

APPLICATION OF PSEUDO-STEADY-STATE APPROXIMATION IN SOLVING CHEMICAL ENGINEERING PROBLEMS

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The concept of pseudo-steady-state approximation (PSSA) has been used quite extensively in solving chemical engineering problems where different steps in an overall process take place at different time scales. Ideally, the process takes place in two consecutive steps, and the PSSA is invoked to eliminate the unsteady-state nature of one of the steps. The effect of invoking such an approximation is to considerably simplify the solution of the problem.

The PSSA solution is an approximate solution and needs to be carefully examined to determine its accuracy and to identify the physical conditions under which the solution is valid. In cases where the rigorous solution is available, it can be compared with the PSSA solution to determine the error involved in invoking the PSSA concept. In cases where the rigorous solution is not available, application of perturbation method may be necessary to determine the accuracy of the PSSA solution.

In this paper, we have chosen a number of examples from fluid mechanics, heat and mass transfer, and reaction kinetics to illustrate the principle of the technique, when and how it can be applied, the importance of checking the accuracy of the PSSA solution, and the physical conditions under which the method may be used.

The general procedure is to identify the steps in the overall process and the corresponding time scales or time constants (e.g., τ_1 and τ_2). The problem may then be examined under the limiting conditions of either

$$\tau_1 / \tau_2 \ll 1 \quad \text{or} \quad \tau_1 / \tau_2 \gg 1$$

This procedure is illustrated with the following examples, the majority of which involve moving boundary problems. The examples chosen are such that their more rigorous analytical solutions are available, and in each case, the PSSA

solution is checked against the more rigorous solution to determine the conditions under which the PSSA solution is valid.

EXAMPLE 1 Draining of a Tank

Draining a tank filled with a liquid is an unsteady-state problem often simplified by the application of the PSSA concept. Here, a tank having height H and radius R is filled with a liquid to a height h . At time $t=0$, the liquid in the tank is allowed to drain through a hole of radius R_0 in the bottom of the tank. We want to determine the time it takes to empty the tank.

There are two time constants: they are determined by V_1 , the velocity of the liquid level in the tank, and V_2 , the efflux velocity through the hole. The exact solution of this problem involves the solution of an unsteady-state mass balance

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coupled with an unsteady-state macroscopic mechanical energy balance. The equations are considerably simplified, however, if one assumes that $R_0 \ll R$. Under this condition, the rate at which the liquid is leaving the tank is much smaller than the total amount of liquid in the tank. The liquid level in the tank may move so slowly that it can be essentially considered as stationary. The rate at which the liquid level in the tank drops is much smaller than the velocity of liquid leaving the tank through the hole (*i.e.*, $V_1 \ll V_2$). As a result, steady-state macroscopic mechanical energy balance can be used instead of the unsteady-state balance. The problem can now be modeled as an unsteady-state mass balance coupled with a steady-state mechanical energy balance. The problem has been solved^[1] and the rigorous solution is given by

$$t = 2 \left(\frac{R}{R_0} \right)^2 \sqrt{\frac{H}{2g}} \phi_N \quad (1)$$

where ϕ_N is a correction factor defined as

$$\phi_N = \frac{1}{2} \sqrt{\frac{(N-2)}{N}} \int_0^1 (\eta - \eta^{N-1})^{-1/2} d\eta \quad (2)$$

Here, N is defined as $(R/R_0)^4$. Since V_1 and V_2 are inversely proportional to R^2 and R_0^2 , the variable N is equivalent to $(V_2/V_1)^2$. The correction factor, ϕ_N , is a direct measure of the accuracy of the PSSA solution. As ϕ_N begins to differ significantly from one, the PSSA solution begins to deviate from the exact solution. The value of ϕ_N is undefined at zero and at one. Numerical integration of ϕ_N has been performed as a function of N between $N=1^{-0.05}$ and 0.99999; the results are shown in Figure 1. For values of $N > 100$ (*i.e.*, when the tank radius is only about 3.16 times the radius of the hole), the PSSA solution is more than 99% accurate. At $N=3$, when the tank radius is only 1.32 times the radius of the hole, the accuracy of the PSSA solution falls to 90%. As the radius of the hole increases in relation to the tank radius, the level in the tank falls faster and the assumption of a steady-state energy balance involves greater errors.

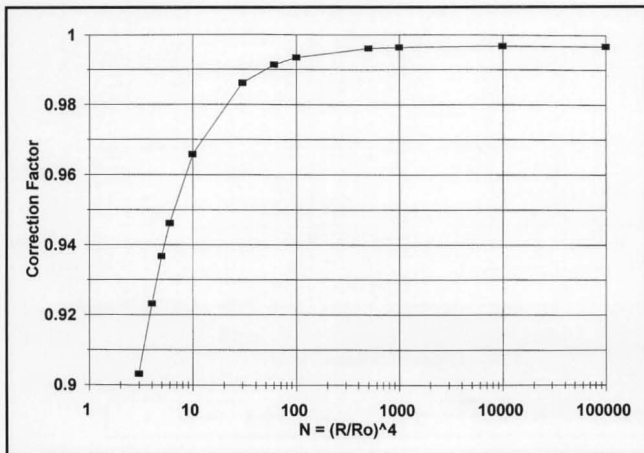


Figure 1. Effect of changing the ratio of tank diameter to hole diameter on the accuracy of PSSA solution.

EXAMPLE 2 Measurement of Diffusion Coefficients by Bulb Technique

The measurement of diffusion coefficients using a two-bulb apparatus is another example where using the PSSA is advantageous. Here, two bulbs are separated by a capillary whose volume is negligible in comparison to the volume of each of the two bulbs. An impermeable membrane located equidistant between the two bulbs separates solutions of different compositions. At time $t=0$, the membrane is ruptured and the two solutions are allowed to diffuse into each other.

Two different time scales are pertinent for this system. One time scale defines how fast the concentrations in the bulbs are changing with time, and the second time scale defines how fast the concentration profile is established in the capillary for a given concentration driving force between the bulbs. Since the volume of the bulbs is much larger than that of the capillary, concentration in the bulbs changes much more slowly. In contrast, the capillary itself contains relatively little material. Changes in its concentration profile occur much more quickly. Even if this profile is initially quite different from that at steady state, it will approach steady state before the concentrations in the bulbs change much. Therefore, the system is modeled as an unsteady-state mass balance for the material in the bulbs combined with a steady-state flux across the capillary, *i.e.*, the PSSA is invoked.

The PSSA solution for the concentration difference between the two chambers as a function of time can be easily found through the solution of Fick's equation. First, two dimensionless variables are defined: dimensionless time and dimensionless volume ratio

$$\tau = \frac{Dt}{L^2} \quad \text{and} \quad N = \frac{AL}{V} \quad (3)$$

where

- D diffusion coefficient
- L distance separating the two bulbs
- A cross-sectional area of the capillary
- V volume of a single bulb.

It is assumed that the two bulbs are of equal volume. The concentration difference between the two chambers at any time under the condition of PSSA is given by^[2]

$$\Delta x(\tau) = \exp(-2N\tau) \quad (4)$$

The more rigorous solution for the concentration difference between the two chambers by the application of perturbation method has been shown to be^[3]

$$\Delta x(\tau) = \exp \left(-2N\tau \left(1 - \frac{N}{2} \right)^{1/2} \right) \quad (5)$$

The ratio of the PSSA solution to the more exact solution is then equal to

$$\exp\left\{-2N\tau\left[1-\left(1-\frac{N}{2}\right)^{1/2}\right]\right\}$$

This factor describes the accuracy of the PSSA solution as a function of the ratio of the volume of the capillary to the volume of the bulbs (N) and dimensionless time τ . Figure 2 shows this relationship. When $N=0.01$, the capillary has 1% of the volume of the bulb, and the PSSA solution is equal to the exact solution for all values of τ . As the value of N increases, the PSSA solution deviates more and more from the "exact" solution. When $N=1$, the capillary has a volume that is equal to the bulb volume. At this N, the exact solution is considerably different from the PSSA solution at all values of τ except for very small values of τ . The PSSA solution has been shown to be valid^[2] when the time constant for the capillary is much smaller than that for the compartments, *i.e.*,

$$\frac{L^2}{D} \gg \frac{1}{D\beta} \quad \text{where} \quad \beta = \frac{2A}{VL}$$

Marrero and Mason^[4] have discussed the effect of factors such as end effects and the presence of Knudsen diffusion in the capillary tube.

EXAMPLE 3
Measurement of Diffusion Coefficients
Using Stefan Tube

One of the common methods of determining D_{AB} , diffusivity of A and B in a binary gas system, is through the use of a Stefan tube. Liquid A is placed at the bottom in a long, relatively small-diameter tube filled with gas B. Gas B is blown across the top of the tube so that any A diffusing to the top of the tube is swept away, maintaining essentially zero partial pressure of A at the top of the tube. As A vaporizes and diffuses into B, the liquid level in the tube drops. Time required for the liquid level to drop from an initial level to a final level is measured and is used to calculate the diffusivity.

As in the previous examples, there are two time scales involved here: the speed with which the concentration profiles are established in the gaseous phase in the tube, and the rate at which the liquid level drops. The length of the diffusion path continually increases. Since the density of liquid is three orders of magnitude higher than that of a gas, we would intuitively surmise that the liquid level would drop quite slowly and, in contrast, the concentration profiles within the gas space would establish much more quickly.

For all practical purposes, the concentration profile in the tube can be approximated as that at steady state. We can, therefore, combine the steady-state flux at the boundary with the unsteady-state macroscopic mass balance. Equating the steady-state flux with the rate of vaporization, we obtain

$$\rho_M \frac{dy}{dt} = N_A = \frac{D_{AB}P}{RTy} \frac{(p_{A1} - p_{A2})}{P_{BM}} \quad (6)$$

Integrating between the limits of y_0 (diffusion path length at $t=0$) and y_t (diffusion path length at $t=t$) and rearranging, we obtain

$$D_{AB} = \frac{RT\rho_{BM}P_M(y_t^2 - y_0^2)}{2P(p_{A1} - p_{A2})t} \quad (7)$$

An obvious error in the analysis is that the initial concentration distribution in the tube may be quite different from the steady-state profile. However, we can easily calculate the time needed to establish the steady-state profile. The ratio of flux at the boundary at time t to flux at steady-state is given by^[5]

$$\frac{N_t}{N_{\tau=\infty}} = 1 - 2e^{-1^2\pi^2\tau} + 2e^{-2^2\pi^2\tau} - 2e^{-3^2\pi^2\tau} + \dots \quad (8)$$

where

$$\tau = \frac{D_{AB}t}{y_0^2}$$

The approach to steady-state profile is depicted in Figure 3. The steady-state profile is established when $\tau = 0.5$. For gaseous systems, with $y_0 = 10$ cm and $D_{AB} = 0.1$ cm²/s, the steady-state profile is approached in about ten minutes. When compared with the experimental time of the order of hours, the PSSA appears quite reasonable.

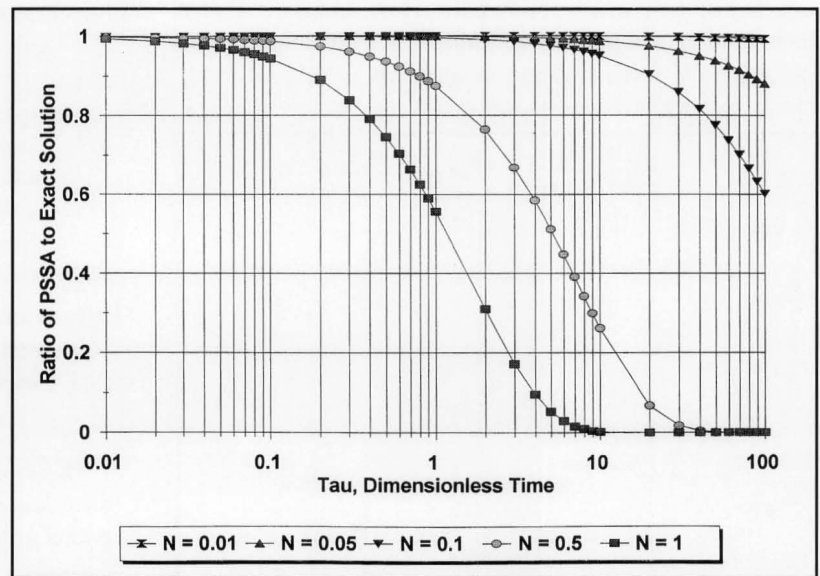
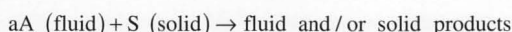


Figure 2. Accuracy of PSSA solution as a function of the ratio of capillary volume to bulb volume.

A second error arises from the fact that the observed drop in the liquid level produces vapor which occupies the space originally filled with liquid and may not diffuse out of the tube. But this error will be small because the partial density of A in the newly created space will be much smaller compared to the density of the liquid.

EXAMPLE 4
Gas-Solid Non-Catalytic Reactions

Gas-solid non-catalytic reactions represent another class of problems where the PSSA has been advantageously exploited. Consider a non-catalytic reaction between gas (A) and solid (S). The reaction may be represented by



The solid particle is in the form of a spherical particle. As the reaction proceeds, the particle may shrink with time, ultimately disappearing completely, or it may retain its size but the unreacted core of the solid continuously shrinks in size with the formation of an ash layer on the outer shell of the particle. Both the reactant A and the boundary of the unreacted core move inward. But since the density of solid differs from that of gas by a factor of about 1000, it is reasonable to assume that the unreacted core moves so slowly towards the center that for all practical purposes it may be considered stationary; *i.e.*, the time constant associated with the movement of unreacted core is so much larger than that for establishing the concentration gradient in the ash layer. The PSSA solution is relatively easy to derive and is given in a number of books.^[6] The exact solution for a spherical particle is not possible, however, and a number of approximate analytical solutions have been derived^[7-10] to determine the adequacy of the PSSA solution. To illustrate the accuracy of the method, we follow the suggestion of Wen^[11] and consider the problem in the Cartesian coordinate system.

Consider the reaction taking place on a horizontal surface that moves inward as the reaction takes place, leaving a porous inert layer at the top. The model equations for such a scenario are

$$\varepsilon \frac{\partial C_A}{\partial t} = D_{eA} \frac{\partial^2 C_A}{\partial Z^2} \quad 0 < Z < S(t) \quad (9)$$

The boundary conditions are

$$C_A = C_{A0} \quad \text{at} \quad Z = 0$$

and at the moving boundary $Z = S(t)$

$$\begin{aligned} C_A &= 0 \\ -D_{eA} \frac{\partial C_A}{\partial Z} &= aC_{S0} \frac{dS}{dt} \end{aligned} \quad (10)$$

The initial condition for the moving boundary is that it occupies the position $Z=0$ at $t=0$. The PSSA solution can be

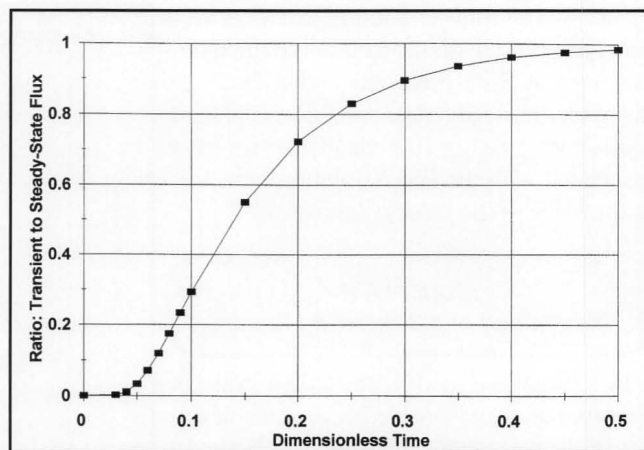


Figure 3. Approach of transient flux to steady-state value as a function of time.

easily shown to be

$$\begin{aligned} S(t) &= \sqrt{\frac{2 C_{A0} D_{eA} t}{a C_{S0}}} \\ C_A &= C_{A0} \left(1 - \sqrt{\frac{a C_{S0}}{2 C_{A0} D_{eA} t}} Z \right) \end{aligned} \quad (11)$$

An analytical expression for the exact case can be obtained as follows. The solution of the differential equation (9) is given by the combination of variables method and has been shown to be^[11]

$$C_A = C_{A0} \left(1 - \frac{\operatorname{erf} \left(\frac{Z}{2 \sqrt{D_{eA} t / \varepsilon}} \right)}{\operatorname{erf} \lambda} \right) \quad (12)$$

where $\lambda = S / (4 D_{eA} t / \varepsilon)^{1/2}$ and is the root of

$$\frac{C_{A0} \varepsilon}{a C_{S0}} = \sqrt{\pi} \lambda e^{\lambda^2} \operatorname{erf} \lambda \quad (13)$$

By expanding the error function in an infinite series, we can show that

$$\frac{C_{A0} \varepsilon}{a C_{S0}} = 2 \lambda \left(\lambda + \frac{2}{3} \lambda^3 + \frac{4}{15} \lambda^5 + \dots \right) \quad (14)$$

If $\lambda \ll 1$, then

$$\lambda \approx (C_{A0} \varepsilon / 2 a C_{S0})^{1/2} \quad \text{and} \quad S(t) \approx (2 C_{A0} D_{eA} t / a C_{S0})^{1/2}$$

This is exactly the same expression for the travel of the moving boundary obtained for the PSSA case. Thus, PSSA is a good approximation if λ is much less than 1. It is indeed the case for gas-solid reactions. Molar density of A is about three orders of magnitude smaller than that for a solid. Hence, $\lambda \approx 10^{-3}$. As the value of λ increases, however, so does the inaccuracy of the PSSA solution. This is depicted in

Figure 4. The ratio of solid reactant conversion (proportional to the location of the moving front at $S(t)$) predicted under PSSA to that under unsteady-state condition is plotted against $\epsilon C_{A0} / aC_{S0}$. It is clear that the error associated with the PSSA solution increases as the value of $\epsilon C_{A0} / aC_{S0}$ increases.

EXAMPLE 5 Dissolution of a Sphere in Liquid^[12]

In Examples 3 and 4, the PSSA concept appeared quite reasonable because the densities of the two phases involved (gas-liquid in Example 3 and gas-solid in Example 4) were different by about three orders of magnitude. Let us now consider the case where the densities of the two phases are of the same order of magnitude. The problem of dissolving a benzoic acid sphere of 1 cm diameter in water at 25°C has been considered by Sherwood, *et al.*^[12] We wish to determine the time required for complete dissolution of the sphere.

Again, there are two time constants involved in the process: one characterizes the rate of movement of the spherical boundary, and the other characterizes how quickly the concentration profiles are established in the aqueous phase. Just as in Examples 3 and 4, it is tempting to assume that the boundary recedes very slowly compared to the time required for the steady-state concentration profile to establish. To determine how quickly the steady-state concentration profiles in the fluid phase are established, we can perform the following analysis. Benzoic acid dissolves at the interface and radially diffuses into water. Assume that the concentration of the aqueous phase at the surface of the sphere is maintained at 0.0278 g moles/l. The flux at the sphere boundary at $r = r_0$ can be shown to be

$$(N_A)_{r=r_0} = \frac{D_{AB}C_S}{r_0} + \frac{D_{AB}C_S}{\sqrt{\pi D_{AB}t}} \quad (15)$$

The transient flux differs from the steady-state flux by 1% when $(\pi D_{AB}t)^{1/2}$ is equal to 100 r_0 . For $D_{AB} = 1.1 \times 10^{-5}$ cm²/s, this time is calculated as 72.2 million seconds. In this analysis, the diameter of the sphere has been assumed to remain constant. But when we integrate the flux equation with time, we find that in 72.2 million seconds the total amount of benzoic acid dissolved will be about twenty-six times that contained in a one-cm sphere.

The use of a steady-state equation, in this case, results in considerable error. The transient concentration profile approaches steady state extremely slowly. First, the value of D_{AB} is small and molar concentration of acid in solution is relatively large, much larger than that of gas A in the gas

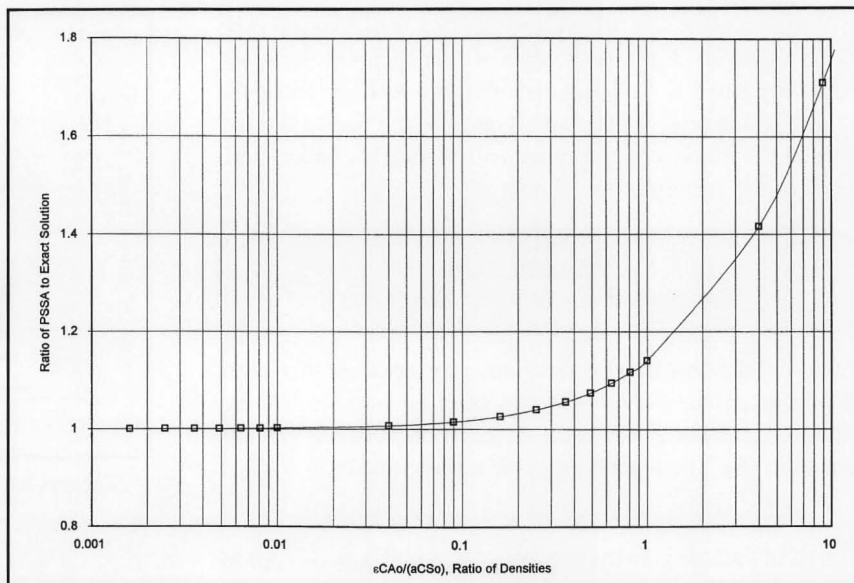


Figure 4. Accuracy of PSSA solution as a function of ratio of two densities.

space in the Stefan tube. The amount of solute contained in the shell originally occupied by solid is significant. In this case, PSSA does not work well. The value of λ (as defined in Example 5) in this case approaches one, and for this condition, the PSSA solution should deviate significantly from the exact solution.

CONCLUDING REMARKS

The PSSA is a powerful concept that can be applied in many transport phenomena problems where multiple time scales are involved. This has been demonstrated with the use of several examples. In every case, however, it is imperative to determine the accuracy of the PSSA solution by comparing it with either an exact solution or an approximate closed form analytical solution or numerical solution. In the first four examples, the PSSA solution is fairly accurate; but for the last example, the concept of PSSA solution results in significant errors.

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