partial c}{\partial t} = \epsilon r_b - \epsilon v_b \frac{\partial c}{\partial x} = -\rho_b \frac{\partial q}{\partial t} - v \frac{\partial c}{\partial x}.$$

The foregoing can now be simplified by redefining the independent variable t as

(7-4)
$$t' = t - \frac{x}{v_b}$$

in which t' is the time elapsed since a plug flow step input has passed through the bed depth at x. This gives the following simple expression commonly used to evaluate processes carried out in fixed-bed reactors (Sherwood *et al.*, 1975):

(7-5)
$$\rho_b \frac{\partial q}{\partial t'} + v \frac{\partial c}{\partial x} = 0.$$

7-2. ION-EXCHANGE KINETICS

The only analytical solution of the ion-exchange process known to this writer is the one published by H. Thomas in 1944 relevant to monovalent ions only (Sherwood, *et al.*, 1975; Perry & Chilton, 1973).

Assume we are interested in exchanging Na^+ and H^+ in water. Expressing the reaction in the form of an homogeneous reversible chemical reaction gives

$$Na^+ + RH \rightleftharpoons H^+ + RNa$$
$$c \quad , \quad q_m - q \qquad c_o - c \quad , \quad q$$

in which R represents the ion-exchange resin, c_o is the concentration of Na^+ in the feed water stream, and q_m is the maximum monovalent ion capacity of the resin. It then can be shown from the laws of mass action that

(7-6)
$$\rho_b \frac{\partial q}{\partial t} = \rho_b \frac{\partial q}{\partial t'} = \kappa a \left[c \left(1 - \frac{q}{q_m} \right) - \frac{1}{K} (c_o - c) \frac{q}{q_m} \right]$$

in which $K = k_f / k_b$ and k_f & k_b are the forward and reverse reaction rates, respectively, with both possessing dimensions of per unit of concentration per unit time. It should be noted that in accord with the derivation of Thomas that the product $q_m k_f \rho_b$ was replaced in Eqn. 7-6 by a kinetic coefficient κa of unknown magnitude to compensate for the resistances to transport of the ions from one phase to the other.

The time required for the mass transport process consists of that needed for a constituent to diffuse from one phase to the other, to diffuse through the pores of a porous solid, and possibly even to diffuse through the solid itself. It may also consist of the time required to overcome any resistance to adsorption at the fluid-solid interface. Resistances of this type are almost always rate controlling in two-phase operations and processes (Sherwood, et al., 1975). The term κa used by Thomas consists of the product of a rate constant κ (length per unit time) and the surface area of the solid a (surface area per unit of bed volume). The utilization of a single constant κ to represent all of these resistances to mass transfer is, of course, a rather gross approximation but subsequent digital analysis showed that while the Thomas solution does yield breakthrough curves which differ somewhat from those obtained employing exact correct mass transfer formulations, the errors are not serious for design purposes (Sherwood, et al., 1975).

The reaction depicted by Eqn. 7-6 will eventually cease upon reaching equilibrium. The ion concentrations at equilibrium are given by

$$(7-7) \qquad \frac{q^*}{q_m} = \frac{K(c/c_o)}{1 + (K-1)(c/c_o)}$$

in which q^* designates the q at equilibrium with c.

Eqns. 7-5 & 7-6 can be simplified considerably upon replacing x and t' with the following dimensionless variables:

$$n = \frac{(\kappa a)}{v}x \qquad \text{(no. of transfer units)}$$

$$T = v\left(\frac{c_o}{\rho_b q_m}\right)\frac{t'}{x}$$

$$nT = (\kappa a)\left(\frac{c_o}{\rho_b q_m}\right)t' \qquad \text{(dimensionless time)}.$$

This gives

$$(7-8) \qquad \frac{\partial(q/q_m)}{\partial(nT)} = -\frac{\partial(c/c_o)}{\partial n}$$

and

$$(7-9) \qquad \frac{\partial(q/q_m)}{\partial(nT)} = \frac{c}{c_o} + \left(\frac{1}{K}-1\right)\frac{c}{c_o}\cdot\frac{q}{q_m} - \frac{1}{K}\cdot\frac{q}{q_m}.$$

It is now readily evident that Eqn. 7-9 is non-linear except for the very special case of $K = 1$.

7-3. THOMAS' SOLUTION

Thomas devised a new dependent variable j defined by

$$(7-10A) \qquad (K^{-1}-1)\frac{q}{q_m} = \frac{\partial \ln(j)}{\partial n} = \frac{1}{j} \cdot \frac{\partial j}{\partial n}$$

$$(7-10B) \qquad (K^{-1}-1)\frac{c}{c_o} = -\frac{\partial \ln(j)}{\partial (nT)} = -\frac{1}{j} \cdot \frac{\partial j}{\partial (nT)}$$

which is a function of both c and q. Eqn. 7-8 was then equated to Eqn. 7-9 and the foregoing expressions substituted into the result as directed. Two terms containing cross-products of n and nT were obtained which cancelled each other out leaving the following single, linear partial differential equation in j.

$$(7-11) \qquad \frac{\partial^2 j}{\partial (nT) \partial n} + \frac{\partial j}{\partial (nT)} + \frac{1}{K} \cdot \frac{\partial j}{\partial n} = 0$$

Boundary Conditions (BCs): Assume that the purpose of the treatment is to replace Na^+ with H^+ in water, and that the bed resin is fully charged with H^+ at time zero so that $q(x, t=0) = 0$. Also assume that the interstitial water in the bed is free of Na^+ at time zero, and that the feed solution contains a concentration c_o of Na^+ which is introduced into the ion-exchange column as a step input at time zero. The concentration of Na^+ within the interstitial water at $x = 0$ will thus always be c_o so that $c(x=0, t) = c_o$.

Changing t to t' does not alter the foregoing BCs. Eqn. 7-4 shows that $x = v_b t$ at $t' = 0$, which demonstrates that the coordinate system stays attached to the plug flow wave front as it moves through the resin bed. This front always encounters fully charged resin so that $q(x, t'=0) = 0$. Also, Eqn. 7-4 shows that $t = t'$ at $x = 0$ so that $c(x=0, t') = c_o$.

Eqns. 7-10A & 7-10B must now be used to adjust the foregoing BCs to the new variable j as follows.

i. $q/q_m = 0$ at $nT = 0$ so that from Eqn. 7-10A

$$\frac{dj}{dn}\Big|_{nT=0} = 0.$$

The L.T. of the foregoing with respect to n is

$$\bar{j}(u,0) = \frac{j(0,0)}{u}$$

in which u is used henceforth to designate the L.T. of n. The inverse is

$$j(n,0) = j(0,0)$$

in which $j(0,0)$ is the value of j at n and $nT = 0$.

ii. $c/c_0 = 1$ at $n = 0$ so that from Eqn. 7-10B

$$\frac{dj}{d(nT)}\Big|_{n=0} = -\left(\frac{1}{K} - 1\right)j(0,nT).$$

The L.T. of the foregoing with respect to nT is

$$\bar{j}(0,s) = \frac{j(0,0)}{s + K^{-1} - 1}$$

in which s is used henceforth to designate the L.T. of nT. The inverse is

$$j(0,nT) = j(0,0) \cdot \exp\left[-\left(\frac{1}{K} - 1\right)nT\right].$$

Integration: The integration of Eqn. 7-11 can be initiated by taking the L.T. with respect to either one of the two independent variables while holding the other constant. For example, commencing with n, one obtains

$$(u+1)\frac{d\bar{j}(u,nT)}{d(nT)} + \frac{u}{K} \cdot \bar{j}(u,nT) = j(0,0)\exp[(1-K^{-1})nT]$$

after utilizing two of the BC relationships listed under BC *ii* of the previous section. Taking the L.T. again with respect to nT one gets

$$\frac{\bar{j}(u,s)}{j(0,0)} = \frac{u+1}{u[s(u+1)+u/K]} + \frac{1}{(s+K^{-1}-1)[s(u+1)+u/K]}$$

after utilizing a BC relationship listed under BC *i*.

Transform Pairs 4 & 8 of Table II, Chapter 2 may now be used to obtain the inverse to the foregoing equation with respect to the transformed variable s, or

$$\frac{\bar{j}(u,nT)}{j(0,0)} = \frac{(1-K^{-1})}{u(u+1-K^{-1})} \cdot \exp\left[-\frac{u \cdot (nT)}{(u+1)K}\right] + \frac{\exp[(1-K^{-1})nT]}{u+1-K^{-1}}.$$

Subtracting unity from each u in accord with Operation 6 of Table I, Chapter 2 then gives

$$\frac{j(n,nT)}{j(0,0)} = (1-K^{-1})e^{-(n+nT/K)} \, L^{-1}\left[\frac{u}{(u-1)(u-K^{-1})} \cdot \frac{e^{nT/Ku}}{u}\right]$$
$$+ \exp[(1-K^{-1})(nT-n)]$$

in which the bracketed terms remain to be inverted. Unfortunately, the function giving this L.T. is unrecognized in the field of mathematics and is not listed in any tables of transform pairs. The only recourse left is convolution as described in Operation 14 of Table I.

One term of the convolution integral is (Roberts & Kaufman, 1966)

$$f_1(n) = L^{-1}\left[\frac{1}{u}\exp\left(\frac{nT/K}{u}\right)\right] = I_0\left(2\sqrt{\frac{nT}{K}n}\right)$$

in which $I_0(z)$ represents the zero order of one of the modified Bessel functions in z. The second term is

$$f_2(n) = L^{-1}\left[\frac{u}{(u-1)(u-K^{-1})}\right] = \frac{1}{(1-K^{-1})}(e^n - K^{-1}\cdot e^{n/K}).$$

The solution to Eqn. 7-11 then becomes

$$(7-12)\quad \frac{j(n,nT)}{j(0,0)} = \exp[(1-K^{-1})(nT-n)] + e^{-nT/K}\int_0^n e^{-\xi}I_0\left(2\sqrt{\frac{nT}{K}\xi}\right)d\xi$$

$$-\exp[(1-K^{-1})(nT-n)]\cdot e^{-nT}\int_0^{n/K} e^{-\xi}I_0(2\sqrt{nT\xi})d\xi.$$

The Thomas J Function: Thomas found that the substitution of the function

$$(7-13)\qquad J(\alpha,\beta) = 1 - e^{-\beta}\int_0^\alpha e^{-\xi}I_0(2\sqrt{\beta\xi})d\xi$$

into Eqn. 7-12 gives the following much simpler appearing expression

$$(7-14)$$

$$\frac{j(n,nT)}{j(0,0)} = 1 - J\left(n,\frac{nT}{K}\right) + J\left(\frac{n}{K},nT\right)\cdot\exp[(1-K^{-1})(nT-n)].$$

Thomas also proved that the **J** function possesses the following useful properties and identity:

$$\frac{\partial J(\alpha,\beta)}{\partial\alpha} = -e^{-(\alpha+\beta)}I_0(2\sqrt{\alpha\beta})$$

$$\frac{\partial J(\alpha,\beta)}{\partial\beta} = +e^{-(\alpha+\beta)}\sqrt{\frac{\alpha}{\beta}}\cdot I_1(2\sqrt{\alpha\beta})$$

$$J(\alpha,\beta) + J(\beta,\alpha) = 1 + e^{-(\alpha+\beta)}I_0(2\sqrt{\alpha\beta})$$

in which $I_1(z)$ designates the first order of a modified Bessel function in z.

Eqn. 7-10B was then employed to convert the variable j back to the original c. This necessitates taking the partial derivative of Eqn. 7-14 with respect to (nT), which gives a result in which two terms containing first order Bessel functions cancel each other out to yield

$$\frac{1}{j(0,0)}\cdot\frac{\partial j(n,nT)}{\partial(nT)} = (1-K^{-1})\cdot\exp[-(1-K^{-1})(nT-n)]\cdot J\left(\frac{n}{K},nT\right).$$

Substituting the foregoing plus Eqn. 7-14 into Eqn. 7-10B then gives the following solution for c (Sherwood, *et al.*, 1975)

$$(7-15) \quad \frac{c}{c_o} = \frac{J(n/K,nT)}{J(n/K,nT) + [1-J(n,nT/K)] \cdot \exp[(1-K^{-1})(n-nT)]}.$$

Utilizing an approach similar to the one above for Eqn. 7-10A, one obtains

$$(7-16) \quad \frac{q}{q_m} = \frac{1 - J(nT,n/K)}{J(n/K,nT) + [1-J(n,nT/K)] \cdot \exp[(1-K^{-1})(n-nT)]}.$$

Evaluation of the Thomas J Function: The modified zero order Bessel function appearing in Eqn. 7-13 can be expanded into an infinite series and then integrated term by term. Unfortunately, nearly every term of the expansion also has to be expanded into an additional infinite series in order to be integrated. The result is the following remarkably complicated expression

$$(7-18) \quad J(\alpha,\beta) = 1 - e^{-\beta} \sum_{i=0}^{\infty} \frac{\beta^i}{i!} + e^{-(\alpha+\beta)} \sum_{m=-2}^{\infty} \frac{(\alpha\beta)^{m+2}}{(m+2)!} \cdot \sum_{i=0}^{\infty} \frac{\beta^i}{(i+2+m)!}$$

in which $i = 0,1,2,3,\ldots$ and $m = -2,-1,0,1,2,3,\ldots$. The rate of convergence is acceptable only when the product $\alpha\beta < 36$.

Thomas developed the following approximation to Eqn. 7-13 which is said to be in error by less than 1% when $\alpha\beta > 36$ (Sherwood, *et al.*, 1975).

$$(7-19) \quad J(\alpha,\beta) \approx \frac{1}{2}[1-\text{erf}(\sqrt{\alpha}-\sqrt{\beta})] + \frac{\exp-(\sqrt{\alpha}-\sqrt{\beta})^2}{2\sqrt{\pi} \cdot [(\alpha\beta)^{1/4}+\sqrt{\beta}]}$$

If $\alpha\beta > 3600$ then the foregoing degenerates to

$$(7-20) \quad J(\alpha,\beta) \approx \frac{1}{2}[1-\text{erf}(\sqrt{\alpha}+\sqrt{\beta})].$$

Note that the term $(\sqrt{\alpha}-\sqrt{\beta})$ appearing with the error function can be either positive or negative. One thus must at times utilize the identity

$$\text{erf}(-z) = -\text{erf}(z)$$

i.e., first set a negative z positive to procure the $\text{erf}(z)$ and then multiply the answer by -1.

Eqns. 7-15 & 7-16 are shown plotted against T in Fig. 7-3 for $K = 2/3$, 1 & 2; and for $n = 20$ transfer units. The value of n selected for this figure was large enough to permit the use of Eqn. 7-19 throughout.

The results illustrate clearly the sensitivity of the ion-exchange process to the ratio k_f/k_b. If $K = 2/3$ then the kinetics of the exchange is unfavorable from a process viewpoint, and c/c_o is considerably greater than q/q_m throughout T. If $K = 2$ then both breakthrough curves sharpen considerably, and become virtually identical.

It should also be noted that if $K = 1$ then the breakthrough curves pass close to $T = 1$ at $c/c_0 = 1/2$. Tables of the Thomas J function published by Sherwood *et al.* (1975) demonstrate clearly that as $n \to \infty$, $T \to 1$ at $c/c_0 = 1/2$ when $K = 1$.

Regeneration of Spent Resin: Referring again to the example of the exchange of Na^+ and H^+ ions, it will be assumed that the resin has become fully saturated with Na^+, and that the residing interstitial fluid possesses no H^+ at time zero so that $q(z, t^{'}=0)$ = q_m. A step input of an aqueous regeneration solution of *HCl* at a concentration c_0 is commenced at time zero so that $c(z=0, t^{'}) = 0$ for the Na^+.

Following the analytical steps already outlined for the treatment mode, one can show that

$$(7\text{-}21) \qquad \frac{c}{c_0} = \frac{1 - J(n/K, nT)}{1 - J(n/K, nT) + J(n, nT/K) \cdot \exp[(1 - K^{-1})(n - nT)]}$$

and

$$(7\text{-}22)$$
$$\frac{q}{q_m} = \frac{1 - J(n/K, nT) + [J(n, nT/K) + J(nT/K, n) - 1] \cdot \exp[(1 - K^{-1})(n - nT)]}{1 - J(n/K, nT) + J(n, nT/K) \cdot \exp[(1 - K^{-1})(n - nT)]}.$$

Plots of Eqns. 7-21 & 7-22 are presented in Fig. 7-4 for $K = 2/3$, 1 & 2; and for $n = 20$ transfer units. It must be recognized, however, that the K for treatment may differ greatly from that for regeneration in the ion-exchange process because the elution solutions commonly are made very strong to hasten regeneration. This increases the ionic strength of the elution solution which in turn affects the rate constants k_f and k_b appreciably (Sherwood *et al.*, 1975).

7-4. COMMENTARY

Unfortunately, the Thomas solution applies strictly to monovalent ions and the water quality engineer must deal primarily with divalent ions. The solution does have further applications, however, as illustrated in the following chapter.
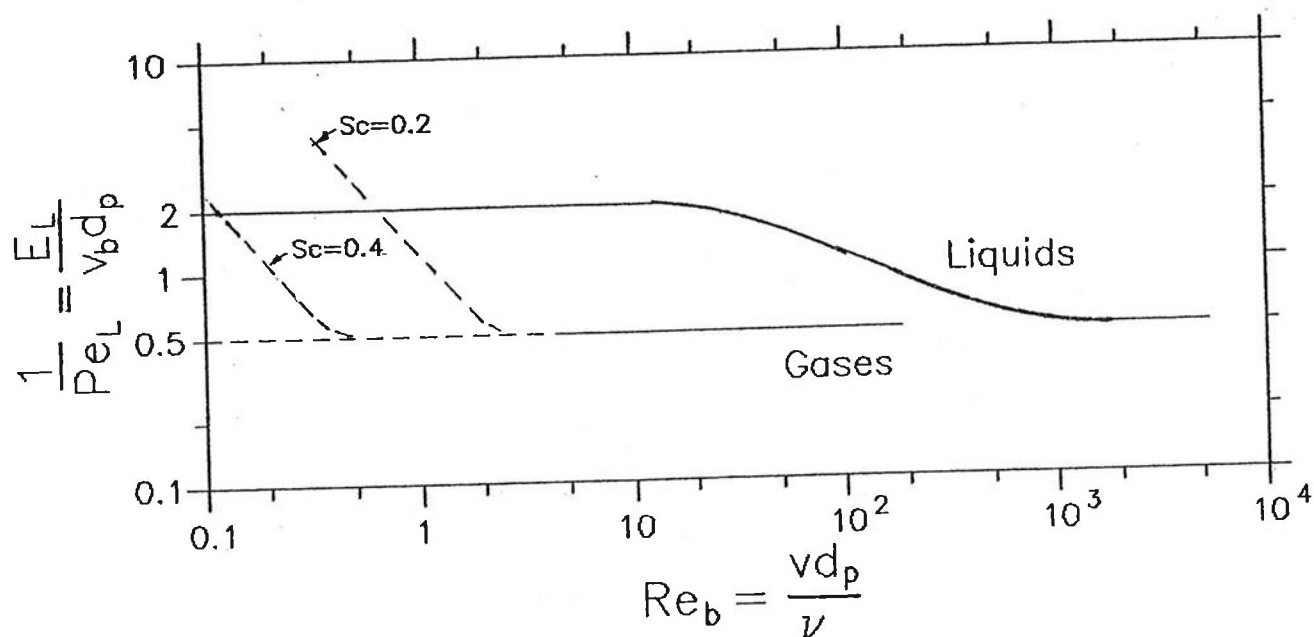
Fig. 7-2. Observed Dispersion of Fluids in Packed Beds (from Levenspiel, 1962).
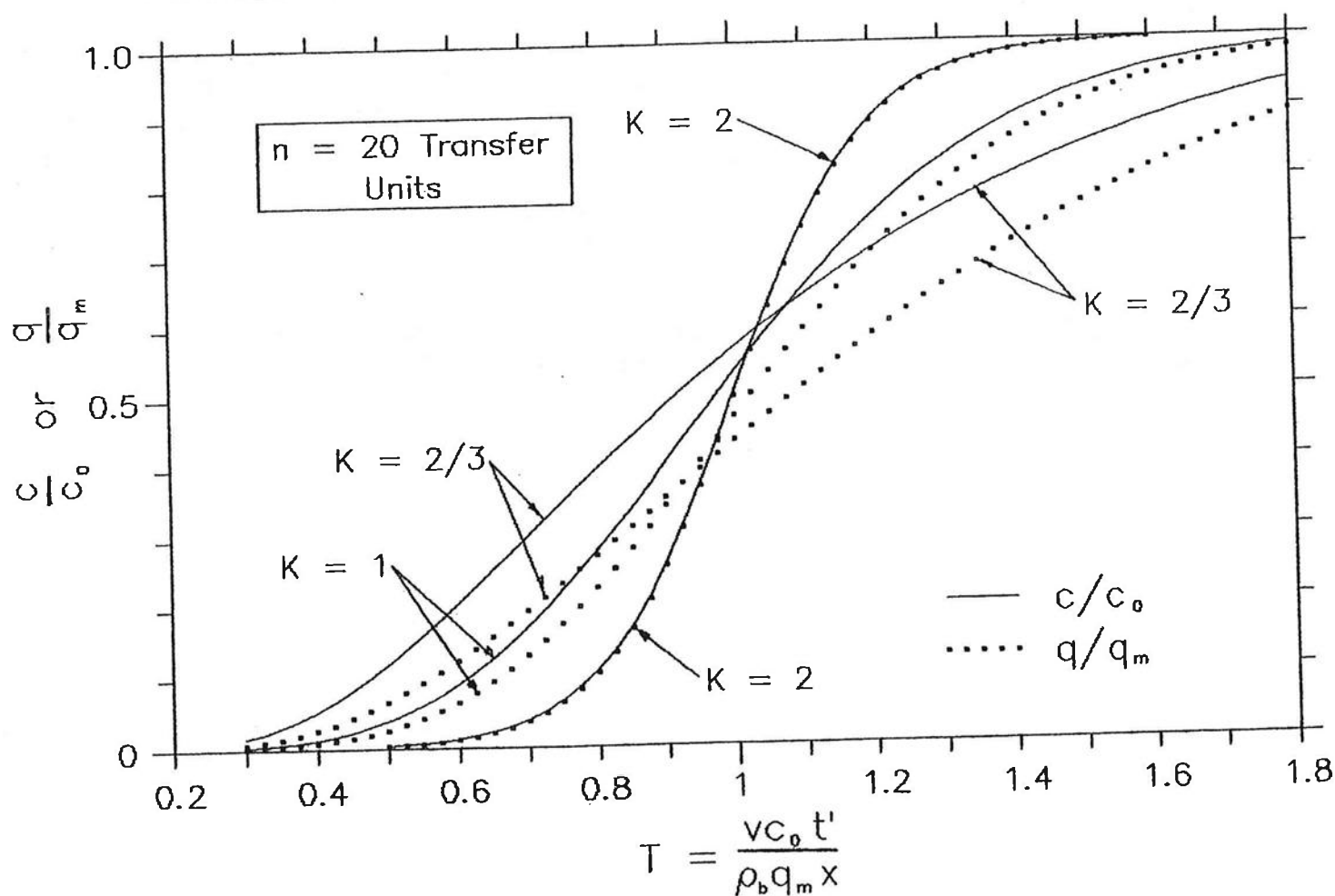

Fig. 7-3. Plots of Thomas' Analytical Solution for the Treatment Mode of Operation of Ion-Exchange Columns.
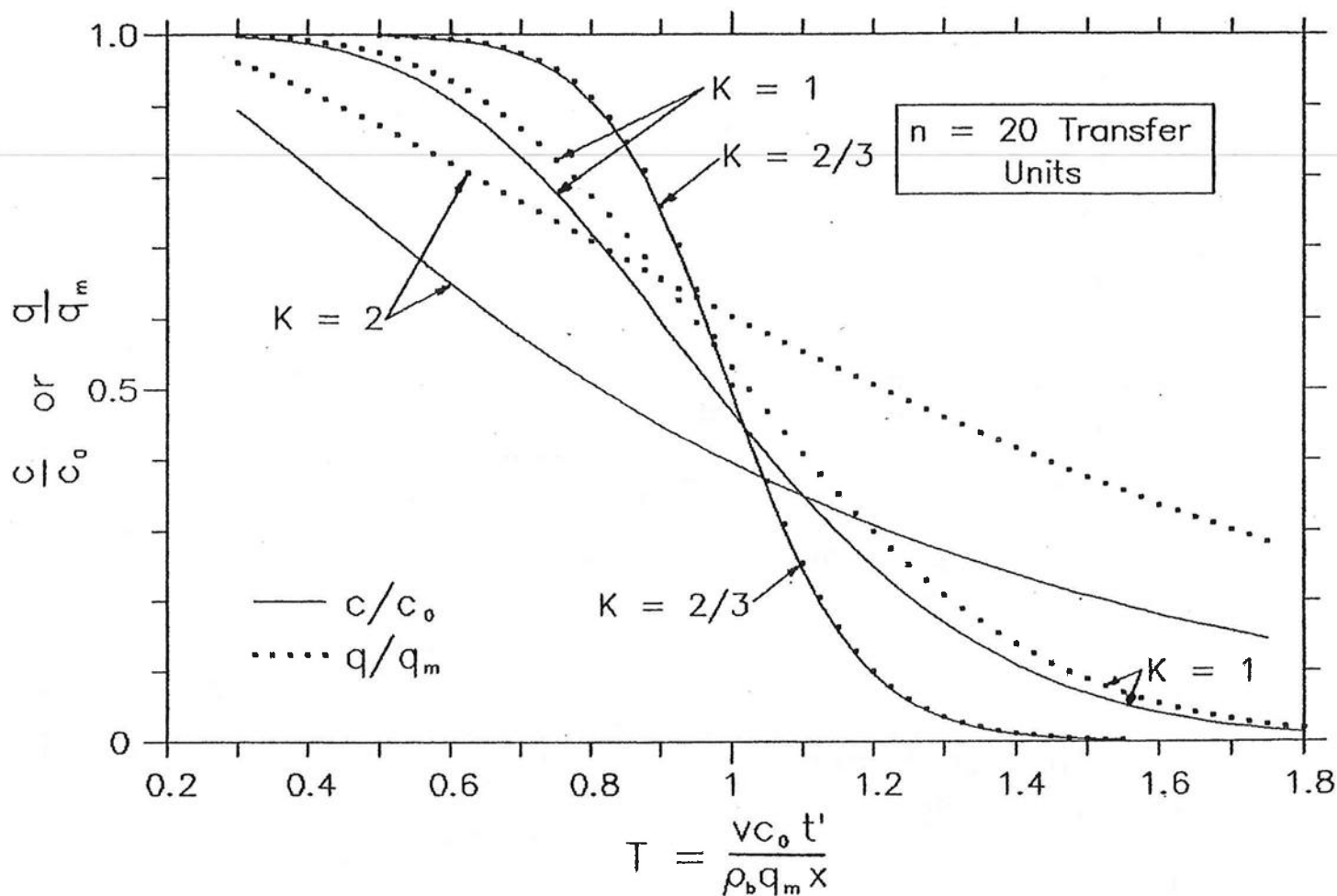
Fig. 7-4. Plots of Thomas' Analytical Solution for the Regeneration of Spent Ion-Exchange Media in Packed Beds.

CHAPTER 8

LANGMUIR ADSORPTION IN FIXED-BED REACTORS

In 1916 Langmuir derived the following isotherm applicable to the adsorption of gas molecules onto completely homogeneous surfaces with negligible interaction between the adsorbed molecules (Perry & Chilton, 1973; Sherwood, *et al.*, 1975);

$$(8-1) \qquad \frac{q^*}{q_m} = \frac{K_A p}{1 + K_A p}$$

in which p is the partial pressure of the adsorbate in the gas phase, K_A the Langmuir equilibrium coefficient of the adsorbate on the solid phase (dimensions of per unit pressure) and the remaining terms are as defined previously.

Now let p_o equal some reference partial pressure such as that of the adsorbate in the gas feed stream, and let q^*_o represent q at equilibrium with p_o. One then obtains from the above

$$K_A q_m = \frac{(1 + K_A p_o) q^*_o}{p_o}$$

which upon substitution back into Eqn. 8-1 gives

$$(8-2) \qquad \frac{q^*}{q^*_o} = \frac{(1 + K_A p_o) p / p_o}{1 + K_A p}.$$

Finally, the substitution of

$$(8-3) \qquad r = 1 + K_A p_o$$

into Eqn. 8-2 yields

$$(8-4) \qquad \frac{q^*}{q^*_o} = \frac{r(p/p_o)}{1 + (r-1)(p/p_o)}$$

which is identical in form to Eqn. 7-7 of Chapter 7 with p, r, and q_o^* replacing c, K, and q_m, respectively. In other words, the Thomas solution for ion-exchange also applies to Langmuir adsorption upon making the foregoing specified substitutions. There also exist some limitations which follow.

The Langmuir equilibrium coefficient K_A must always be finite and positive; thus, r (or K) as defined by Eqn. 8-3 is always > 1. The partial pressure p_o of the adsorbate must be modest relative to the total to prevent a substantial change in v_b which was held constant by Thomas. Finally, the Langmuir adsorption isotherm has also been used to describe adsorption from liquids, but adsorption from liquids usually proves to be much less ideal than from gases (Sherwood, *et al.*, 1975).

EXERCISE 8-1: In 1939 E. Wicke investigated the desorption of CO_2 gas from a fixed-bed column containing porous carbon particles (Sherwood, *et al.*, 1975). Use the Thomas solution combined with the Langmuir adsorption isotherm to analyze the study results.

Description: Wicke employed a column having a cross-sectional area A_x of 0.405 cm^2 with a total bed depth of 72 cm. The carbon bed had a bulk density ρ_b of 0.36 g/cm^3 and a void ratio ϵ of 0.345. The total pressure and temperature of the gas phase were maintained at about 1 atm and 0°C, respectively.

The bed carbon was first brought to equilibrium with CO_2 at a partial pressure (p_o) of 100 mm of Hg. A carrier gas free of CO_2 was then introduced as a step input into the column at a flow rate Q_s of 1.85 cm^3/s, and the column effluent was monitored for CO_2. The study results are shown graphically in Fig. 8-1.

Procedure: Note first that $v = Q_s/A_x = 4.57$ cm/s; $v_b = v/\epsilon = 13.24$ cm/s and $t' = t - x/v_b = t - 5.44$ s. Also, Fig. 8-1 shows that it took about 650 s for the ratio c/c_o to decrease by one-half, or $t_{1/2} = 650$ s.

Eqn. 7-21 was used to compute the ratio c/c_o after picking the parameters n and K by trial and error. The value of $T_{1/2}$ was also carefully ascertained. The definition of T given in Chapter 7 was then used to relate $T_{1/2}$ to $t_{1/2}$, or

$$(8\text{-}5) \qquad T_{1/2} = \left(\frac{c_o}{\rho_b q_o^*}\right) \times \frac{4.57}{72} \times (t'_{1/2} - 5.44).$$

Now if $n = 25$ and $K = 1.6$ as stated in Fig. 8-1 then $T_{1/2} = 0.894$ and the foregoing gives

$$0.894 = \left(\frac{c_o}{\rho_b q_o^*}\right) \times \frac{4.57}{72} \times (650 - 5.44) \quad \& \quad \frac{c_o}{\rho_b q_o^*} = 0.0219.$$

This shows that the value of q at equilibrium with 100 mm Hg of CO_2 is

$$q_o^* = \frac{(c_o)}{0.0219 \rho_b} = \left(\frac{100}{62.36 \times 10^3 \times 273}\right) \times \frac{1}{0.0219} \times \frac{1}{0.36} = 7.45 \times 10^{-4} \text{ moles/g}.$$

Eqn. 8-3 shows that $K = 1.6 = r = 1 + K_A p_o$; consequently, $K_A = 0.6 \times 10^{-2}$ per mm Hg, and the maximum adsorptive capacity q_m of the carbon for CO_2 is found to be

$$q_m = \frac{K q_o^*}{K - 1} = \frac{1.6}{0.6} q_o^* = 2 \times 10^{-3} \text{ moles/g}.$$

Finally, the Langmuir adsorption isotherm producing the response depicted in Fig. 8-1 is

$$q^{\bullet} = 2 \times 10^{-3} \cdot \frac{0.6 \times 10^{-2} p}{1 + 0.6 \times 10^{-2} p}$$

at 0°C.

Commentary: No doubt the correspondence between the observed data and the computed curve shown in Fig. 8-1 could be improved with a fine tuning of the parameters n and K. Still the results suffice to show that the desorption of carbon dioxide from porous carbon is near ideal except at the very beginning and end of the process. This was noted by Sherwood *et al.*, (1975) employing an entirely different method of analysis, and it was suggested that the discrepancy at long times probably is due to the deficiency of the Langmuir formulation at small values of c.

EXERCISE 8-2: Oil shale contains appreciable amounts of high molecular weight kerogen which is recovered by first breaking up the raw shale and then retorting it in situ or above ground at 950°F or higher. Various hydrocarbon vapors and liquids are produced which are then captured and processed further for the market. The spent shale fragments are extremely heterogeneous in both size and shape as well as the degree of water soluble total organic carbon (TOC) content (Hall, 1982).

Hall investigated the leaching of the TOC into water employing column studies, with the results of one such study shown in Fig. 8-2. Ascertain the ability of the Thomas solution combined with the Langmuir adsorption isotherm to depict the data presented thereon.

Description: The spent shale fragments used in the column study depicted in Fig. 8-2 were those which passed through a 1/2 inch sieve but not a 1/8 inch sieve. Because the raw shale tended to fracture along planes of stratification, they were roughly cylindrical in shape with an average diameter and thickness of about 0.7 cm and 0.2 cm, respectively.

The column used had a diameter of 11.4 cm and a total bed depth of one meter. The dry bulk density ρ_b of the bed was 0.88 g/cm³ with a total void ratio including the pores within the solids of about 0.59. The external void ratio ϵ exclusive of the pore volume was 0.44.

Distilled water was first allowed to stand within the bed for an hour or so at ambient temperature with the concentration c_0 of TOC in the water increasing to an average of 34.7 mg/L. A step input of distilled water was then commenced at a flow rate Q_L of

55 ml/min and water samples were collected periodically for analysis at bed depths of 25, 55 and 85 cm. Note that the foregoing data give an approach velocity v of 32.3 cm/h and a bed velocity $v_b = v/\epsilon$ of 73.5 cm/h.

Procedure: Particular attention was paid to the data collected at the 85 cm depth because they gave the most complete pattern. A trial and error approach indicated that n and K should be around 14 and 2.5, respectively. Also, the value of the group of constants $c_o/(\rho_b q_o^*)$ contained in the definition of T used to relate T to real time t was about 2.5.

These values were held constant for the remaining two depths sampled except n was set proportional to the sampling depth x in accord with the definition of n given in Chapter 7. This gave n transfer units of 9 and 4 for the 55 and 25 cm depths, respectively. Additionally, the time t' had to be varied with sampling depth in accord with $t' = t - x/v_b$. The results obtained at the three depths sampled are shown in Fig. 8-2.

Commentary: Additional studies performed by Hall showed that the TOC in the water had in no way attained full equilibrium with the shale fragments within an hour's time frame. This commonly is the case for studies made on *liquid-solid* equilibria, with experimental measurements of q pertaining primarily to the mass of solute contained within the exterior outlines of the solid phase only (Sherwood *et al.*, 1975).

Additionally there probably existed some longitudinal dispersion in the column combined with wall effects. It also would be naive to expect that the heterogeneity of the shale fragments would be exactly the same at all bed depths. Even so, the Thomas solution combined with the Langmuir adsorption isotherm worked remarkably well in explaining the observed data patterns.

Discrepancies appear at relatively long operation times, however, with the TOC concentrations tailing off at a much slower pace than predicted. This likely results from the extensive time required for the TOC to diffuse out from the centers of the relatively large shale fragments. Thomas' assumption of a constant resistance to mass transfer makes it impossible to account for such an effect, and a second stage of diffusion from the solid phase particles has to be added to account for the entire length of observation as was done by Hall (1982).
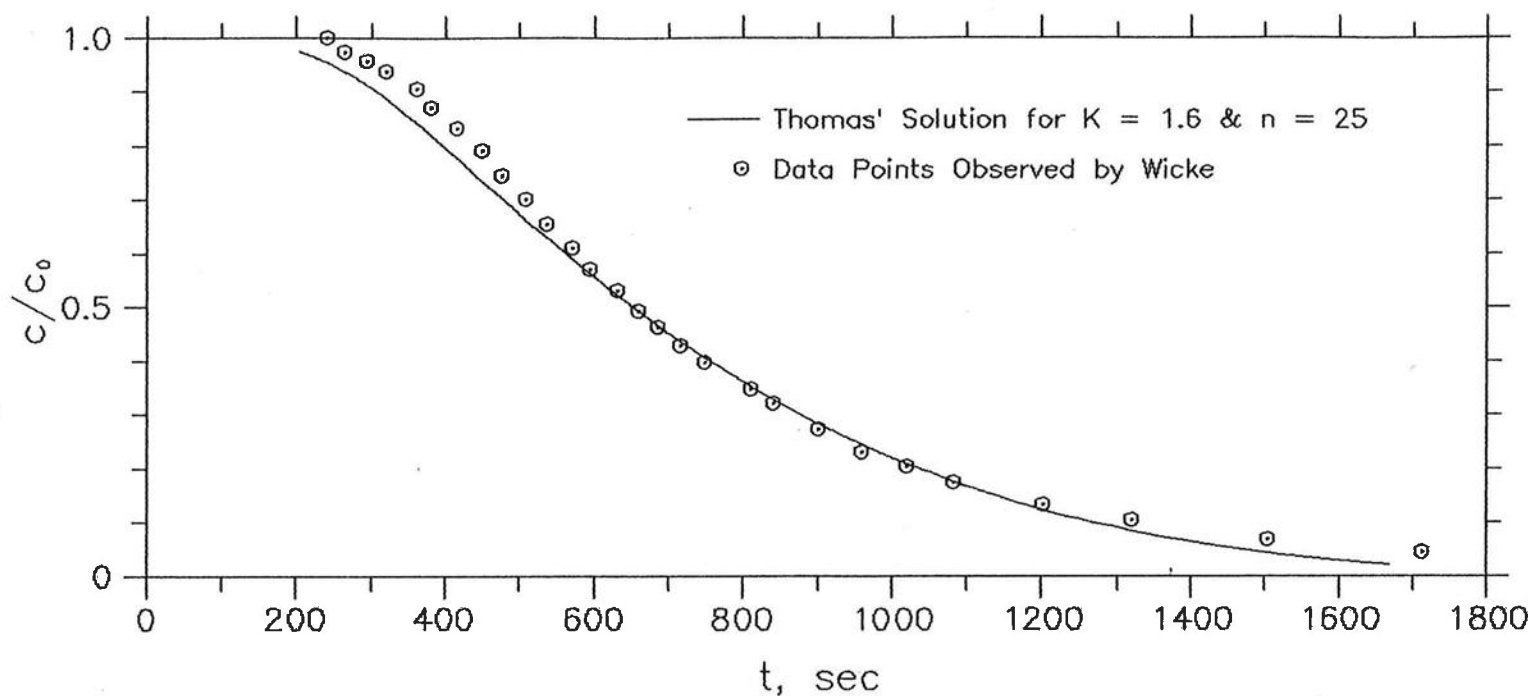
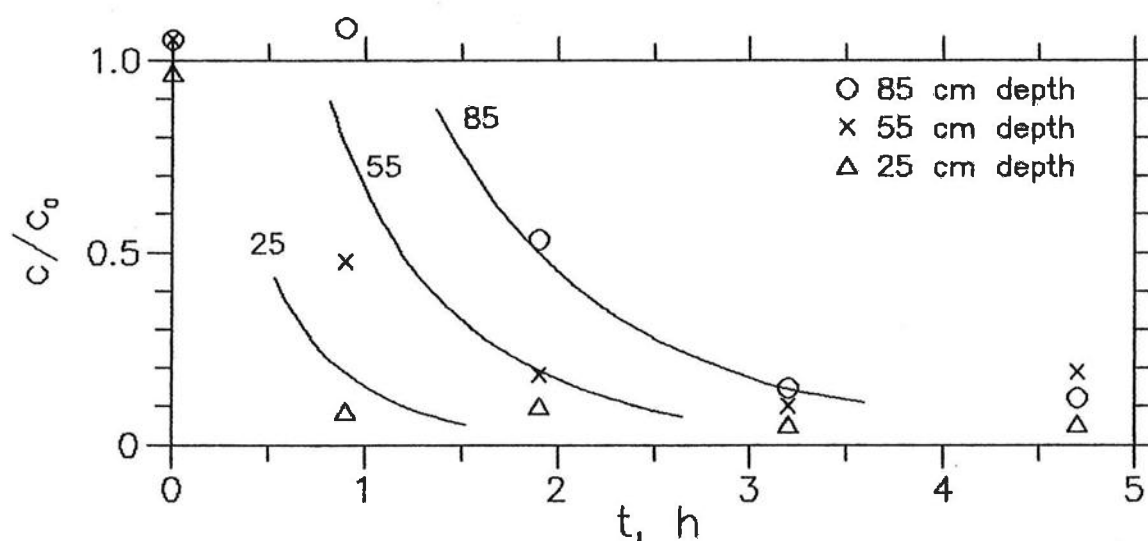Fig. 8-1. Desorption of Carbon Dioxide Gas from Porous Carbon.

Fig. 8-2. Contamination of Water with Total Organic Carbon
Derived from Spent Oil Shale; Data of Hall (1982).

APPENDIX A

A STANDARD METHOD OF OBTAINING THE INVERSE TO RATIONAL s-DOMAIN FUNCTIONS

The <u>method of residues</u> is used to invert s-domain functions of the type

$$(A-1) \qquad g(s) = \frac{P(s)}{Q(s)}$$

in which $P(s)$ and $Q(s)$ are <u>rational</u> polynomials possessing no common factors, and $P(s)$ is at least one order less than $Q(s)$ (otherwise the problem cannot be real). This method is limited only by the ability to determine the zeros to $Q(s)$.

The general approach is to ascertain first the values of s in the denominator $Q(s)$ which cause $g(s)$ to go to infinity. Such values are called the <u>poles</u> of the function, and each pole yields a <u>residue</u>. The sum of all such residues then gives the completed solution.

To illustrate, let $Q(s) = (s+\alpha)^2(s+\beta)$ where $\alpha \neq \beta$. This polynomial equals zero at $s = -\alpha$ and $s = -\beta$. These <u>zeros</u> of $Q(s)$ equal the poles of $g(s)$ but we must distinguish between the pole at $s = -\alpha$ which occurs twice in $Q(s)$, and $s = -\beta$ which occurs just once. The former is called a <u>multiple</u> pole and the later a <u>simple</u> pole.

The residue for a multiple pole at $s = s_1$ appearing m times is (Reed & Reed, 1968)

$$(A-2) \qquad \text{res } g(s_1) = \frac{1}{(m-1)!} \lim_{s \to s_1} \frac{d^{m-1}[(s-s_1)^m g(s)e^{+ts}]}{ds^{m-1}}$$

This type of residue may equal zero, but it must always be finite.

If $m = 1$ for a simple pole then Eqn. A-2 reduces to

$$(A-3) \qquad \text{res } g(s_1) = \lim_{s \to s_1} (s-s_1)g(s)e^{+ts}$$

This kind of residue must be finite and other than zero.

Another very convenient method of procuring the residue of a simple pole is

$$(A-4) \qquad \text{res } g(s_1) = \frac{P(s)}{Q'(s)}e^{+st}\Big|_{s=s_1}$$

provided that $P(s)$ is finite.

EXERCISE A-1: Use the method of residues to determine the inverse to Eqn. 2-24 of Chapter 2; i.e.,

$$(2-24) \qquad \bar{r}(s) = \frac{a^2/(1+\beta)}{s^2+2as+a^2/(1+\beta)} = \frac{a^2/(1+\beta)}{(s-r_1)(s-r_2)}$$

where $a = 2(1+\beta)/\bar{\tau}$, the roots r_1 and r_2 are $-a(1+q)$ and $-a(1-q)$, respectively, and $q = \sqrt{\beta/(1+\beta)}$.

Clearly, this s-domain function possesses two simple poles at $s = r_1$ and $s = r_2$, and the two residues may be computed with either Eqn. A-3 or A-4. For Eqn. A-4:

$$Q(s) = s^2-(r_1+r_2)s+r_1r_2 \quad \text{so that} \quad Q'(s) = \frac{dQ(s)}{ds} = 2s-r_1-r_2.$$

Consequently,

$$\text{res } \bar{r}(r_1) = \frac{a^2}{1+\beta} \cdot \lim_{s \to r_1} \frac{1}{2s-r_1-r_2} \cdot e^{+ts} = \frac{a^2}{1+\beta} \cdot \frac{1}{r_1-r_2} \cdot e^{r_1 t}$$

Likewise, for root r_2

$$\text{res } \bar{r}(r_2) = \frac{a^2}{1+\beta} \cdot \frac{1}{r_2-r_1} \cdot e^{r_2 t}$$

The complete solution is

$$r(t) = \frac{a^2}{1+\beta} \cdot \frac{e^{r_1 t} - e^{r_2 t}}{r_1-r_2}.$$

which yields Eqn. 2-25 of Chapter 2 upon the substitution of the formulations for a, r_1, and r_2 into the above.

EXERCISE A-2: Use the method of residues to prove that the inverse of the $g(s)$ function $(s+a)^{-n}$ is as given by Transform Pair 6 of Table II.

One has to use Eqn. A-2 to obtain the inverse to this $g(s)$ function because it possesses just one pole at $s = -a$ repeated n times. Eqn. A-2 shows that

$$\text{res } g(-a) = \frac{1}{(n-1)!} \cdot \lim_{s \to -a} \left\{ d^{n-1} \left[\frac{(s+a)^n e^{+ts}}{(s+a)^n} \right] / ds^{n-1} \right\}$$

$$= \frac{1}{(n-1)!} \cdot \lim_{s \to -a} \frac{d^{n-1} e^{+ts}}{ds^{n-1}} = \frac{t^{n-1}}{(n-1)!} \cdot \lim_{s \to -a} e^{+ts} = \frac{t^{n-1}}{(n-1)!} e^{-at}$$

which matches Transform Pair 6.

EXERCISE A-3: Use the method of residues to determine the periodic output from a single CSTR subjected to a sinusoidal input of tracer defined by the function $A \sin \omega t$ in which A is the amplitude and ω the angular velocity.

The L.T. of the output $g(s)$ from the CSTR consists of the product of $\bar{r}(s)$ for a CSTR and $g_i(s)$ for the input function. Transform Pair 7 of Table II shows that

$$g_i(s) = \frac{A\omega}{s^2 + \omega^2}.$$

and so,

$$g(s) = \frac{aA\omega}{(s+a)(s^2+\omega^2)} = \frac{aA\omega}{(s+a)(s+i\omega)(s-i\omega)}$$

in which $a = 1/\bar{\tau}$ for the CSTR. This shows that the s-domain function has three simple poles at $s = -a$, $s = -i\omega$, and $s = +i\omega$. Employing Eqn. A-4, one obtains the following three residues:

$i.$ res $g(-a)$ $= aA\omega \cdot \lim_{s \to -a} \frac{e^{+ts}}{s^2+\omega^2+2s(s+a)} = \left(\frac{Aa\omega}{a^2+\omega^2}\right)\exp-\frac{t}{\tau}$

This residue disappears exponentially with time because it represents a perturbation resulting from tracer start-up at time zero. It is of no interest here and is ignored henceforth.

$ii.$ res $g(-i\omega)$ $= aA\omega \cdot \lim_{s \to -i\omega} \frac{e^{+ts}}{s^2+\omega^2+2s(s+a)} = -\frac{aA}{2i \cdot (a-i\omega)} \cdot e^{-i\omega t}$

Also, in a like manner,

$iii.$ res $g(+i\omega)$ $= \frac{aA}{2i \cdot (a+i\omega)} \cdot e^{+i\omega t}$

The completed solution is thus

$$f(t) = aAi\left[\frac{e^{-i\omega t}}{2(a-i\omega)} - \frac{e^{+i\omega t}}{2(a+i\omega)}\right] = \frac{aA}{a^2+\omega^2}(a \cdot \sin\omega t - \omega \cdot \cos\omega t)$$

Now letting $\cos\beta = a/\sqrt{a^2+\omega^2}$, $\sin\beta = \omega/\sqrt{a^2+\omega^2}$, and $\tan\beta = \omega/a$, one can show that the foregoing reduces to

$$f(t) = \frac{aA}{\sqrt{a^2+\omega^2}}(\sin\omega t \cdot \cos\beta - \cos\omega t \cdot \sin\beta)$$

$$= \frac{aA}{\sqrt{a^2+\omega^2}}\sin(\omega t - \tan^{-1}\omega/a) = \frac{A}{\sqrt{1+(\omega\bar{\tau})^2}}\sin(\omega t - \tan^{-1}\omega\bar{\tau})$$

This shows that the input sinusoidal function is attenuated by $1/\sqrt{1+(\omega\bar{\tau})^2}$ and its phase delayed by the angle whose tangent is $\omega\bar{\tau}$ as it passes through a CSTR.

To make this solution appropriate for a tracer study, one must add on an average concentration where $<c> \geq A$, or

(A-5) $c(t) = <c> + \dfrac{A}{\sqrt{1+(\omega\bar{\tau})^2}}\sin(\omega t - \tan^{-1}\omega\bar{\tau})$

If a periodic input of this type is used to evaluate the internal mixing of a real system, then it is customary to vary the frequency ω and then plot the resulting amplitude change and phase shift against frequency. A plot of this type is called a Bode plot (Seinfeld & Lapidus, 1974).

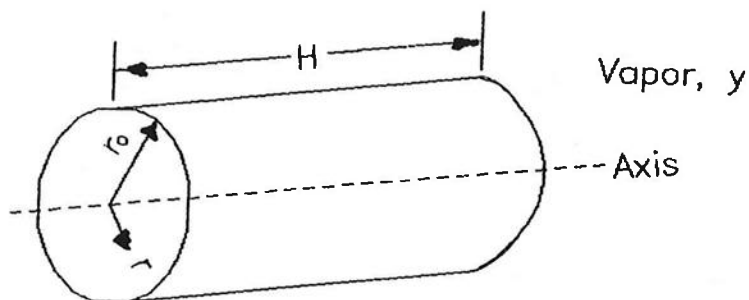## APPENDIX B

PERMEATION OF SOLIDS

B-1.   A SLENDER ROD

Fig. B-1

Referring to Fig. B-1, the mass flux of a VOC into a slender plastic rod is

$$\frac{dm}{dt} = 2\pi r_0 H D_M \frac{dc}{dr}\Big|_{r=r_0}$$

in which r_0 is the radius and H the length of the rod. Now

$$m_\infty = c_\infty V = c_\infty \pi r_0^2 H$$

so that

$$\frac{d(m/m_\infty)}{dt} = \frac{df_s}{dt} = \frac{2}{c_\infty}\frac{D_M}{r_0}\cdot\frac{dc}{dr}\Big|_{r=r_0}$$

in which f_s is the fraction of rod saturation, or in dimensionless coordinates

$$\frac{df_s}{d\theta} = \frac{2}{c_\infty}\cdot\frac{dc}{d\lambda}\Big|_{\lambda=1} \quad \text{in which} \quad \theta = \frac{D_M t}{r_0^2} \quad \& \quad \lambda = \frac{r}{r_0}.$$

The boundary conditions match those listed in Chapter 5 for the derivation of Barrer's equation. Taking the L.T. of the above function with respect to time and setting $c = 0$ at $t = 0$ gives

(B-1) $$F_s(s) = \frac{2}{c_\infty}\cdot\frac{1}{s}\cdot\frac{dC(s)}{d\lambda}\Big|_{\lambda=1}.$$

The Fickian diffusion equation written in cylindrical coordinates is

(B-2) $$\frac{\partial c}{\partial\theta} = \frac{1}{\lambda}\cdot\frac{\partial c}{\partial\lambda} + \frac{\partial^2 c}{\partial\lambda^2}$$

which has a L.T. with respect to time of

$$\frac{d^2C(s)}{d\lambda^2} + \frac{1}{\lambda}\frac{dC(s)}{d\lambda} - sC(s) = 0$$

or

(B-3)
$$z^2\frac{d^2C(s)}{dz^2} + z\frac{dC(s)}{dz} + z^2C(s) = 0$$

upon standardization by setting $z = p\lambda$ in which $p^2 = -s$.

    Eqn. B-3 is Bessel's differential equation of zero order which is not amenable to integration by the L.T. technique due to its variable coefficients (Reed & Reed, 1968). The general solution is (Sokolnikoff & Sokolnikoff, 1941)

(B-4)
$$C(s) = A \cdot J_0(z) + B \cdot Y_0(z)$$

in which $J_0(z)$ and $Y_0(z)$ are zero order Bessel functions of the first and second kind, respectively; and A & B are arbitrary constants.

    Taking the derivative of Eqn. B-4 with respect to z gives
$$\frac{dC(s)}{dz} = -A \cdot J_1(z) - B \cdot Y_1(z)$$

which must equal zero at $z = 0$ thanks to the symmetry in concentration about the axis of the rod. Thus,
$$A \cdot J_1(0) + B \cdot Y_1(0) = 0.$$

Now $J_1(0) = 0$ and $Y_1(0) = -\infty$ so that the constant B must always equal zero; hence,
$$A = \frac{C(1,s)}{J_0(p)} = \frac{c_\infty}{s} \cdot \frac{1}{J_0(p)} \quad \text{where} \quad c_\infty = K \cdot y$$

in accord with an ideal step input of VOC vapor pressure at time zero, and Eqn. B-4 becomes

(B-5)
$$\frac{C(s)}{c_\infty} = \frac{1}{s} \cdot \frac{J_0(p\lambda)}{J_0(p)}.$$

    Taking the derivative of the foregoing with respect to λ gives
$$\frac{dC(s)}{d\lambda}\bigg|_{\lambda=1} = \frac{c_\infty}{p} \cdot \frac{J_1(p)}{J_0(p)}$$

at $\lambda = 1$, which in turn yields the following s-domain solution for f_θ upon substitution back into Eqn. B-1:

(B-6)
$$F_s(s) = \frac{2}{sp} \cdot \frac{J_1(p)}{J_0(p)}.$$

An Inverse: The periodic Bessel functions appearing in Eqn. B-6 can be expanded into infinite products (Abramowitz & Stegun, 1966) to obtain

$$F_s(s) = \frac{\prod_{n=1}^{\infty}(1 + s/\alpha_{1,n}^2)}{s\prod_{n=1}^{\infty}(1 + s/\alpha_{0,n}^2)}.$$

A simple pole exists at $s = 0$, and an infinite number of simple poles s_n at $-\alpha_{0,n}^2$ in which $\alpha_{0,n}$ represents the n'th zero of $Jo(p)$. Utilization of Eqn. A-3 of Appendix A shows that the residue at $s = 0$ is plus unity.

Employing Eqn. A-4, the n'th residue of Eqn. B-6 is

$$\text{res } g(s_n) = \frac{4J_1(p)}{3pJ_0(p) + sJ_1(p)}e^{+s\theta}\Big|_{s=s_n} = -\frac{4}{\alpha_{0,n}^2}e^{-\alpha_{0,n}^2\theta}$$

because $Jo(p)$ always equals zero at the poles. The sum of all residues then gives the inverse

(B-7) $\qquad f_s = 1 - 4\sum_{n=1}^{\infty}\frac{1}{\alpha_{0,n}^2}\exp{-\alpha_{0,n}^2\theta}$ in which $\theta = \frac{D_M t}{r_0^2}$.

Unlike the trigonometric functions, the zeros of the Bessel function are not evenly spaced as shown in Table III for the first ten zeros of $Jo(p)$.

A plot of Eqn. B-7 is shown in Fig. B-2. The first term of Eqn. B-7 suffices when $f_e > 0.75$, or

(B-8) $\qquad f_s = 1 - 0.6917 \cdot \exp{-5.783\theta}$ when $f_s > 0.75$.

Otherwise, convergence becomes slow if one ventures too close to $\theta = 0$.

TABLE III. FIRST TEN ZEROS TO BESSEL'S FUNCTION $Jo(x)$*

n	$\alpha_{0,n}$	n	$\alpha_{0,n}$
1	2.40482556	6	18.07106397
2	5.52007811	7	21.21163663
3	8.65372791	8	24.35247153
4	11.79153444	9	27.49347913
5	14.93091771	10	30.63460647

* From Abramowitz & Stegun (1966).

B-2. A SPHERE

The developments for a sphere parallel those discussed previously herein for slabs and cylinders, and utilize equivalent boundary conditions.

The mass flux of a VOC into a sphere is

$$\frac{dm}{dt} = 4\pi r_o^2 D_M \cdot \frac{dc}{dr}\Big|_{r=r_o}.$$

Now

$$m_\infty = \frac{4}{3}\pi r_o^3 c_\infty$$

so that

$$\frac{d(m/m_0)}{dt} = \frac{df_s}{dt} = \frac{3D_M}{r_o c_\infty}\cdot\frac{dc}{dr}\Big|_{r=r_o}$$

or in dimensionless coordinates

$$\frac{df_s}{d\theta} = \frac{3}{c_\infty}\cdot\frac{dc}{d\lambda}\Big|_{\lambda=1} \quad \text{in which} \quad \theta = \frac{D_M t}{r_o^2} \quad \& \quad \lambda = \frac{r}{r_o}.$$

Taking the L.T. of the foregoing with respect to time and setting $c = 0$ at $t = 0$ gives

(B-9)
$$F_s(s) = \frac{3}{c_\infty}\cdot\frac{1}{s}\cdot\frac{dC(s)}{d\lambda}\Big|_{\lambda=1}.$$

The Fickian diffusion equation written in spherical coordinates is

$$\frac{\partial c}{\partial \theta} = \frac{2}{\lambda}\cdot\frac{\partial c}{\partial \lambda} + \frac{\partial^2 c}{\partial \lambda^2}$$

which has a L.T. with respect to time of

(B-10)
$$z^2\frac{d^2 C(s)}{dz^2} + 2z\frac{dC(s)}{dz} + z^2 C(s) = 0$$

upon standardization by setting $z = p\lambda$ in which $s = -p^2$.

The general solution to Eqn. B-10 is (Abramowitz & Stegun, 1966)

(B-11)
$$C(s) = A\left(\frac{\sin z}{z}\right) - B\left(\frac{\cos z}{z}\right)$$

in which A & B are arbitrary constants. The derivative of the foregoing with respect to z is

$$\frac{dC(s)}{dz} = \frac{A}{z}\left(-\frac{1}{z}\sin z + \cos z\right) + \frac{B}{z}\left(\frac{1}{z}\cos z + \sin z\right)$$

which must equal zero at $z = 0$ thanks to the symmetry in concentration about the center of the sphere. This can only occur if $B = 0$. Additionally,

$$A = \frac{C(p,s)\cdot p}{\sin p} = \frac{c_\infty}{s}\cdot\frac{p}{\sin p} \quad \text{where} \quad c_\infty = K\cdot y$$

and Eqn. B-11 becomes

(B-12)
$$\frac{C(s)}{c_\infty} = \frac{1}{s\lambda}\frac{\sin p\lambda}{\sin p}.$$

Taking the derivative of Eqn. B-12 with respect to λ gives

$$\frac{dC(s)}{d\lambda}\Big|_{\lambda=1} = \frac{c_\infty}{s}\left(\frac{p \cdot \cos p}{\sin p} - 1\right)$$

at $\lambda = 1$, which upon substituting back into Eqn. B-9 yields the following solution for f_s in the s-domain:

(B-13) $\qquad F_s(s) = \frac{3}{s^2}\left(\frac{p \cdot \cos p}{\sin p} - 1\right)$ in which $p^2 = -s$.

Inverses: Eqn. B-13 may be written in the following forms to expedite the process of obtaining its inverse;

(B-14) $\qquad F_s(s) = \frac{3}{s^2}\left(\frac{\sqrt{s}\cosh\sqrt{s}}{\sinh\sqrt{s}} - 1\right) = \frac{3}{s^2}(\sqrt{s}\,\mathrm{ctnh}\sqrt{s} - 1)$

$$= \frac{3}{s^{3/2}}\left(\frac{1 + e^{-2\sqrt{s}}}{1 - e^{-2\sqrt{s}}}\right) - \frac{3}{s^2}.$$

The binomial series may now be used to expand the last of these forms into the infinite series

$$F_s(s) = \frac{3}{s^{3/2}} - \frac{3}{s^2} + 6\sum_{n=1}^{\infty}\frac{1}{s^{3/2}}e^{-2n\sqrt{s}}$$

which has the inverse (refer to the development of Eqn. 5-8 in Chapter 5)

(B-15) $\quad f_s = 6\sqrt{\dfrac{\theta}{\pi}} - 3\theta + 12\sqrt{\dfrac{\theta}{\pi}}\cdot\sum_{n=1}^{\infty}e^{-n^2/\theta} - 12\sum_{n=1}^{\infty}n\cdot\mathrm{erfc}\dfrac{n}{\sqrt{\theta}}.$

B-3

Fig. ~~B-2~~ shows a plot of Eqn. B-15. Just the first two terms suffice when $f_s < 0.70$, or

(B-16) $\qquad f_s \approx 6\sqrt{\dfrac{\theta}{\pi}} - 3\theta$ when $f_s < 0.70$.

Convergence is slow, however, for a f_s much in excess of 0.70.

Expansion of the periodic functions appearing in the first of the three forms of Eqn. B-14 into infinite products yields

$$F_s(s) = \frac{3}{s^2}\left\{\frac{\displaystyle\prod_{n=1}^{\infty}(1 + 4s/(n-1)^2\pi^2) - \prod_{n=1}^{\infty}(1 + s/n^2\pi^2)}{\displaystyle\prod_{n=1}^{\infty}(1 + s/n^2\pi^2)}\right\}$$

which shows that Eqn. B-13 possesses a double pole at $s = 0$, and an infinite number of simple poles s_n at $-\alpha_n^2 = -n^2\pi^2$. The residue of the double pole can be ascertained by applying Eqn. A-2 of Appendix A to Eqn. B-14 plus a liberal application of L'Hospital's rule. After considerable work, however, one finds that this residue is simply plus unity.

Eqn. A-4 may now be used to derive the n'th residue by setting $Q(s) = s^2\sinh\sqrt{s}$ as shown in Eqn. B-14 so that

$$\operatorname{res}\ g(s_n)\ =\ \frac{P(s)}{Q'(s)}e^{+s\theta}\Big|_{s=s_n}\ =\ \frac{6(\sqrt{s}\cosh\sqrt{s}-\sinh\sqrt{s})}{s(4\sinh\sqrt{s}+\sqrt{s}\cosh\sqrt{s})}e^{+s\theta}\Big|_{s=s_n}\ =\ -\frac{6}{\alpha_n^2}e^{-\alpha_n^2\theta}$$

because $\sinh\sqrt{s_n} = 0$. Summing up all of the residues then gives the solution

$$(\text{B-17})\quad f_s\ =\ 1\ -\ 6\sum_{n=1}^{\infty}\frac{1}{\alpha_n^2}\cdot\exp-\alpha_n^2\theta\ \text{ in which }\ \theta=\frac{D_M t}{r_o^2}\ \&\ \alpha_n^2=n^2\pi^2$$

Just the first term of this function suffices when $f_\theta > 0.85$; i.e.,

$$(\text{B-18})\qquad\qquad f_s\ \approx\ 1\ -\ \frac{6}{\pi^2}\exp-\pi^2\theta\qquad\text{when}\qquad f_s>0.85.$$

Xi

$$\Theta = \frac{D_M t}{r_o^2}$$
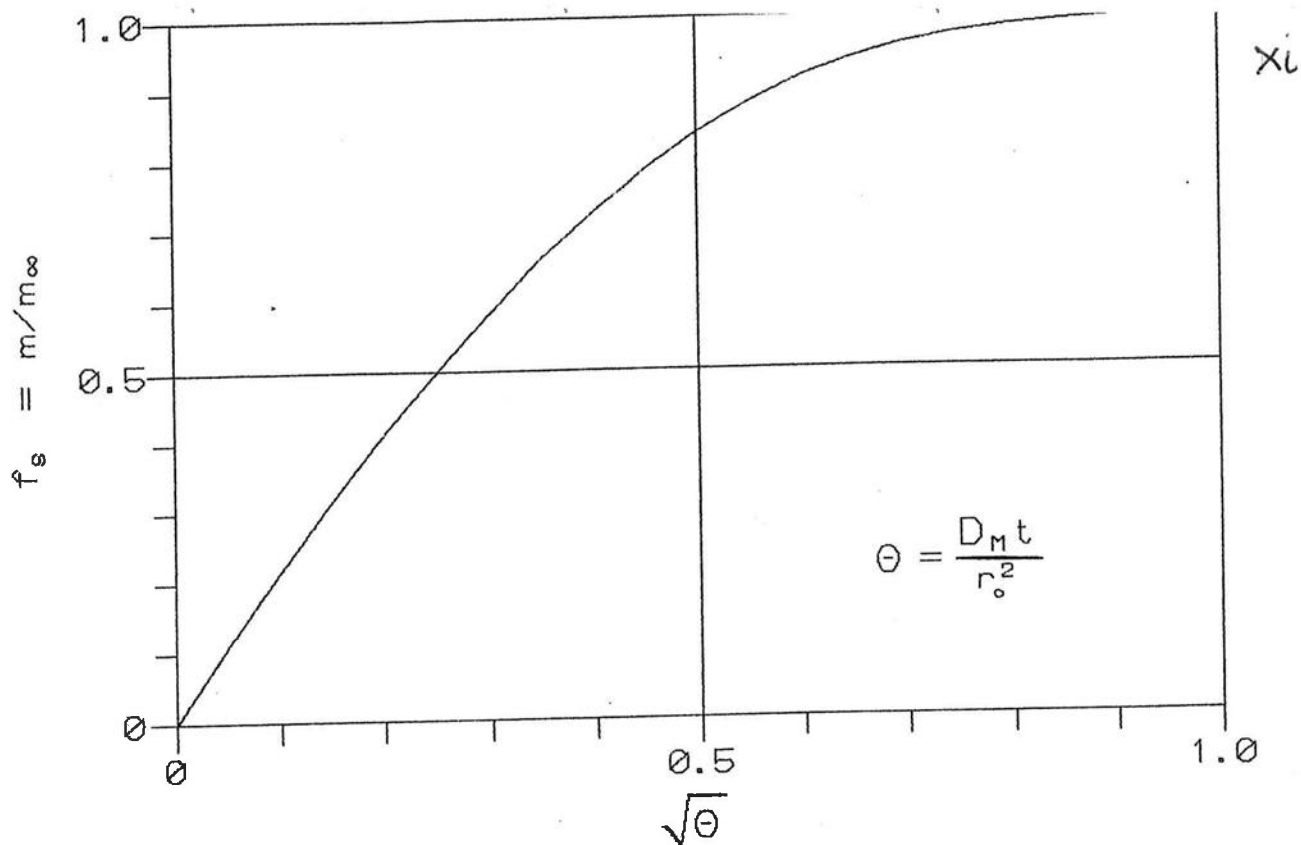
Fig. B-2. Gain in Weight of a Slender Plastic Rod Exposed to the Vapor of a VOC.

$$\Theta = \frac{D_M t}{r_o^2}$$
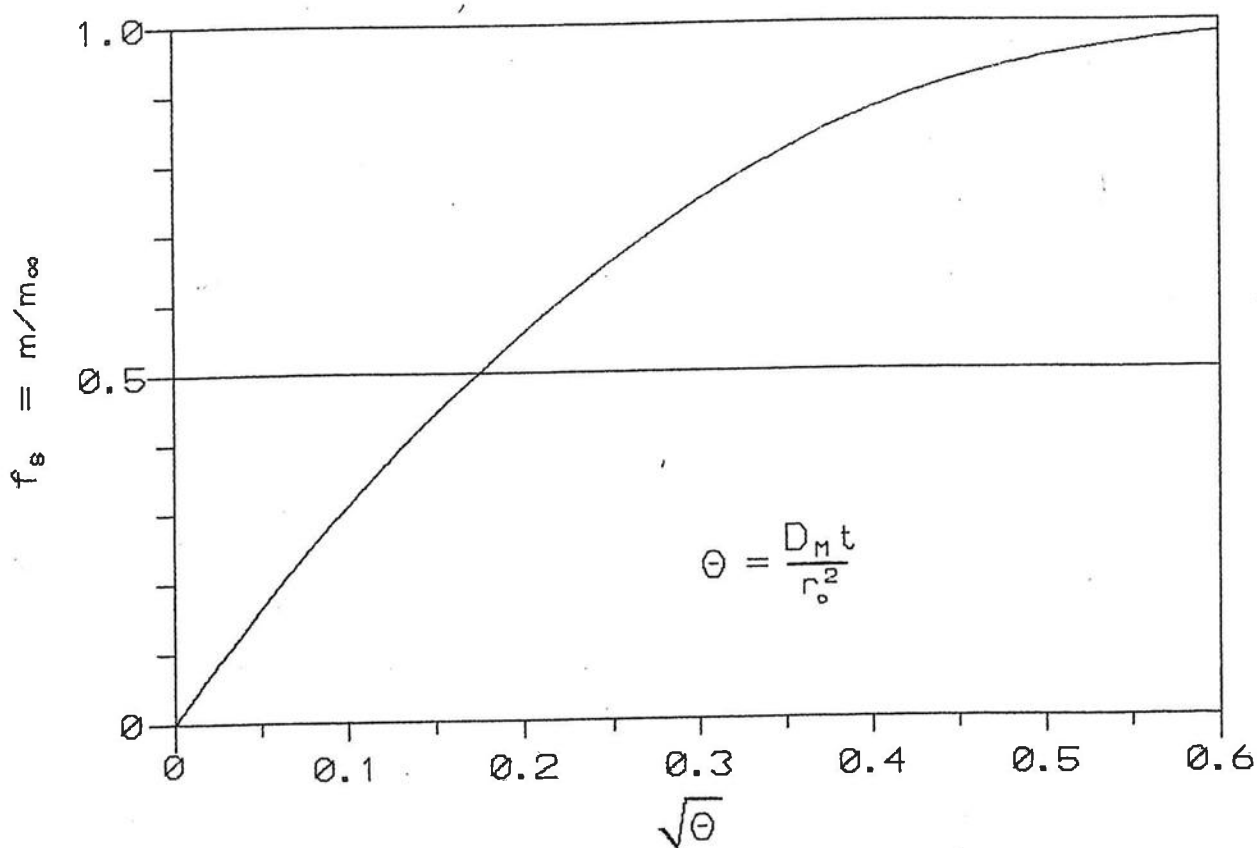
Fig. B-3. Gain in Weight of a Plastic Sphere Exposed to the Vapor of a VOC.

LIST OF SYMBOLS

A_s	Surface area (L^2)
A_x	Cross-sectional area (L^2)
c	Concentration $(M\ L^{-3}$ or moles $L^{-3})$
c_d	Concentration in reactor effluent stream
c_i	Concentration in reactor feed stream
c_J	Concentration of reactant J
c_o	Concentration at time zero
$C(s)$	Laplace transform of any of above
d_P	Particle diameter (L)
d_t	I.D. of a tubular reactor (L)
D_M	Coefficient of molecular diffusion $(L^2\ T^{-1})$
E_L	Coefficient of longitudinal dispersion $(L^2\ T^{-1})$
$f(t)$	A function of a real variable t
F_F	Mass flux of a fluid $(M\ T^{-1})$
$g(s)$	Laplace transform of $f(t)$
j	A function dependent on two variables
k	A reaction rate constant
K	Partition or equilibrium coefficient
K_A	Langmuir equilibrium coefficient (per unit of pressure)
L	A fixed distance (L)
m	Mass (M) or a number in a series expansion
m_o	Mass at time zero
m_T	Total mass of tracer added to a reactor system
n	Number of transfer units in a fixed-bed reactor
N	Number of reactors in a CSTR cascade
N'	A dimensionless parameter of dispersion or number of transfer units
p	Partial pressure of a gas
p_o	A reference partial pressure
$P(t)$	Probability of a particle remaining in a reactor during the time t
q	Mass or moles of adsorbate adsorbed to solids (M/M or moles/M)
q_m	Maximum adsorptive capacity of solids
Q	Volumetric flow rate $(L^3\ T^{-1})$
$r(t)$	The RTD-function (T^{-1})

$\bar{r}(s)$	Laplace transform of the RTD-function
$R(t)$	Probability of a particle being removed from a reactor during the time t
$\bar{R}(s)$	Laplace transform of the $R(t)$ probability function
s	Complex variable
t	Forward time (T), or any real variable
u	Complex variable
v	Velocity (L T^{-1})
v_b	Velocity of a fluid through a fixed-bed reactor (L T^{-1})
V	Volume (L^3)
x	Coordinate in direction of flow or mass flux
y	Concentration in gas phase (M L^{-3})
y_i	Concentration in reactor gas feed stream
z	A coordinate direction or an unknown function
ϵ	Fractional void space in a fixed-bed reactor
ζ	Relative degree of conversion
θ	Dimensionless time
κa	Thomas' kinetic coefficient (T^{-1})
ν	Kinematic fluid viscosity (L^{2}s^{-1})
ρ	Density (M L^{-3})
ρ_b	Bulk density of solids in a fixed-bed reactor (M L^{-3})
σ^2	Variance of a distribution taken about the mean
τ	Backwards in time (T)
$\bar{\tau}$	Mean residence time (T)
ω	Angular velocity or frequency (T^{-1})
$< >$	Designates an average quantity

REFERENCES CITED

Abramowitz, M. and Stegun, I. A., Editors, *Handbook of Mathematical Functions* National Bureau of Standards, Applied Mathematics Series . 55, Washington, D.C., 1966.

Barrer, R. H., *Diffusion In and Through Solids* University Press, Cambridge, 1951.

Bird, R. B., Stewart, W. L., Lightfoot, E. N., *Transport Phenomena* Wiley, New York, 1960.

Bontoux, L. G., *Basic Concepts of the Permeation of Organic Chemicals through Polybutylene* Ph. D. Thesis, University of California, Berkeley, 1990.

Burington, R. S., *Mathematical Tables and Formulas* Handbook Publishers, Inc., Sandusky, Ohio, 1949.

Crank, J. and Park, G. S., *Diffusion in Polymers* Academic Press, London & New York, 1968.

Danckwerts, P. V., *Chem. Engr. Sci., 2,* 1, 1953.

Denbigh, K. G., *Chemical Reactor Theory – An Introduction* Cambridge University Press, London, 1965.

Hall, W. G., *The Kinetics of Leaching of Organic Carbon from In-Situ Spent Oil Shale* Ph. D. Thesis, University of California, Berkeley, 1982.

Kramer, H. and Westerterp, K. R., *Elements of Chemical Reactor Design and Operation* Academic Press Inc., New York, 1963.

Levenspiel, O., *Chemical Reaction Engineering* Wiley, New York, 1962.

Levenspiel, O., *The Chemical Reactor Omibook* ? , 1979.

Little, J. C., Hodgson, A. T., Gadgil, A. J., *Atmospheric Environment 28,* 227, 1994.

Perry, R. H. and Chilton, C. H., *Chemical Engineer's Handbook* 5th Ed. McGraw-Hill Book Co., New York and London, 1973.

Reed, M. B. and Reed, G. B., *Electrical Network Theory, Laplace Transform Technique* International Textbook Co., Scranton, PA, 1968.

Roberts, G. H. and Kaufman, H., *Table of Laplace Transforms* W. B. Saunders Co., Philadelphia, 1966.

Seinfeld, J. H. and Lapidus, L., *Mathematical Methods in Chemical Engineering – Volume 3, Process Modeling, Estimation, and Identification* Prentice-Hall, Inc., New Jersey, 1974.

Sherwood, T. K., Pigford, R. L., Wilke, C. R., *Mass Transfer* McGraw-Hill Book Co., New York and London, 1975.

Sokolnikoff, I. S. and Sokolnikoff, E. S., *Higher Mathematics for Engineers and Physicists* McGraw-Hill Book Co., New York and London, 1941.

Spalding, D. B., *Chem. Engr. Sci., 9,* 74, 1958.