

"PRODUCT IN THE WAY" PROCESSES

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Many processes in chemical engineering have the same basic physical description—that the thing produced (or something proportional to it) gets in the way of the process. These diverse processes all lead to the same mathematics and optimization, as will be shown here.

A wide variety of chemical engineering processes lead to rate equations of the form

$$\frac{1}{(\text{production rate})^2} = a(\text{time}) + b \quad (1)$$

or

$$\text{time} = g \left(\frac{\text{cumulative product}}{\text{product}} \right)^2 + h \left(\frac{\text{cumulative product}}{\text{product}} \right) \quad (2)$$

Here time is measured from the start of production or of the current production cycle, and a , b , g , and h are constants (all symbols are defined in the nomenclature at the end of this paper). Although the processes described by these equations cover the whole range of chemical engineering (including heat transfer, filtration, condensation, freezing, chemical reactions, oxidations, etc.), the underlying mechanism is the same for all. This paper is about that mechanism, its mathematics, and the wide range of places where a chemical engineer can encounter it.

In all of these processes, the characteristic physical fact is that the product, or something proportional to it, gets in our way and the more we pro-

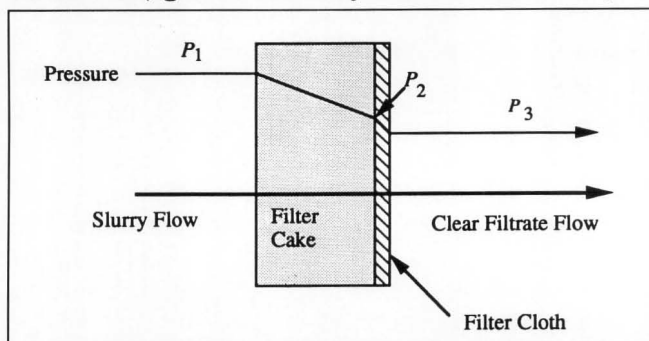


Figure 1. Flow through a simple filter



Noel de Nevers has been a faculty member at the University of Utah since 1963. His principal interests are fluid mechanics, thermodynamics, and air pollution. He has also developed a course and edited a book of readings on Technology and Society. He recently won local fame by discovering a previously unknown major arch in Arches National Park.

duce, the more the product is in our way and the slower the process rate becomes.

One may easily show that Eqs. (1) and (2) are the same by writing

$$\text{cumulative product} = \int_0^t (\text{production rate}) d(\text{time}) \quad (3)$$

and then differentiating Eq. (2) and comparing it term-by-term with Eq. (1). The two equations are the same if $a = 4g$ and $b = h^2$.

FILTRATION

It is easy to see how these equations arise in the classical treatment of constant-pressure filtration of a solid from a liquid, to form an incompressible cake.^[1] The flow through a filter and its pressure profile are shown schematically in Figure 1. A slurry (a fluid containing suspended solids) flows through a filter medium (most often a cloth, but sometimes paper, porous metal, or a bed of sand). The solid particles in the slurry deposit on the face of the filter medium, forming the "filter cake." The liquid, free from solids, flows through both cake and filter medium. The flow is laminar in almost all filters, and the changes in potential and kinetic energies are negligible, so that the pressure drop is given by Darcy's equation [$(-\Delta P/\Delta x) = \mu V/k$]. Solving that equation for the superficial velocity, we find

$$V_s = \frac{Q}{A} = \frac{-\Delta P}{\mu} \frac{k}{\Delta x} \quad (4)$$

where μ is the fluid viscosity and k is the cake permeability. Here there are two resistances in se-

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ries with the same flow rate through them. If we let the subscript "f.m." indicate "filter medium," we can write Eq. (4) twice and equate the identical flow rates (see Figure 1)

$$V_s = \frac{P_1 - P_2}{\mu} \left(\frac{k}{\Delta x} \right)_{\text{cake}} = \frac{P_2 - P_3}{\mu} \left(\frac{k}{\Delta x} \right)_{\text{f.m.}} \quad (5)$$

When we solve for P_2 , we get

$$P_2 = P_1 - \mu V_s \left(\frac{\Delta x}{k} \right)_{\text{cake}} = P_3 + \mu V_s \left(\frac{\Delta x}{k} \right)_{\text{f.m.}} \quad (6)$$

and then, solving this equation for V_s , we get

$$V_s = \frac{P_1 - P_3}{\mu \left[\left(\frac{\Delta x}{k} \right)_{\text{cake}} + \left(\frac{\Delta x}{k} \right)_{\text{f.m.}} \right]} = \frac{Q}{A_{\text{filter}}} \quad (7)$$

This equation describes the instantaneous flow rate through a filter; it is analogous to Ohm's law for two resistors in series, so the $\mu \Delta x/k$ terms are called the *cake resistance* and the *cloth resistance*.

The resistance of the filter medium is normally assumed to be a constant independent of time, so $(\Delta x/k)_{\text{f.m.}}$ is replaced with a constant, α . If the filter cake is uniform, then its instantaneous flow resistance is proportional to its instantaneous thickness. However, this thickness is related to the volume of filtrate which has passed through the cake by the material balance

$$\Delta x_{\text{cake}} = \left(\frac{\text{mass of cake}}{\text{area}} \right) \left(\frac{1}{\rho_{\text{cake}}} \right) = \frac{1}{\rho_{\text{cake}}} \left(\frac{\text{volume of filtrate}}{\text{area}} \right) \left(\frac{\text{mass of solids}}{\text{volume of filtrate}} \right) \quad (8)$$

Customarily we define

$$W = \left(\frac{\text{mass of solids}}{\text{volume of filtrate}} \right) \left(\frac{1}{\rho_{\text{cake}}} \right) = \frac{\text{volume of cake}}{\text{volume of filtrate}} \quad (9)$$

so that

$$\Delta x_{\text{cake}} = \frac{V}{A} W \quad (10)$$

Here the cake is assumed to be incompressible, $\rho_{\text{cake}} = \text{constant}$, which is a good assumption for most filtrations but not for filtration of flocs and gels. The volume of filtrate here is V . (This implies 100% collection efficiency for the solids in the slurry, which is generally observed.) When we substitute Eq. (10) for the cake thickness in Eq. (7), we find

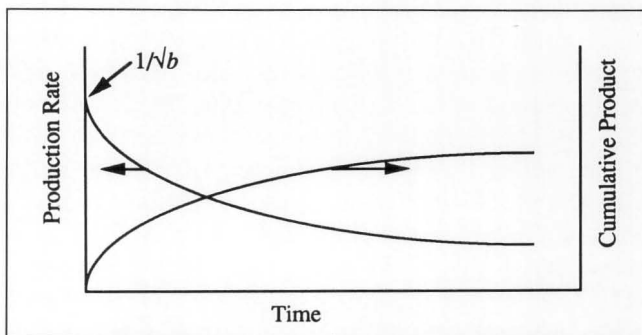


Figure 2. Relation between production rate and cumulative production

$$\frac{Q}{A} = \frac{1}{A} \left(\frac{dV}{dt} \right) = \frac{P_1 - P_3}{\mu \left(\frac{VW}{kA} + \alpha \right)} \quad (11)$$

For most industrial filtrations the filter is supplied by a centrifugal pump or blower at practically constant pressure, so $(P_1 - P_3)$ is a constant, and Eq. (11) may be rearranged and integrated to

$$\frac{1}{2} \left(\frac{V}{A} \right)^2 \frac{\mu W}{k} + \frac{V}{A} \mu \alpha = (P_1 - P_3)t \quad (12)$$

Eq. (2) and Eq. (12) are identical if

$$\begin{aligned} \text{product} &= V/A \\ g &= (\mu W)/2k(P_1 - P_3) \\ h &= \mu \alpha / (P_1 - P_3) \end{aligned}$$

Intuitively, we can see what is happening in Figure 2. At time zero there is no cumulative product and the production rate equals $1/(\sqrt{b})$. As soon as we begin to produce filtrate, we also produce filter cake. This increases the resistance, so the production rate declines. The more filtrate we produce, the thicker the filter cake and the higher the resistance. The product (filter cake) gets in the way of producing more filter cake.

Often one sees Eq. (2) rewritten as

$$\frac{\text{time}}{\text{cumulative product}} = g(\text{cumulative product}) + h \quad (13)$$

This allows us to plot (time/cumulative product) vs. cumulative product and to read the values of g and h as the slope and intercept of the straight line which results. This is shown for filtration (using Eq. 12) by McCabe and Smith.^[2] It is equally applicable to other processes described in this paper. That type of plot has less intuitive content than Figure 2, but it makes

possible a visual check of whether or not the experimental data agree with Eqs. (1) or (2) and allow a direct determination of g and h from those data.

FREEZING

The second example of Eqs. (1) or (2) is the formation of ice on a cooled surface, such as occurs in an ice maker.^[3] Referring again to Figure 1, we see that in this situation the flow is of heat, not fluid. We would relabel that figure by replacing the slurry with fluid being frozen, replacing the filter cake with the ice which has formed, replacing the filter cloth with the chiller surface (normally a highly conductive metal), and at the right the recipient of the heat (normally a chilled brine or evaporating refrigerant). The pressure-distance curve would be replaced by a temperature-distance curve, with the same shape. If we ignore the heat transfer resistances other than those due to conduction (which is an excellent approximation for this case), then we can rewrite Eq. (7) as

$$\text{heat flux} = \frac{q}{A} = \frac{dQ}{dt} = \frac{T_1 - T_3}{\left[\left(\frac{\Delta x}{k} \right)_{\text{ice}} + \left(\frac{\Delta x}{k} \right)_{\text{metal wall}} \right]} \quad (14)$$

Where

T = temperature

k = (which were permeabilities in Eqs. 4 to 12) are now thermal conductivities of ice and metal, respectively

Q/A = total heat transferred per unit area (analogous to the volume, V , of filtrate)

q/A = the instantaneous heat flux (analogous to $V_s = (1/A)(dV/dt)$ for filtration)

Here the analogs of Eqs. (8) to (10) are

$$\begin{aligned} \Delta x_{\text{ice}} &= \frac{\text{mass of ice}}{\text{area}} \left(\frac{1}{\rho_{\text{ice}}} \right) \\ &= \left(\frac{1}{\rho_{\text{ice}}} \right) \left(\frac{\text{heat transferred}}{\text{area}} \right) \left(\frac{\text{mass of ice}}{\text{heat transferred}} \right) = \left(\frac{Q}{A} \right) \left(\frac{1}{\rho \lambda} \right) \end{aligned} \quad (15)$$

where λ is the latent heat of fusion. If we substitute this value of Δx_{ice} into Eq. (14) and perform the integration, we find

$$\frac{1}{2} \left(\frac{Q}{A} \right)^2 \frac{1}{(\rho \lambda k)_{\text{ice}}} + \left(\frac{Q}{A} \right) \left(\frac{\Delta x}{k_{\text{metal}}} \right) = (T_1 - T_3)t \quad (16)$$

which is identical to Eq. (2) if

$$\text{product} = Q/A$$

$$g = 1/[2(\rho \lambda k)_{\text{ice}}(T_1 - T_3)]$$

$$h = \Delta x_{\text{metal}}/[k_{\text{metal}}(T_1 - T_3)]$$

Again—the product (ice) gets in our way. The thermal conductivity of ice is about 1% that of aluminum (the common metal in freezers) so the accumulated amount of what we are producing (ice) is the determinant of the rate of producing it.

This analysis ignores the sensible heat of the ice and any convective heat transfer resistances. Kreith^[3] applies the same analysis to the freezing of ice layers on ponds in cold weather. That situation is sketched in Figure 3, which is practically the same as Figure 1 if it were rotated by 90°. However, in Figure 3 the resistance of the metal wall is replaced by 1/(the ice-to-air heat transfer coefficient), which is practically a constant. The resulting equations are the same as above, with $(\Delta x_{\text{metal}}/k_{\text{metal}})$ being replaced by an ice-to-air heat transfer resistance, $(1/h_o)$. This analysis applies to any solidification process if the solid is a poor heat conductor, but not necessarily to the solidification of metals like aluminum or copper.

EVAPORATOR SCALE FORMATION

The third example is scale formation in evaporators.^[4] In many such evaporators a scale layer forms on the evaporator surfaces. This scale layer is normally a poor heat conductor, so its resistance to heat flow largely determines the overall heat flow rate. The experimental observation is that the thickness of the scale is proportional to the amount of heat which has been transferred to the evaporating solution since the last cleaning of the heating surface. Clearly, this is the same as the previous example with the variables renamed, *i.e.*,

$$\text{heat flux} = \frac{q}{A} = \frac{dQ}{dt} = \frac{T_1 - T_3}{\left[\left(\frac{\Delta x}{k} \right)_{\text{scale}} + \left(\frac{\Delta x}{k} \right)_{\text{metal wall}} \right]} \quad (17)$$

Normally, the scale thickness is taken as some constant α times the cumulative amount of heat transferred per unit area, and the two fluid-film heat transfer resistances are added to that of the metal wall, so that the analog of Eq. (11) becomes

$$\frac{q}{A} = \frac{dQ}{dt} = \frac{T_1 - T_3}{\left[\left(\frac{\alpha}{k_{\text{scale}}} \right) \frac{Q}{A} + \left(\frac{\Delta x}{k} \right)_{\text{metal wall}} + \frac{1}{h_o} + \frac{1}{h_i} \right]} \quad (18)$$

and the analog of Eq. (12) becomes

$$\frac{1}{2} \left(\frac{Q}{A} \right)^2 \left(\frac{\alpha}{k_{\text{scale}}} \right) + \frac{Q}{A} (\text{sum of other resistances}) = (T_1 - T_3)t \quad (19)$$

Normally this is seen in the form of Eq. (1).^[4,5] The

transition from Eq. (2) to Eq. (1) may be made by solving Eq. (2) as a quadratic for the cumulative product, finding

$$(\text{cumulative product}) = \frac{-h}{2g} + \frac{\sqrt{h^2 + 4gt}}{2g} \quad (20)$$

then differentiating, and noting that the production rate is $d(\text{cumulative production})/dt$. Thus

$$\frac{q}{A} = \text{heat transfer rate} = \frac{1}{\sqrt{h^2 + 4gt}} \quad (21)$$

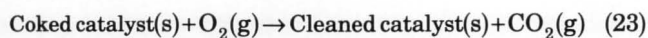
Squaring and taking the reciprocals leads to Eq. (1).

GAS-SOLID CHEMICAL REACTIONS

The next application is a gas-solid chemical reaction which forms or leaves a solid residue, *e.g.*



which is important in some gas-phase sulfur dioxide capture processes, *e.g.*, fluidized bed combustion, or in catalyst regeneration, *e.g.*



in which carbon is burned off a solid porous petroleum cracking catalyst, leaving behind a cleaned catalyst. In the first of these cases, the product of the reaction is a less porous solid than is the solid reactant, so that the layer of product forms the principal barrier to diffusion of the gaseous reactant inward to the surface of the unreacted solid. In the second case, the reaction increases the porosity of the solid, but as the regeneration continues the oxygen must diffuse further inward to get to the unregenerated part of the catalyst, and the carbon dioxide must diffuse further to get out, so that the diffusion resistance of the steadily growing cleaned catalyst layer is the principal resistance in the process.

In general, such a reaction is described as^[6]

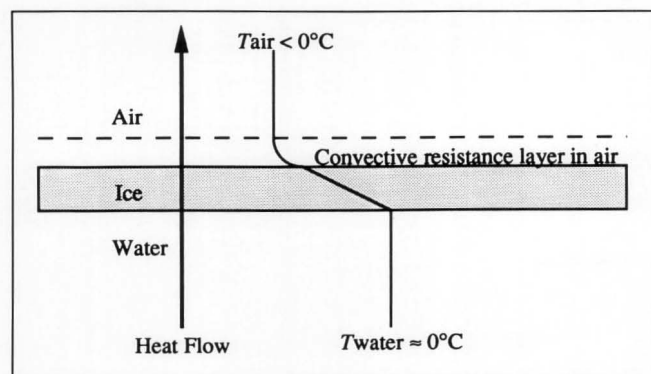
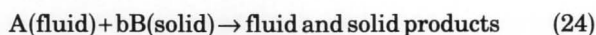


Figure 3. Solid ice formation on a body of water

where b is the stoichiometric coefficient.

We may visualize these two reactions on Figure 3 if we visualize the ice as being replaced by the reaction product (CaSO_3 or Cleaned catalyst), visualize the unfrozen liquid being replaced by the unreacted solid reactant (CaO or Coked catalyst), and visualize the air-to-ice heat transfer coefficient being replaced by a gas-to-solid mass transfer coefficient. In place of the heat flow we will have gaseous reactant diffusing to the solid surface and then diffusing through the reacted solid to the surface of the unreacted solid; there will be no flow of anything beyond that surface.

For this general reaction, the analog of Eq. (7) is

$$\frac{1}{A} \frac{dN_A}{dt} = \frac{C_{A_o} - C_{A_i}}{\left[\frac{(N_A/A)b}{D\rho_{\text{solid product}}} + \frac{1}{k_G} \right]} \quad (25)$$

where

$(1/A)(dN_A/dt)$ = rate at which reactant A is delivered to the surface of unreacted B

D = diffusivity of the gas

k_G = an external mass transfer coefficient,

subscripts o, i = bulk gas phase and reaction interface, respectively

The analog of Eqs. (8) to (10) is

$$\Delta x_{\text{solid product}} = \frac{N_A}{A} \frac{b}{\rho_{\text{solid product}}} \quad (26)$$

N_A is normally stated in moles, so that $\rho_{\text{solid product}}$ must be the molar density of the solid product. Substituting Eq. (26) into Eq. (25), we find the analog of Eq. (11)

$$\frac{1}{2} \left(\frac{N_A}{A} \right)^2 + \frac{N_A}{A} \left(\frac{1}{k_G} \right) = (C_{A_o} - C_{A_i}) \left(\frac{D\rho_{\text{solid product}}}{b} \right) \quad (27)$$

In most applications of Eq. (27) it is further assumed that the concentration of A at the surface of B, (C_{A_i}), is negligible, and that $(1/k_G)$ is negligible, so that we have

$$\Delta x_{\text{solid product}} = \sqrt{\frac{2C_{A_o} D b t}{\rho_{\text{solid product}}}} \quad (28)$$

or, solved for t

$$t = \frac{\rho_{\text{solid product}} \Delta x^2}{2bDC_{A_o}} \quad (29)$$

Most often one sees this equation applied not to a flat surface, but rather to a spherical particle.^[6] There one sees^[6, Chap. 12, Eq. 14]

$$t = \frac{\rho_B R^2}{6bDC_{A_0}} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right] \quad (30)$$

where R is the radius of the particle (assumed constant, which implies that $\rho_B/b = \rho_{\text{solid product}}$), and r_c is the radius of the unreacted core of B . This is the "shrinking core—ash diffusion controls" kinetic model. In it, the attention is focused on the unreacted B rather than on the reacted material

We may see how Eqs. (29) and (30) compare by writing

$$r_c = R - \Delta x \quad (31)$$

substituting in Eq. (30), and simplifying to find

$$t = \frac{\rho_B \Delta x^2}{2bDC_{A_0}} \left[1 - \frac{2}{3} \frac{\Delta x}{R} \right] \quad (32)$$

If, as assumed above, $\rho_B/b = \rho_{\text{solid product}}$, then Eq. (32) is simply Eq. (29) multiplied by $[1 - (2/3)(\Delta x/R)]$, which accounts for the spherical rather than planar shape. For the planar configuration shown in Figures 1 and 3, R is infinite and Eqs. (29) and (32) are identical. For spherical particles, Eq. (29) describes only the initial stages of the process during which Δx is small compared to R .

This same set of equations applies to the formation of oxide films on metals (*e.g.*, rusting, but also solid oxide formation on non-ferrous metals) if the film is coherent and does not flake away,^[7] and to processes like fluidized bed powder coating and various steps in the production of integrated circuits if the deposited or diffused film is more resistant to the flow of heat or material than the substrate.

FILM CONDENSATION

Nusselt's classic derivation of the behavior of a vapor condensing on a vertical wall in laminar flow,^[8] as shown in Figure 4, provides the final example. The derivation normally shown does not make clear that this is one of the class of processes discussed here. If we take the viewpoint of an observer riding with a batch of fluid down the wall (the Lagrangian view), we can see that the situation is exactly the same as the problem of freezing of ice on a solid surface and that Eq. (15) applies, with the properties of the condensate replacing those of the ice. In the derivation, the heat transfer resistance of the metal wall is normally ignored, as we do here, so by combining Eqs. (15) and (16) we find

$$\frac{1}{2} \Delta x^2 = \frac{k\Delta T}{\rho\lambda} t \quad (33)$$

Here the appropriate value of t is the time it has

taken this batch of condensate to flow downward from $z = 0$. At any value of z , for a slice perpendicular to the flow we may compute the average velocity from the assumption of laminar flow as

$$V_{\text{avg}} = \frac{\rho(\Delta x)^2 g}{3\mu} \quad (34)$$

(which ignores the buoyant effect of the vapor and the shear stress between vapor and condensate film). We assume that the piece of fluid we are riding with begins at $t = 0$, at $z = 0$, with $V = 0$. At time t it will be at location z and have the average velocity given by Eq. (34). To find the value of t corresponding to any z , we assume that the average velocity since $t = 0$ is one-half of the velocity at $t = t$, which leads to $t = z / (V_{\text{avg}}/2)$. Substituting this value into Eq. (33) and solving for Δx , we find

$$\Delta x = \left[\frac{12\Delta T \mu z}{k\lambda\rho^2 g} \right]^{1/4} \quad (35)$$

This is $(3)^{1/4} = 1.3$ times the value derived by Nusselt and shown in most heat transfer books. The difference results from the approximation made in treating a laminar flow as if it were a plug flow. That approximation is not as large a source of error in the derivation as some of the other approximations.^[8]

OPTIMIZATION

One benefit of seeing that all these processes have the same form is that we can then use the optimization equations developed for any one of them for all of them. For any of the processes which require regular shutdown and cleanout (*e.g.*, batch filtration, batch freezing, evaporator operation with peri-

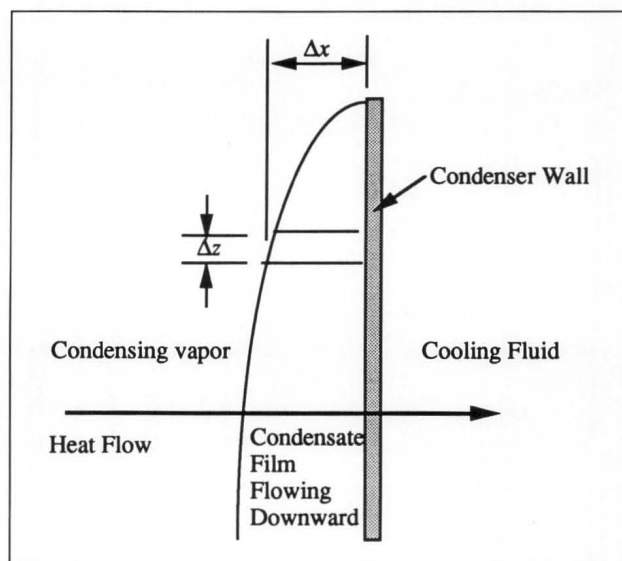


Figure 4. Laminar film condensation

odic shutdown and scale removal) if t is the operating time and t_c is the time required to shut down, clean out and restart, the average production rate is

$$\text{average production rate} = \frac{\text{cumulative product}}{t + t_c} \quad (36)$$

If we substitute Eq. (20) for cumulative product, set $[d(\text{cumulative product})/dt]$ equal to zero, and solve for t , we find (after some algebra)

$$t = t_c + h \sqrt{\frac{t_c}{g}} \quad (37)$$

or, if the rate is formulated in terms of Eq. (1),

$$t = t_c + 2 \sqrt{\frac{bt_c}{a}} \quad (38)$$

The latter solution is shown in Peters and Timmerhaus^[5] for an evaporator with scale formation and regular shutdowns for cleaning, but it is obviously equally applicable to all of the batch processes shown here.

CONCLUSION

One fundamental kind of process—product gets in the way of production—appears in many places in chemical engineering. The mathematical presentations of these processes vary, but all can be shown to fit a single pattern. By using that pattern, we can use the results and ideas for any one of these processes for all of them.

Where Should this Fit in the ChE Curriculum?

This material is regularly discussed in our senior-year process design class. The students have previously taken courses in fluid mechanics, heat transfer, mass transfer, and chemical reaction kinetics, so the examples should all be review for them. The design course seems a good place for them to see this integration of several diverse topics in their previous courses. Professors who use the process design book of Peters and Timmerhaus can introduce the discussion of this topic by assigning the following homework problem:

Problems 11-5 (page 417) and 14-16 (page 578) of Peters and Timmerhaus have very different-looking rate equations, for processes which are physically similar. Show the choice of symbols which makes the rate equations for these two problems the same.

NOMENCLATURE

- a = rate constant in Eq. (1):
 $1/[(\text{production rate})^2 (\text{time})]$
 A = area: m^2

- b = rate constant in Eq. (1): $1/(\text{production rate}^2)$
 b = stoichiometric coefficient: mols/mol
 C_A = concentration of A: mols/ m^3
 D = diffusivity: m^2/s
 g = rate constant in Eq. (2): (cumulative product²)(time)
 g = acceleration of gravity: m/s^2
 h = rate constant in Eq. (2):(cumulative product)(time)
 h = heat transfer coefficients: $J/[(m^2)(s)(K)]$
 k = permeability: m^2
 k = thermal conductivity: $J/[(m)(s)(K)]$
 k_G = external mass transfer coefficient: m/s
 N_A = moles of A: mols
 P = pressure: Pa
 Q = cumulative heat transferred: J
 Q = volumetric flowrate: m^3/s
 q = heat flow: J/s
 R = radius (of spherical particle): m
 r_c = radius of unreacted core of spherical particle: m
 T = temperature: K
 t = time: s
 x = distance or thickness: m
 z = vertical distance: m
 V = volume of filtrate: m^3
 V = velocity: m/s
 V_s = superficial velocity: m/s
 W = cake volume/filtrate volume
 α = cloth resistance/ $\mu = (\Delta x/k)_{f.m.}$: $1/m$
 α = scale formation constant: m^3/J
 λ = latent heat: J/kg
 μ = viscosity: Pa s
 ρ = density or molar density: kg/m_3 or $mols/m^3$

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