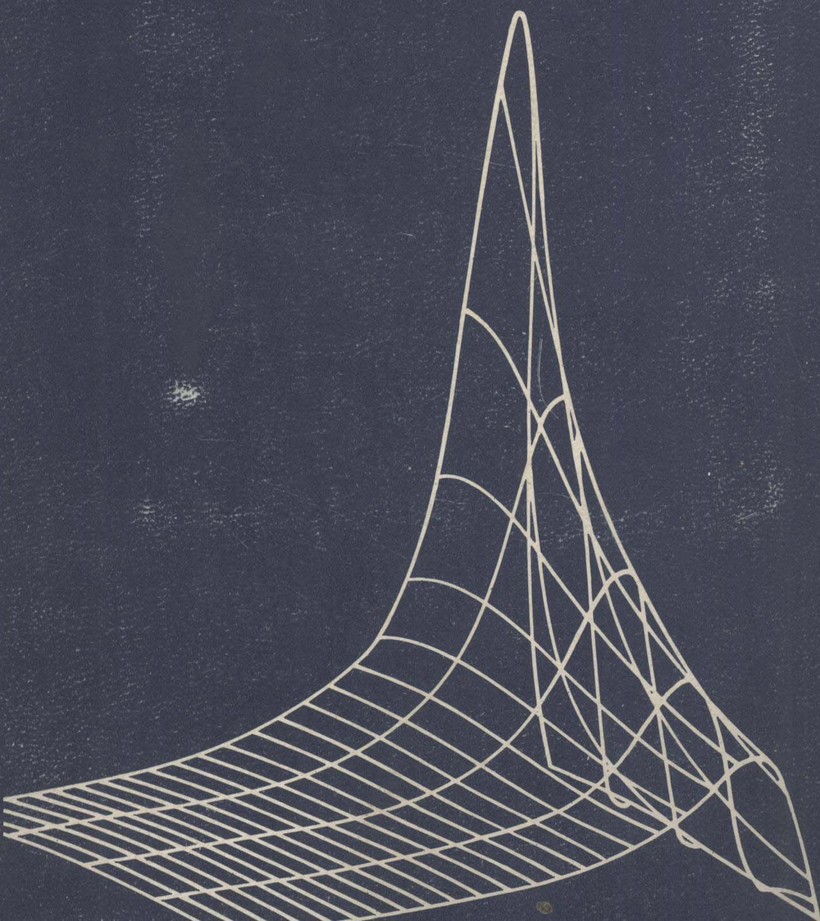
Residence Time Distribution Theory in Chemical Engineering

Edited by
A. Pethö and R. D. Noble



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In Memoriam

Chin-Yung Wen
1928-1982

Preface

In the last two or three decades a new branch of chemical engineering has been synthesized. "This transition from descriptive technology to modern engineering came ... at the First Symposium on Chemical Reaction Engineering (1957), where a number of earlier developments were brought together ... into a discipline ... called Chemical Reaction Engineering" [O. Levenspiel, Chem. Engng. Sci. *35* (1980) p. 1821].

Physical effects in chemical reactors, however, are difficult to separate from the chemical rate processes. In trying to do so one usually distinguishes between chemical kinetics and fluid dynamics, putting down the "performance equation" of a chemical reactor as follows:

output = f (input, kinetics, flow pattern)

When constructing a flow model for a given reactor, we must know the pattern of fluid passage through the reactor. This flow behavior could be determined by finding the complete history of each fluid element. However, Danckwerts pointed out in his famous paper (1953) that, instead of this complexity of the flow pattern, it is enough to know how long the fluid elements stay in the reactor, in other words, to determine the residence time distribution of the fluid particles in the exit stream. We can then select a model to represent the real process which has the same or similar type of residence time distribution.

The primary goal of the Bad Honnef Summer School 1982 is to offer the possibility of basic unterstanding of the above system identification process, which is, however, by far not as simple as it may seem, through lecturers who are experts of world niveau in the field. General mathematical background, both deterministic and stochastic, are being taught besides the more sophisticated, newly developed techniques. However, another principal aim of the Summer School is to draw attention to the various fields of application.

A. Pethö
R. D. Noble

Contents

The Scope of R.T.D. Theory

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SUMMARY

An attempt is made to survey the scope of RTD theory discussing first the general concepts and broad principles, the looking at some of the systems considered and their applications to mixing, reaction. The stochastic approach and the direct derivation of moments are discussed.

1. Introduction- general concepts

This workshop is the lineal descendent of that oldest of symposia, the English tea-break. For it was during such an interlude of praiseworthy academic indolence that the central idea of Danckwerts' paper on continuous flow systems came to him [1]. The paper that he subsequently wrote [2] is not as often cited as it might be for it has become so primary a reference, that like ignorance of Latin, it is usually taken for granted.

In it he defined the internal and external age distributions, $I(t)$ and $E(t)$, and related them to the F-diagram, the fraction of material introduced after a given instant that emerges at a time t later. This is the response of the system to a step change of tracer concentration in the input. The C-diagram is the response to an impulse of tracer at the inlet and thus gives $E(t)$ directly on normalization. The relations between these functions and the intensity function $\Lambda(t)$, later introduced by Shinnar and Naor [3], are given by:

$$E(t) = F'(t) = -\theta I'(t) = \Lambda(t) \exp - [\int_0^t \Lambda(t')dt'] \tag{1}$$

$$\int_0^t E(t')dt' = F(t) = 1 - \theta I(t) = 1 - \exp - [\int_0^t \Lambda(t')dt'] \tag{2}$$

$$\theta^{-1} \int_t^\infty E(t')dt' = \theta^{-1}(1-F(t)) = I(t) = \theta^{-1} \exp - [\int_0^t \Lambda(t')dt'] \tag{3}$$

$$E(t)/\int_t^\infty E(t')dt' = -\frac{d}{dt} \ell n\{1-F(t)\} = -\frac{d}{dt} \ell n\ \theta I(t) = \Lambda(t) \tag{4}$$

where $\theta = V/q$ = volume of system/perfusion rate. We note in passing that

$$\mu = \int_0^\infty tE(t)dt = -\theta \int_0^\infty tI'(t)dt = \theta \int_0^\infty I(t)dt = \theta \tag{5}$$

Danckwerts went on to discuss two parameters which might give indications of the physical situation from the inspection of the F or E curves. The first is the hold-back

$$H = \frac{1}{2} \int_0^\theta F(t)dt \tag{6}$$

which is zero for plug flow and might approach 1 if there is much dead space in the system. Thus it is a comparison of the residence time distribution with the plug-flow system. The other parameter compares the F-curve with that of the perfectly mixed single stage by the integral

$$S = \frac{1}{2} \int_0^\infty \left| F(t) - 1 + e^{-t/\theta} \right| dt \tag{7}$$

He called this the segregation and gave it the sign of $\{1 - e^{-t/\theta} - F(t)\}$ for small t. He then discussed flow through a bed of solids with longitudinal dispersion obtaining

$$F(t) = \frac{1}{2} \operatorname{erfc} \frac{(L-vt)}{2\sqrt{Dt}} = \frac{1}{2} \operatorname{erfc} \frac{1-(t/\theta)}{2\sqrt{\Delta t/\theta}}, \quad \Delta = D\theta/L^2 , \tag{8}$$

and laminar flow in pipes for which

$$F(t) = \begin{cases} 0 & t \leqslant \frac{1}{2}\theta \\ 1 - \theta^2/4t^2 & t \geqslant \frac{1}{2}\theta \end{cases} \tag{9}$$

In a later paper [4] Danckwerts used the idea of local residence times based on the observation of Spalding [5] that in a tracer test the $\int_0^\infty c\ dt$ is constant throughout the system and equal to Q/q, where Q is the total quantity of tracer and q the volumetric flow rate. This gives a local average age of particles

$$\mu(\mathbf{x}) = \int_0^\infty tc(\mathbf{x},t)dt/\int_0^\infty c(\mathbf{x},t)dt \tag{10}$$

In 1963, Shinnar and Naor [3] introduced the escape probability or intensity function, $\Lambda(t)dt$, or the fraction of material of age t that will leave the system in the interval $(t,t+dt)$ to give a clearer insight into stagnancy. A system with stagnancy has an escape probability that decreases over some interval for in such an interval the longer a particle stays the less likely is it to leave. The intensity function shows a maximum when there is stagnancy both in experimental and model situations.

As probability densities the functions $E(t)$ etc. have their characteristic functions and the Laplace transform has often been used in this one. It serves usefully as a moment generating function for $\bar{E}(s)$, the Laplace transform of $E(t)$, is analytic in the right half plane. Denoting by μ and σ^2 the mean residence time and the variance of residence times

$$\mu = \int_0^\infty tE(t)dt \quad , \quad \sigma^2 = \int_0^\infty (t-\mu)2E(t)dt \tag{10}$$

we have

$$\bar{E}(s) = 1 - \mu s + \frac{1}{2}(\sigma^2 + \mu^2)s^2 - \ldots \tag{11}$$

and

$$\mu = -\bar{E}'(0) = -\frac{d}{ds}[\ln E(s)]_{s=0} \tag{12}$$

$$\sigma^2 = \bar{E}''(0) - [\bar{E}'(0)]^2 = \frac{d^2}{ds^2}[\ln \bar{E}(s)]_{s=0} \tag{13}$$

When a model is governed by linear equations the Laplace transform can be used to obtain $E(t)$ and if only the moments are required a difficult inversion may often be avoided. Matching moments is one technique that can be used for parameter estimation though it needs to be used with care (Seinfeld and Lapidus give a careful treatment in their text [5]).

Following Spalding [6] it is worth commenting on the general structure of the linear process. Let the system of volume V occupy a region Ω with boundary $\partial\Omega$, which consists of three types of region: $\partial\Omega_o$, over which no transport takes place; $\partial\Omega_i$, over which fluid enters the system; and $\partial\Omega_e$, over which it leaves the system. Thus if $c(\mathbf{x},t)$ is the concentration of tracer at a point $\mathbf{x}$ within Ω

$$\frac{\partial c}{\partial t} = \nabla\cdot D\nabla c - \nabla\cdot\mathbf{v}c \tag{14}$$

where D is a local Fickian coefficient and $\mathbf{v}$ the local velocity. Both of these can be functions of position but we assume the fluid is incompressible.

$$\nabla\cdot\mathbf{v} = 0$$

and that there are no density partitions in the system — a condition that can be relaxed — so that c = constant is a solution of the equations. Then (14) has to be solved subject to

$$c(\mathbf{x},0) = 0 \tag{15}$$

$$\mathbf{v}\cdot\mathbf{n} = 0 \text{ and } D(\partial c/\partial n) = 0 \text{ on } \partial\Omega_o \tag{16}$$

$$D(\partial c/\partial n) - \mathbf{n}\cdot\mathbf{v}c = f \text{ on } \partial\Omega_i \tag{17}$$

$$\partial c/\partial n = 0 \text{ on } \partial\Omega_e \tag{18}$$

where $\mathbf{n}$ is the outward normal to $\partial\Omega$. The function f is the local flux into the system over $\partial\Omega_i$ and

$$\iint_{\partial\Omega_i} - \mathbf{n}\cdot\mathbf{v}\, dS = q \tag{19}$$

$$\iint_{\partial\Omega_i} - f\, dS = q\,\delta(t) \tag{20}$$

$\delta(t)$ being the unit Dirac measure. Then

$$E(t) = \frac{1}{q}\iint_{\partial\Omega_e} \mathbf{n}\cdot\mathbf{v}\, c\, dS \tag{21}$$

Of these equations we take the Laplace transform and use the expansion

$$\bar{c}(\mathbf{x},s) = \bar{c}_o(\mathbf{x}) - s\bar{c}_1(\mathbf{x}) + \frac{1}{2}s^2\bar{c}^2(\mathbf{x}) - \cdots \tag{22}$$

Then

$$\nabla\cdot(D\nabla\bar{c}_o) - \nabla\cdot\mathbf{v}\bar{c}_o = 0 \tag{23}$$

$$\nabla\cdot(D\nabla\bar{c}_1) - \nabla\cdot\mathbf{v}\bar{c}_1 = -\bar{c}_o \tag{24}$$

$$\nabla\cdot(D\nabla\bar{c}_2) - \nabla\cdot\mathbf{v}\bar{c}_2 = -2\bar{c}_1 \tag{25}$$

and the boundary conditions (16) and (18) carry over immediately whilst (17) becomes

$$D(\partial\bar{c}_o/\partial n) - \mathbf{n}\cdot\mathbf{v}\bar{c}_o = -\mathbf{n}\cdot\mathbf{v} \tag{26}$$

$$D(\partial\bar{c}_i/\partial n) - \mathbf{n}\cdot\mathbf{v}\bar{c}_i = 0 \quad , i = 1,2 \tag{27}$$

Now

$$\bar{E}(s) = \frac{1}{q}\iint_{\partial\Omega_e} \mathbf{n}\cdot\mathbf{v}c\,dS$$

$$= 1 - \mu s + \frac{1}{2}(\sigma^2 + \mu^2)s^2 - \cdots$$

so we should find

$$\frac{1}{q}\iint_{\partial\Omega_e} \bar{c}_o\mathbf{n}\cdot\mathbf{v}dS = 1 \ , \ \frac{1}{q}\iint_{\partial\Omega_e} \bar{c}_1\mathbf{n}\cdot\mathbf{v}dS = \mu \ , \ \frac{1}{q}\iint_{\partial\Omega_e} \bar{c}_2\mathbf{n}\cdot\mathbf{v}dS = \sigma^2 + \mu^2 \tag{28}$$

The first follows from the fact that $\bar{c}_o \equiv 1$ is a solution of (23), (16), (26) and (18). Then integrating (24) over Ω and using Green's theorem and the boundary conditions, gives

$$V = \iiint_{\Omega} \bar{c}_o dV = - \iiint_{\Omega} (\nabla \cdot D\nabla\bar{c}_1 - \nabla\cdot\mathbf{v}\bar{c}_1)dV$$

$$= \iint_{\partial\Omega_e} \mathbf{n}\cdot\mathbf{v}\bar{c}_1 dS = q\mu$$

Thus

$$\mu = \theta = V/q \tag{29}$$

Now the partial differential equation (24)

$$\nabla\cdot(D\nabla\bar{c}_1) - \nabla\cdot\mathbf{v}\bar{c}_1 = -1 \tag{30}$$

has to be solved before we can calculate the second moment. Again the use of (25) and Green's theorem gives

$$q(\sigma^2 + \mu^2) = \iint_{\partial\Omega_e} \mathbf{n}\cdot\mathbf{v}\bar{c}_2 dS = 2\iiint_{\Omega} \bar{c}_1 dV$$

$$= -2\iiint\{\bar{c}_1\nabla\cdot D\nabla\bar{c}_1 - \bar{c}_1\nabla\cdot\mathbf{v}\bar{c}_1\}dV$$

$$= 2\iiint D(\nabla\bar{c}_1)^2 dV - \iint \bar{c}_1^2\mathbf{v}\cdot\mathbf{n}dS \tag{31}$$

Horn [7] has shown how important the modification to a positive integrand can be for accurate computation of dispersion coefficients. If the system has internal partitions the volume is weighted according to the equilibrium concentration of each [24].

Independent of the linearity however is the additivity of moments of systems in series, for if these have individual distributions $E_1(t)$ and $E_2(t)$ their joint distribution is

$$E(t) = \int_0^t E_1(\tau)E_2(t-\tau)d\tau \tag{32}$$

Thus

$$\bar{E}(s) = \bar{E}_1(s)\bar{E}_2(s) \tag{33}$$

and by (12) and (13)

$$\mu = \mu_1 + \mu_2 \quad , \quad \sigma^2 = \sigma_1^2 + \sigma_2^2 \quad . \tag{34}$$

If the systems are in parallel with probability p_i that an incoming particle goes to the system with R.T.D. $E_i(t)$, then

$$E(t) = \lambda_1 E_1(t) + \lambda_2 E_2(t) \quad , \quad \lambda_1 + \lambda_2 = 1 \quad . \tag{35}$$

Thus

$$\mu = \lambda_1\mu_1 + \lambda_2\mu_2 \quad , \quad \sigma^2 = \lambda_1\sigma_1^2 + \lambda_2\sigma_2^2 + \lambda_1\lambda_2(\mu_1 - \mu_2)^2 \tag{36}$$

If the stream passing through the first system is recycled in such a way that $\lambda/(1+\lambda)$ is the probability of passing through the second system and round to the first again, then

$$E(t) = \frac{1}{1+\lambda} E_1(t) + \frac{\lambda}{(1+\lambda)^2} \int_0^t \int_0^{t'} E_1(t-t') \int_0^{t'} E_2(t'-t'')\, E_1(t'')dt''dt' + \frac{\lambda^2}{(1+\lambda)^3} \int \cdots$$

or

$$\overline{E}(s) = \frac{1}{1+\lambda} \overline{E}_1(s)\left\{1 + \frac{\lambda}{1+\lambda} \overline{E}_2(s)\overline{E}_1(s) + \frac{\lambda^2}{(1+\lambda)^2} \overline{E}_2^2(s)\overline{E}_1^2(s) + \cdots\right\} = \frac{\overline{E}_1(s)}{1+\lambda-\lambda\overline{E}_1(s)\overline{E}_2(s)} \quad (37)$$

Hence

$$\mu = \mu_1 + \lambda(\mu_1 + \mu_2) \quad , \quad \sigma^2 = \sigma_1^2 + \lambda(\sigma_1^2 + \sigma_2^2) + \lambda(1+\lambda)(\mu_1 + \mu_2)^2 \quad , \quad (38)$$

Note that $\mu_1 = V_1/q_1 = V_1/(t+\lambda)q$, $\mu_2 = V_2/q_2 = V_2/\lambda q$ so that $\mu = (V_1+V_2)/q = \theta_1 + \theta_2$. Note also that $\lambda \to \infty$

$$\overline{E}(s) \longrightarrow \frac{1}{1+(\theta_1 + \theta_2)s} \quad (39)$$

Systems Considered

So many possible systems have been considered that it is almost impossible to organize them, let alone record them in detail. The table which follows is but the very roughest outline and makes no claim to completeness. A worth-while task would be to compile a reference list of systems together with what is known of their distributions and moments. This has been done for certain subclasses [16] or for systems that might be relevant in particular contexts [8,60,61], but not comprehensively. In particular the connection has never been well made to the very considerable biological literature on compartmental analysis [24,54,62]. When Sheppard's book was published in 1962, the chemical engineer would probably have recognized but one of its references, Taylor's 1953 paper on longitudinal dispersion in laminar flow through a tube and the overlap is still not a large one though such a distinguished worker as K. B. Bischoff has made important contributions in both areas.

System		References
Single stirred tank or Plug flow with no diffusion		2, everybody!
Sequences of stirred tanks,		
	with by pass	3,5,8,9,46,48
	in parallel	5,9,60,61
	with cross-flow	3,53,60,61
	with back mixing	5,8,11,19,47
	with end reflux	5,61
	with stagnant regions	45,61
	with transport delay	5,10,12,44
Arrays of stirred tanks		8,14,15
General networks		6,13,17,19,28,30,43,49,50,52
Systems of compartments		24,54-59,62
Stochastic flows		13,58
Recycle systems		31-40
Zone models		6,17,23
Plug-flow with diffusion		2,5,8,16
Flow in helical coils		41,42,51
Combined stirred tanks and plug flow		10,13,18,21

Zweitering's concept of the degree of mixing

Zweitering [18] noted that two very different systems might have the same residence time distribution. For example a plug-flow tubular reactor of holding time θ_1 followed by a mixed reactor of holding time θ_2 would give

$$E(t) = \begin{cases} 0 & 0 \leqslant t \leqslant \theta_1 \\ \frac{1}{\theta_2} e^{-\frac{t-\theta_1}{\theta_2}} , & t > \theta_1 \end{cases} \tag{40}$$

If the tank preceeded the tube then R.T.D. would be exactly the same, yet the conversions in the two schemes for anything but a first-order reaction would be different. Zweitering observed that the residence time t was the sum of the age, α, and the life expectancy, β. Now during $(t,t+\delta t)$ a volume $q\delta t$ leaves the system of which a fraction $\{1-F(\beta)\}$ were already in the system at time $t-\beta = \alpha$. These had a life expectancy of β so that if $I^*(\beta)\delta\beta$ = fraction within the system with expectancy $(\beta,\beta+\delta\beta)$, $VI^*(\beta)\delta\beta = \{1-F(\beta)\}q\delta t$. But $\delta\beta = \delta t$ so $\theta I^*(\beta) = 1-F(\beta) = \theta I(\beta)$ and α and β are distributed in the same way. We note in passing that $\overline{\alpha} = \int_0^\infty \alpha I(\alpha)d\alpha = (\mu^2+\sigma^2)/2\mu$ so that the average residence time of all particle in the system is $\mu + (\sigma^2/\mu)$, which is greater than μ, the average residence time of those entering or leaving the system.

We have noted above that, since, in a tracer test, $\int_0^\infty c(\mathbf{x},t)dt = 1$ everywhere, a local mean age; $\mu(\mathbf{x})$, can be defined by

$$\mu_a(\mathbf{x}) = \int_0^\infty tc(\mathbf{x},t)dt \; . \tag{10 bis}$$

Now except in the case of complete mixing $\mu_a(\mathbf{x})$ will vary and this variation may be measured by

$$\Sigma_a^2 = \langle(\mu_a(\mathbf{x}) - \overline{\alpha})^2\rangle = \frac{1}{V}\iiint (\mu_a(\mathbf{x}) - \overline{\alpha})^2 dV \tag{41}$$

This is called the age variance between points. The age variance within points is

$$\Sigma_a^2 = \langle \int_0^\infty \{t - \mu_a(\mathbf{x})\}^2 c(\mathbf{x},t)dt\rangle \tag{42}$$

and it can be shown that

$$\sigma_a^2 = \int_0^\infty (\alpha-\overline{\alpha})^2 \; I(\alpha)d\alpha = s_a^2 + \Sigma_a^2 \tag{43}$$

Zweitering shows how to attain any required residence time distribution in a plug-flow reactor with side-stream take off. Then the section of the tubular reactor which contains material of ages in $(\alpha, \alpha+d\alpha)$ has a volume = dV $VI(\alpha)d\alpha$ =

$[1-F(\alpha)]d\alpha$. The volume drawn off must contribute that moiety of effluent with residence time in $(\alpha, \alpha+d\alpha)$ i.e. $qE(\alpha)d\alpha$, so that the flow rate at α is $q - \int_0^\infty qE(t)dt = q(1-F(\alpha))$. If $c(\alpha)$ is the concentration of a reactant disappearing by reaction at a rate $r(c)$

$$q[1-F(\alpha)]c(\alpha) - q[1-F(\alpha+d\alpha)]c(\alpha+d\alpha) = qE(\alpha)d\alpha c(\alpha) + r(c(\alpha))dV$$

which reduces to

$$\frac{dc}{d\alpha} = - r(c) \tag{44}$$

with an effluent concentration

$$\overline{c} = \int_0^\infty E(\alpha)c(\alpha)d\alpha \tag{45}$$

This is the condition of complete segregation; eqn. (44) is solved subject to $c(0) = c_f$.

On the other hand Zweitering claimed maximum mixedness for the scheme whereby the residence time distribution is attained by a sidestream of flow rate $qE(\beta)d\beta$ being added to a plug flow reactor at a point of life expectancy β. Since the distribution of expectancy is the same the volume element is the same as before and a balance gives

$$q[1-F(\beta+d\beta)]c(\beta+d\beta) - q[1-F(\beta)]c(\beta) = qE(\beta)d\beta c_f - r(c(\beta))dV$$

or

$$\frac{dc}{d\beta} = r(c(\beta)) - \Lambda(\beta)[c_f - c(\beta)] \tag{46}$$

This equation should be solved subject to the condition

$$\frac{dc}{d\beta} \to 0 \qquad \beta \to \infty \quad ,$$

since c is bounded. Thus in the limit

$$c_f - c_\infty = \left[\underset{\beta\to\infty}{\text{Lt}} \; \frac{1-F(\beta)}{E(\beta)} \right] r(c_\infty) \tag{47}$$

which for a stirred tank is

$$c_f - c_\infty = \theta r(c_\infty) \; . \tag{48}$$

Since $\Lambda(\beta)$ is constant for the stirred tank, the solution of (46) is a constant and $c(0) = c_\infty$ satisfies (48).

For first order reaction $r(c) = kc$

$$\frac{dc}{d\beta} = kc - \Lambda(\beta)(c_f-c)$$

or

$$c(\beta) = \frac{c_o e^{k\beta}}{1-F(\beta)} \int_{\beta}^{\infty} E(t)\, e^{-kt}\, dt \tag{49}$$

whence

$$c(0) = c_o \int_0^{\infty} E(t) e^{-kt}\, dt \tag{50}$$

Zweitering showed that $J = \Sigma_a^2/\sigma_a^2$, Danckwert's segregation parameter [20], would be minimized under conditions of maximum mixedness.

Combinations of these models have been made by Weinstein and Adler [21], Villermaux and Zoulalian [22] and Ng and Rippin [23]. Asbjørnsen [15] has used a network model and Kranbeck, Shinnar and Katz [13] a general assemblage of units in their stochastic model (vide inra).

Reaction transforms

If c is the concentration of a reactant disappearing at a rate r(c), the fraction remaining after time t is $\gamma(t)$ the solution of

$$\frac{d\gamma}{dt} = - k\, R(\gamma) \tag{51}$$

$$k = R(c_o)/c_o \quad , \quad R(\gamma) = r(c_o\gamma)/r(c_o) \tag{52}$$

Then, by (44) and (45) a completely segregated reactor will give a product with a fraction of

$$\Gamma = \int_0^{\infty} \gamma(t)\, E(t) dt$$

$$= \int_0^1 \frac{\gamma}{kR(\gamma)}\, E\left(\frac{1}{k} \int_{\gamma}^{1} \frac{d\gamma'}{R(\gamma')}\right) d\gamma \quad . \tag{53}$$

This may be regarded as an integral transform of the residence time distribution which is best expressed in dimensionless form. Let θ be the mean residence time and

$$\tau = t/\theta \ , \quad f(\tau) = \theta E(\theta\tau) \ , \quad \kappa = k\theta = R(c_o)\theta/c_o \tag{54}$$

Then $\gamma(\tau) = \gamma(\tau;\kappa,R)$ satisfies

$$\frac{d\gamma}{d\tau} = - \kappa R(\gamma) \quad , \ \gamma(0) = 1 \tag{55}$$

and

$$\Gamma(\kappa) = \int_0^\infty \gamma(\tau)f(\tau)d\tau \quad . \tag{56}$$

For example, a pth order reaction with $R(\gamma) = \gamma^p$ gives

$$\gamma(\tau) = \{1 + (p-1)\kappa\tau\}^{-1} \tag{57}$$

when

$$q = 1/(p-1), \; k = k\, c_o^{\,p-1} \tag{58}$$

we can unite

$$\Gamma(\rho) = p^q \int_0^\infty \frac{f(\tau)}{(\rho+\tau)^q}\, d\tau \tag{59}$$

with

$$\rho^{-1} = (p-1)\kappa \tag{60}$$

and $\Gamma(\rho)$ is the generalized Stieltjes transform of f. Cf. [25,26]. When p = 1 this degenerates into the Laplace transform as $\gamma(\tau) = \exp{-\kappa\tau}$.

Some generalized Stieltjes transform pairs are given in [26]. The most important one for our purposes is given by the formula

$$\int_0^\infty x^\lambda e^{-\alpha x}(x+y)^{-\mu}dx = \Gamma(\lambda+1)\alpha^{(\mu-\lambda-2)/2}\, y^{(\lambda-\mu)/2}\, e^{\alpha y/2}\, e^{\alpha 7/2} W_{k,m}(\alpha y) \tag{61}$$

where $2k = -\lambda - \mu$, $2m = \lambda - \mu + 1$. The Whittaker function

$$W_{k,m}(\alpha y) = \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} M_{k,m}(\alpha y) + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} M_{k,-m}(\alpha y)$$

$$= \frac{\Gamma(\mu-\lambda-1)}{\Gamma(\mu)} M_{k,m}(\alpha y) + \frac{\Gamma(\lambda-\mu+1)}{\Gamma(\lambda+1)} M_{k,-m}(\alpha y) \tag{62}$$

and

$$M_{k,m}(\alpha y) = (\alpha y)^{\frac{1}{2}+m}\, e^{-\alpha y/2}\, {}_1F_1(\tfrac{1}{2}+m-k;\; 2m+1;\; \alpha y) \quad . \tag{63}$$

Combining these formulae gives

$$\int_0^\infty x^\lambda e^{-\alpha x}(x+y)^{-\mu}dx = \frac{\Gamma(\lambda+1)\Gamma(\mu-\lambda-1)}{\Gamma(\mu)}\, y^{\lambda-\mu+1}\, {}_1F_1(\lambda+1;\; \lambda-\mu+2;\; \alpha y)$$

$$+ \Gamma(\lambda-\mu+1)\, \alpha^{\mu-\lambda-1}\, {}_1F_1(\mu;\; \mu-\lambda;\; \alpha y) \tag{64}$$

where

$${}_1F_1(\alpha;\beta;z) = 1 + \frac{\alpha}{\beta}\frac{z}{1!} + \frac{\alpha(\alpha+1)}{\beta(\beta+1)}\frac{z^2}{2!} + - + \frac{(\alpha)^n}{(\beta)^n}\frac{z^n}{n!} + \cdots \tag{65}$$

is Kummer's hypergeometric function