the dispersed phase, according to the availability ratio criterion.

NOTATION

C_{ij} = concentration of the i-th reactant in the j-th phase $[ML^{-3}]$
d = reaction zone thickness $[L]$
D_{ij} = diffusivity of the i-th reactant in the j-th phase $[L^2T^{-1}]$
k_j = reaction rate constant in the j-th phase $[M^{-1}L^3T^{-1}]$
m = equilibrium distribution ratio for A, C_{A1}/C_{A2}
M = equilibrium distribution ratio for B, C_{B2}/C_{B1}
N_i = transfer rate of the i-th reactant across the interface $[ML^{-2}T^{-1}]$
R = availability ratio, $\frac{C^\circ_{B2}}{\nu C^\circ_{A1}}\sqrt{\frac{D_{B2}}{D_{A1}}}$
S_i = consumption rate of the i-th reactant at the reaction front $[ML^{-2}T^{-1}]$
t = time coordinate $[T]$
x = position coordinate $[L]$
x' = position coordinate of the reaction zone $[L]$

Greek Letters

α = proportionality constant $[L^2T^{-1}]$
γ = $\sqrt{D_{A2}/D_{A1}}$
Γ = $\sqrt{D_{B1}/D_{B2}}$
η = $x/2\sqrt{D_{A2}t}$
λ = $\sqrt{\alpha/D_{A2}}$
Λ = $\sqrt{\alpha/D_{B1}}$
ν = stoichiometric coefficient
ω = $\sqrt{D_{A2}/D_{B2}}$
Ω = $\sqrt{D_{B1}/D_{A1}}$

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Finite-Difference Transforms for Application to Stage by Stage Processes

P. G. MURDOCH

Dow Chemical Company, Midland, Michigan

The stage by stage operations of chemical engineering may be calculated by iterative means, or handled by graphical manipulations. The former is tedious; the latter is often useful but leads to somewhat uncertain results when many-stage processes are treated. An analytical method for solving stage by stage problems would have obvious advantages. Such a method has been devised for linear systems (*3, 4, 5*); the method involves finite-difference transforms that are analogous to the Laplace transform. The basis of this method was developed originally in the electrical engineering field for application to control problems. The transform was called the *z-Transform,* corresponding to the $\sigma(p)$ function defined below. There are also alternate transform techniques (*1, 2, 7, 8*) which are more powerful for some applications.

Let y_n denote a function of stage number n. Define the finite-difference transform as follows:

$$F(y_n) = \gamma(p) = \frac{p-1}{p}\left(y_0 + \frac{y_1}{p} + \frac{y_2}{p^2} + \ldots\right) = \frac{p-1}{p}\cdot\sigma(p)$$

or

$$\gamma(p) = \frac{p-1}{p}\sum_{n=0}^{\infty}\frac{y_n}{p^n} = \frac{p-1}{p}\cdot\sigma(p)$$

where

$$p = \text{a parameter}$$

$$\sigma(p) = y_0 + \frac{y_1}{p} + \frac{y_2}{p^2} + \ldots.$$

The transform of $y_n = 1$ is 1:

$$F(1) = \gamma(p) = \frac{p-1}{p}\left(1 + \frac{1}{p} + \frac{1}{p^2} + \ldots\right) = \frac{p-1}{p}\cdot\frac{1}{1-\frac{1}{p}} = 1$$

The transform of $y_n = n$ is $1/(p-1)$.

$$F(n) = \gamma(p) = \frac{p-1}{p}\left(0 + \frac{1}{p} + \frac{2}{p^2} + \ldots\right) = -(p-1)\frac{\partial}{\partial p}\left(1 + \frac{1}{p} + \frac{1}{p^2} + \ldots\right)$$
$$= -(p-1)\frac{\partial}{\partial p}(p/p-1) = \frac{p-1}{(p-1)^2} = \frac{1}{p-1}$$

If the transform of y_n is $\gamma(p)$, the transform of y_{n+1} is

$$F(y_{n+1}) = \frac{p-1}{p}\left(y_1 + \frac{y_2}{p} + \frac{y_3}{p^2} + \ldots\right) = p\left(F(y_n) - \frac{p-1}{p}y_0\right) = p\,\gamma(p) - (p-1)y_0$$

The transform of $\Delta y = y_{n+1} - y_n$ is $F(y_{n+1}) - F(y_n) = (p-1)(\gamma(p) - y_0)$. The transform of $n\,y_n$ is found by noting that

TABLE 1. SOME FINITE DIFFERENCE TRANSFORMS

$$\gamma(p) = \frac{p-1}{p}\sum_{n=o}^{\infty}\frac{y_n}{p^n} = F_n(y_n) \qquad\qquad \frac{p}{p-1}\gamma(p) = \sigma(p)$$

Function of n	Transform	Function of n	Transform
$B_o = 1$	1		
$B_1 = n$	$\frac{1}{p-1}$		
$B_2 = n(n-1)/2!$	$\frac{1}{(p-1)^2}$		
$B_k = n(n-1)\ldots(n-k+1)/k!$	$\frac{1}{(p-1)^k}$	$\frac{n(n+1)\ldots(n+k-1)}{k!} = \frac{(n+k-1)!}{k!(n-1)!} = b_k$	$\frac{p^{k-1}}{(p-1)^k}$ $\quad k \geqq 1$
y_n	$\gamma(p)$		
y_{n+1}	$p\gamma(p) - (p-1)y_o$		
y_{n+2}	$p^2\gamma(p) - p(p-1)y_o - (p-1)y_1$		
$\Delta y = y_{n+1} - y_n$	$(p-1)(\gamma(p) - y_o)$		
$\Delta_2 y = y_{n+2} - 2y_{n+1} + y_n$	$(p-1)^2(\gamma(p) - y_o) + (p-1)(y_o - y_1)$		
$\Delta_3 y = y_{n+3} - 3y_{n+2} + 3y_{n+1} - y_n$	$(p-1)^3(\gamma(p) - y_o) + (p-1)(p-2)(y_o - y_1) + (p-1)(y_1 - y_2)$		
a^n	$\frac{p-1}{p-a}$		
$\frac{a^n}{n!}$	$\frac{p-1}{p}e^{a/p}$	$\frac{a^{n+1}}{(n+1)!}$	$(p-1)(e^{\frac{a}{p}} - 1)$
ny_n	$-(p-1)\left(\frac{\partial\sigma(p)}{\partial p}\right)$	$\frac{y_n}{n+1}$	$(p-1)\int_p^{\infty}\frac{\gamma(p)}{p(p-1)}dp$
$\frac{n(n+1)}{2!}y_n$	$\frac{+p(p-1)}{2!}\frac{\partial^2\sigma(p)}{\partial p^2}$	$\sum_o^n y_n$	$\frac{p}{p-1}\gamma(p)$, that is $\sigma(p)$
$\frac{n(n+1)(n+2)}{3!}y_n$	$\frac{-p^2(p-1)}{3!}\frac{\partial^3\sigma(p)}{\partial p^3}$	$\sum_n^{\infty} y_n$	$\sum_o^{\infty} u_n - \frac{\gamma(p)}{p-1}$
$a^n y_n$	$\frac{p-1}{p-a}\gamma\left(\frac{p}{a}\right)$	$\left[\sum_o^{\infty} y_n = \lim_{p=1}\sigma(p)\right]$	
na^n	$\frac{a(p-1)}{(p-a)^2}$		
$a^{n-1}\cdot\sum_{k=o}^{n-1}\frac{y_k}{a^k}$ ($n = o$ term is o)	$\frac{\gamma(p)}{p-a}$	$\frac{1}{n!}\int_o^z e^{-az}z^n dz$ (Incomplete gamma integral)	$\frac{p-1}{p}\frac{\left(e^{\left(\frac{1}{p}-a\right)z} - 1\right)}{\frac{1}{p} - a}$
$\frac{(-1)^n\left(\frac{a}{2}\right)^{2n}}{(n!)^2}$	$\frac{p-1}{p}J_o\left(\frac{a}{\sqrt{p}}\right)$	$\frac{b^n}{n!}\int_o^z e^{-az}\cdot z^n dz$	$\frac{p-1}{p}\left[\frac{e^{\left(\frac{b}{p}-a\right)z} - 1}{\frac{b}{p} - a}\right]$ $\quad b \neq o$
$1, o, o, o, \ldots$	$\frac{p-1}{p}$		
$0, 1, 1, 1, \ldots$	$1/p$		
$o, o, 1, 1, \ldots$	$1/p^2$		

$$\frac{\partial\sigma}{\partial p} = -\left(\frac{y_1}{p^2} + \frac{2y_2}{p^3} + \frac{3y_3}{p^4} + \ldots\right)$$

$$F(n\,y_n) = \frac{p-1}{p}\left(0 + \frac{y_1}{p} + \frac{2y_2}{p^2} + \frac{3y_3}{p^3} + \ldots\right) = -(p-1)\frac{\partial\sigma}{\partial p}$$

The transform of n is a special case of this relation. By differentiating again one finds that the transform of $n(n+1)y_n$ is $p(p-1)\ \partial^2\sigma/\partial p^2$.

By simple algebra a list of transforms can be developed (see Table 1). This list is by no means exhaustive but is adequate for the solution of many problems involving stage by stage processes. Also many other related transforms can be developed by using the table. For example what is the transform of $a^n - 1$? Answer: $\frac{p-1}{p-a} - 1 = \frac{a-1}{p-a}$. What is the transform of $\frac{n(n+1)a^n}{2!}$? Answer: $\frac{p(p-1)}{2!}\frac{\partial^2}{\partial p^2}\left(\frac{p}{p-a}\right) = \frac{a\,p(p-1)}{(p-a)^3}$.

The utility of the transforms is best shown by example.

Example 1: What is the sum of the first n terms of a geometric progression?

Solution:

$$y_n = \sum_{k=0}^{n} a^k \quad \text{where } a = \text{constant.}$$

By difference

$$y_{n+1} - y_n = a^{n+1}$$

From the table $(p-1)(\gamma - y_0) = a \cdot p - 1/p - a$.

But $y_0 = 1$. Therefore

$$\gamma = \frac{a}{p-a} + 1$$

$$y_n = \frac{a}{a-1}(a^n - 1) + 1 = \frac{a^{n+1}-1}{a-1}$$

Example 2: What is the sum of all terms of the series $(a + 4a^2 + 9a^3 + \ldots)$? That is what is the value of $\sum_{n=0}^{\infty} n^2 a^n$ (where a is less than unity)?

Solution: $F(a^n) = \dfrac{p-1}{p-a}$

$$\sigma = \frac{p}{p-a} = 1 + \frac{a}{p-a}$$

$$F(n^2a^n) = F([n(n+1) - n]a^n)$$

$$= p(p-1)\frac{\partial^2\sigma}{\partial p^2} + (p-1)\frac{\partial \sigma}{\partial p}$$

$$= (p-1)\left[\frac{2\,ap}{(p-a)^3} - \frac{a}{(p-a)^2}\right]$$

Corresponding σ is $\dfrac{p}{p-1} F(n^2a^n) =$

$$\frac{2\,ap^2}{(p-a)^3} - \frac{ap}{(p-a)^2}$$

Desired sum $= \lim_{p \to 1} \sigma = \dfrac{2a}{(1-a)^3} -$

$$\frac{a}{(1-a)^2} = \frac{a(1+a)}{(1-a)^3}$$

Example 3: A series of reactions occurs as follows:

	Reaction rate
1. $A + C = N_1$	$r_1 = k_1 c_A \cdot f(c's)$
2. $N_1 + C = N_2$	$r_2 = k_2 c_{N1} \cdot f(c's)$
3. $N_2 + C = N_3$	$r_3 = k_2 c_{N2} \cdot f(c's)$
.	.
.	.
.	.

where c = concentration, k_1, k_2 = reaction rate constants, $f(c's)$ is a function of concentrations, the same for all reactions. C is the common component; it takes part in all reactions. This type of reaction sequence is fairly common in the chemical industry. The problem: Pure A and C are mixed and reacted batch by batch. What is the yield of product N_n?

Solution: Let $A, N_1, N_2, \ldots$ = moles of $A, N_1, \ldots$. $A_F = A$ in reactor feed.

$$m = k_2/k_1 \qquad a = m - 1$$

$$z = -\ln\frac{A}{A_F}$$

r_A = disappearance rate of A

$$v_n = \frac{N_n}{A_F}$$

r_n = net formation rate of N_n

$$n = 1: \quad \frac{r_1}{r_A} = \frac{dN_1}{-dA} = \frac{dv_1}{dz} \cdot e^z$$

$$= \frac{r_1 - r_2}{r_1} = 1 - mv_1e^z$$

$$n > 1: \quad \frac{r_n}{r_A} = \frac{dN_n}{-dA} = \frac{dv_n}{dz}e^z$$

$$= \frac{r_n - r_{n+1}}{r_1} = m(v_{n-1} - v_n)e^z$$

Or

$$n = 1: \quad \frac{dv_1}{dz} + mv_1 = e^{-z}$$

$$n > 1: \quad \frac{dv_{n+1}}{dz} = m(v_n - v_{n+1})$$

In these equations v_0 is not defined (there is no product N_0). But the subscript $n = 0$ occurs in the transforms. Remove this difficulty by letting $v_n = V_{n-1}$, which amounts in effect to merely renumbering the v's. Then

$$\text{for } n = 0 \qquad \frac{dV_0}{dz} + mV_0 = e^{-z} \tag{1}$$

$$n > 0 \qquad \frac{dV_{n+1}}{dz} = m(V_n - V_{n+1}) \tag{2}$$

Equation (1) is a linear, first-order differential equation. Its solution is

$$V_0 = \frac{e^{-z} - e^{-mz}}{a} \tag{3}$$

so

$$\frac{dV_0}{dz} = \frac{-e^{-z} + me^{-mz}}{a} \tag{4}$$

Take the transform of Equation (2):

$$\frac{d}{dz}[p\gamma - (p-1)V_0] =$$

$$-m(p-1)(\gamma - V_0)$$

Substituting from Equations (3) and (4) and simplifying one gets

$$\frac{d\gamma}{dz} + m\frac{p-1}{p}\gamma = \frac{p-1}{p}e^{-z}$$

This is a linear, first-order differential equation. The solution is

$$\gamma = Ke^{-mz + (mz/p)} + \frac{(p-1)e^{-z}}{ap - m}$$

At $z = 0$ $(A = A_F)$, $N_1 = N_2 = \ldots = 0$. Therefore $\gamma = 0$ at $z = 0$ and

$$K = -\frac{p-1}{ap - m}$$

so

$$\gamma = e^{-z}\frac{p-1}{ap-m}\left(1 - e^{\left(\frac{m}{p} - a\right)z}\right)$$

$$= e^{-z} \cdot \frac{p-1}{p} \; \frac{e^{\left(\frac{m}{p} - a\right)z} - 1}{\frac{m}{p} - a}$$

From the table

$$V_n = \frac{m^n e^{-z}}{n!}\int_0^z e^{-az} z^n dz$$

Since $v_n = V_{n-1}$

$$v_n = \frac{m^{n-1} e^{-z}}{(n-1)!}\int_0^z e^{-az} z^{n-1} dz$$

This is a modified incomplete gamma integral, which can be found in mathematical tables.

The yield of N_n, based on the A reacted, is

$$(Y_n)_A = \frac{N_n}{A_F - A} = \frac{v_n}{1 - e^{-z}} = \frac{e^z v_n}{e^z - 1}$$

where conversion of $A = 1 - e^{-z}$.

Example 4: In the theory of constant α, constant L/V distillation columns, certain finite difference equations are involved (6). These are much more easily solved by use of the transforms than by iterative methods, as will be shown. Assume a total condenser is used. What is the mole fraction of any component in the vapor (y_n) on any plate n in the rectifying section, if top product composition is fixed?

Solution: Let top plate = plate no. zero. Plates numbered down the column.

$$y_0 = x_D$$

L, V, D = molal flow rates of liquid, vapor, top product, respectively

$$\frac{L}{V} = R, \; \frac{D}{V} = 1 - R$$

$$K_n = \frac{y_n}{x_n} = \alpha K_{b_n}$$

α = volatility ratio

K_{b_n} = K of component having $\alpha = 1$; on plate n

$$K_{b_n} = \sum_{j=1}^{c} \frac{(y_n)_j}{\alpha_j}$$

c = number of components

$$K_{b_0} \cdot K_{b_1} \cdot K_{b_2} \ldots K_{b_n} = z_n$$

$$z_{n-1} \frac{y_n}{\alpha} = \theta_n$$

$$\sum^c \theta_n = z_{n-1} K_{b_n} = z_n$$

One has

$$y_{n+1} = Rx_n + (1-R)x_D$$

$$K_{b_n} = \sum^c \frac{y_n}{\alpha}$$

where $\sum^c$ = sum over all components. Therefore

$$K_{b_n} \, y_{n+1} = R \, K_{b_n} \frac{y_n}{\alpha K_{b_n}} + (1-R) \, K_{b_n} \, x_D \quad (5)$$

Multiply by z_{n-1}/α one gets

$$\theta_{n+1} = \frac{R}{\alpha} \theta_n + (1-R) \frac{x_D}{\alpha} z_n \quad (6)$$

If $n = 0$

$$K_{b_0} \frac{y_1}{\alpha} = \frac{R}{\alpha} \theta_0 + (1-R) \frac{x_D}{\alpha} K_{b_0} \quad (7)$$

By comparison of Equations (5) and (7)

$$\theta_0 = \frac{y_0}{\alpha} = \frac{x_D}{\alpha}$$

Let the transform of θ_n be $\gamma(p)$ and the transform of z_n be $G(p)$: Take the transform of Equation (6):

$$p\gamma - (p-1) \frac{x_D}{\alpha} = \frac{R}{\alpha} \gamma + (1-R) \frac{x_D}{\alpha} G$$

$$\gamma = \frac{(p-1) + (1-R)G}{p - \dfrac{R}{\alpha}} \frac{x_D}{\alpha} \quad (8)$$

Since $z_n = \sum^c \theta_n$, $G = \sum^c \gamma$

$$G = [(p-1) + (1-R)G] \sum_{i=1}^{c} \frac{(x_D/\alpha)_i}{p - \dfrac{R}{\alpha_i}}$$

or

$$G = \frac{(p-1) \cdot S}{1 - (1-R) \cdot S} \quad (9)$$

where

$$S = \sum_{i=1}^{c} \frac{(x_D/\alpha)_i}{p - \dfrac{R}{\alpha_i}}$$

Substitute Equation (9) in Equation (8) and obtain

$$\gamma_i = \frac{(p-1) \, (x_D/\alpha)_i}{\left(p - \dfrac{R}{\alpha_i}\right) [1 - (1-R)S]} \quad (10)$$

where the subscript i is used to indicate that γ_i is the transform of the θ_n for any particular component i.

To invert G clear numerator and denominator of fractions by multiplying both by the product of $p - R/\alpha$ values for all components; that is by

$$\prod_{i=1}^{c} \left(p - \frac{R}{\alpha_i}\right)$$

The result for the denominator is a polynomial of degree c (= number of components). The numerator is $(p - 1)$. (a polynomial of degree $c - 1$). Find the c roots p_k ($k = 1$ to c) of the denominator. Then expand by the Heaviside partial fractions method, just as for a Laplace transform inversion. The result is

$$G = \frac{p-1}{1-R} \cdot \sum_{k=1}^{c} \frac{a_k}{p - p_k}$$

where

$$a_k = \frac{\prod_{j=1}^{c} \left(p_k - \dfrac{R}{\alpha_j}\right)}{\prod_{j \neq k} (p_k - p_j)}$$

giving

$$z_n = \frac{1}{1-R} \sum_{k=1}^{c} a_k \, p_k^{\,n}$$

Invert γ_i similarly. The result is

$$(\theta_n)_i = \left(\frac{x_D}{\alpha}\right)_i \sum_{k=1}^{c} (b_k)_i \, p_k^{\,n}$$

where

$$(b_k)_i = \frac{a_k}{p_k - \dfrac{R}{\alpha_i}}$$

To find y_n note that $y_0 = x_D$. For $n =$ 1 or more

$$y_{n_i} = \frac{\alpha \, \theta_n}{z_{n-1}} = (1-R) x_{D_i} \frac{\sum_{k=1}^{c} (b_k)_i \, p_k^{\,n}}{\sum_{k=1}^{c} a_k \, p_k^{\,n-1}}$$

This is the desired relation.
Also

$$(K_b)_n = z_n / z_{n-1} = \Sigma \, a_k \, p_k^{\,n} / \Sigma \, a_k \, p_k^{\,n-1} \quad (n > 0)$$

$$x_{n_i} = \frac{y_{n_i}}{\alpha_i \, (K_b)_n} = (1-R) \frac{x_{D_i}}{\alpha_i} \frac{\sum_{k=1}^{c} (b_k)_i \, p_k^{\,n}}{\sum_{k=1}^{c} a_k \, p_k^{\,n}}$$

Conclusion: The transform method enables straightforward solutions to be developed for many finite difference equations. Though limited to linear equations it should be useful in solving many chemical engineering problems.

NOTATION

$F(y_n)$	=	finite difference transform of y_n $F(y_n) = \gamma(p)$
J_o	=	Bessel function of zero order
k	=	integer
k_i	=	reaction rate constant for ith reaction
m	=	k_2/k_1
n	=	integer
p	=	parameter
r_i	=	rate of ith reaction
y_n	=	function of n
α	=	volatility ratio
$\gamma(p)$	=	$\dfrac{p-1}{p} \sigma(p) = F(y_n)$
$\sigma(p)$	=	$y_o + \dfrac{y_1}{p} + \dfrac{y_2}{p^2} \ldots = \sum_{n=o}^{\infty} \dfrac{y_n}{p^n}$

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