THE APPLICABILITY OF THE PSEUDO-STeadY STATE APPROXIMATION TO MOVING BOUNDARY PROBLEMS FOR SPHERES*

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The equations of diffusion and heat transfer for moving boundary problems in spherical particles were computed in order to test the applicability of the pseudo-steady state approximation, which is usually believed to be valid for the case of gas diffusion. This approximation, however, may sometimes induce considerable errors for the case of heat transfer.

In this study, figures are presented to test such applicability in the literature data and further to correct the experimental data under those conditions.

Introduction

The formation of ice, the melting of solids, the drying of porous materials during the second falling-rate period, the thermal decomposition of solids, and many other solid-gas reactions are often treated as problems of moving boundaries, i.e., (1) a clear boundary always exists between the unreacted core and the reacted layer, (2) the reaction and the phase change take place only at the surface of this boundary, and (3) through the reacted layer the gas diffuses and the heat is transferred.

The analysis of the above-mentioned phenomena for spherical particles can be started from the following partial differential equations for diffusion and heat transfer, respectively.

\[
\varepsilon \frac{\partial C_s}{\partial t} = F(D_s \frac{\partial C_s}{\partial r})
\]

\[
\frac{\partial T}{\partial t} = F(k \frac{\partial T}{\partial r})
\]

with the following initial and boundary conditions,

\[
D_s \frac{\partial C_s}{\partial r} = \alpha C_s (\frac{\partial r_e}{\partial t})
\]

or \( k \frac{\partial T}{\partial r} = C_s \Delta H_e (\frac{\partial r_e}{\partial t}) \) at \( r = r_e \)

\[
r_e = R \quad \text{at} \quad t = 0
\]

Since exact analytical solutions of Eqs. (1) and (2) are impossible except for flat plate, they are often solved under the pseudo-steady state (P. S. S.) approximation, in which the moving rate of the boundary within the solid is assumed to be far slower than the rate of diffusion and heat transfer, and accordingly the left-hand terms of Eqs. (1) and (2) are negligible.

Several investigators have studied and discussed the applicability of the P. S. S. approximation. Pekeris and Slichter applied the perturbation method to the problem of freezing soil around the external surface of a long cylinder, and derived an approximate solution which showed that the maximum error to be introduced by
neglecting the unsteady terms on the left-hand side of Eqs. (1) and (2) was less than 7% in the case of 30% moisture content and a temperature amplitude of 25°C.

Extending their method to the spherical shape, Bischoff\(^7\) derived an approximate solution for the unsteady diffusion equation and showed that the P. S. S. approximation was usually valid for solid-gas systems under the control of product layer diffusion but might often induce remarkable errors for solid-liquid systems.

Recently, by using a computer, Tao\(^8\) presented the numerical solution of the partial differential Eq. (2) for ice formation within a long cylinder as well as within a sphere. His solution included the effect of the external gas film on heat transfer.

Although the subject considered by Bischoff was mass transfer and that by Tao was heat transfer, both results are compared in Fig. 6 for the spherical shape, because their basic equations are mathematically identical. This figure shows that these results cannot well be compared with each other and that they are insufficient to test the accuracy of P. S. S. approximation.

In this study, the basic Eqs. (1) and (2) in partial differential forms for spherical particles were transformed into ordinary differential equations and were computed numerically to get more accurate solutions than those by Bischoff and Tao. Based upon those computed results, figures are presented further to test the applicability of P. S. S. approximation with some numerical illustrations of how to correct the literature data under such conditions.

1. Mathematical Analysis

Consider a reaction of a spherical solid particle S of radius \(R\) with gas stream A flowing around it.

\[
a A C_{0} + S C_{0} \rightarrow T \quad \text{(Solid Products)}
\]

The fundamental diffusion equation of gas component A within the reacted product layer is represented by Eq. (1). Since the P. S. S. approximation is usually valid for the case under the controls of chemical reaction and of external gas-film diffusion\(^2\), only the case under the control of ash layer is taken hereafter. When the rate of chemical reaction is very fast and the resistance to diffusion through the ash layer controls the rate of reaction, the boundary conditions become as follows:

\[
C_{4} = C_{40} \quad \text{at} \quad r = R
\]

\[
C_{4} = 0 \quad \text{at} \quad r = r_{c}
\]

Introducing the following dimensionless variables,

\[
C_{4}^{*} = C_{4}/C_{40}, \quad t^{*} = (t_{D}^{*} / R^{*}) (C_{40} / a C_{40})
\]

\[
r^{*} = r / R, \quad r_{c}^{*} = r_{c} / R
\]

\[
\tau^{*} = \frac{a C_{40}}{(a C_{40})}
\]

we get;

\[
\tau^{*} = \frac{\partial C_{4}^{*}}{\partial t} + \frac{2}{r^{*}} \frac{\partial C_{4}^{*}}{\partial r^{*}}
\]

\[C_{4}^{*} = 1 \quad \text{at} \quad r^{*} = 1\]

\[C_{4}^{*} = 0 \quad \text{at} \quad r^{*} = r_{c}^{*}\]

\[
dr_{c}^{*} / dt^{*} = - (\partial C_{4}^{*} / \partial r^{*}) \quad \text{at} \quad r^{*} = r_{c}^{*}\]

\[
r_{c}^{*} = 1 \quad \text{at} \quad t^{*} = 0\]

Eq. (2) can also be transformed to a similar form as Eq. (7), if \(\tau^{*} = C_{4}^{*} (T_{0} - T_{c}) / (C_{40} D H_{2})\) and \(T^{*} = (T_{m} - T_{c}) / (T_{c} - T_{c})\) are introduced instead of \(\tau^{*}\) and \(C_{4}^{*}\), respectively, since such treatment in heat transfer is entirely analogous to that in diffusion (=mass transfer).

Transforming Eq. (7) to an ordinary differential equation by the method shown in Appendix 1, the concentration profile of the gas component A within the reacted product layer can be obtained as follows:

\[
C_{4}^{*} = \frac{1}{r_{c}^{*}} \left( 1 - \text{erf} \left( \frac{(1 - r_{c}^{*}) / 2 \sqrt{t^{*} / \tau^{*}}}{\tau^{*}} \right) \right)
\]

(10)

Differentiating Eq. (10) by \(r^{*}\) and putting it into the first condition in Eq. (9), we have

\[
dr_{c}^{*} / dt^{*} = - \frac{1}{r_{c}^{*} (1 - r_{c}^{*})} \times 2 \sqrt{t^{*} / \tau^{*}} \text{erf} \left( \frac{\lambda_{c}}{\sqrt{t^{*} / \tau^{*}}} \right)
\]

(11)

where \(\lambda_{c}\) is a variable defined by Eq. (A 1-6). Hence, the solution of Eq. (7) is reduced to solve Eq. (11) under the second condition of Eq. (9). The numerical computation of an ordinary differential Eq. (11) is obviously much easier than that of a partial differential Eq. (7).

As an example of Eq. (11), let us examine the particular case where the value of \(\lambda_{c}\) is relatively small. If the concentration of reactant gas component A is much more diluted than that of solid component S, \(\tau^{*}\) defined by Eq. (6) and \(\lambda_{c}\) defined by Eq. (A 1-6) are both far less than unity, and the error function can be approximated by the following expression:

\[
\text{erf} \left( \frac{\lambda_{c}}{\sqrt{t^{*} / \tau^{*}}} \right) = \frac{2}{\sqrt{\pi}} \lambda_{c} \exp \left( - \lambda_{c}^{2} \right)
\]

(12)

Then Eq. (11) can be reduced to:

\[
dr_{c}^{*} / dt^{*} = - \frac{1}{r_{c}^{*} (1 - r_{c}^{*})} \left( 1 / r_{c}^{*} - 1 \right)
\]

(13)

Integration of the above equation gives

\[
t^{*} = (1/2) (1 - r_{c}^{*2}) - (1/3) (1 - r_{c}^{*3})
\]

(14)

This solution is exactly identical with that by the P. S. S. approximation, which may be derived by neglecting the left-hand term of Eq. (7). The concentration profile of gas component A for such case can be represented by

\[
C_{4}^{*} = \frac{1}{(1/r_{c}^{*} - 1/r_{c}^{*})} / \left( (1/r_{c}^{*}) - 1 \right)
\]

(15)

2. Numerical Computations

The right-hand term of Eq. (11) will become infinite at the onset of the reaction, (i.e., \(t^{*} = 0\) and \(r_{c}^{*} = 1\)). Accordingly, it is impossible at first to start the numerical computation. However, during the period with extremely thin product layer, the differential surface of a spherical shell may be considered as a part of a flat plate or slab, as shown in Appendix 2. Hence, the reaction time required for \(r_{c}^{*} = 0.99999\) was calculated by the following Eq. (16) for the infinite flat plate\(^{12}\) and was then applied to the initial condition of Eq. (11) for the sphere.

\[
\tau_{m} = \sqrt{\pi} \lambda_{c} \exp \left( - \lambda_{c}^{2} \right)
\]

(16)

Since the calculated value of \(t^{*}\) for \(r_{c}^{*} = 0.99999\) is about \(0.5 \times 10^{-14}\) and is very much smaller than \(t^{*} \approx 0.25\) for the complete conversion, \(X = 1\) or \(r_{c}^{*} = 0\), it does not affect the following computations.

Runge-Kutta-Gill method was used for the practical computations. The grid size was taken as \(X = 0.01X + 0.001\) for the range of conversion \(X = 1 - r_{c}^{*}\) less
than 0.2, and as \( X = 0.002 \) for \( X > 0.2 \). The computation was performed by an IBM360 for \( r_m = 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, \) and 3.0.

3. Illustrations of the Results Computed

Fig. 1 shows the ratio of the reaction time by P. S. S. solution of Eq. (14) to that computed by the present method mentioned in the preceding Section 2. The curve for \( X = 0 \) or \( r_e = R \) is based on Eq. (16) for an infinite flat plate (slab). As shown in Fig. 1, the value of such ratio for the sphere is dependent on the conversion and is always less than that for the flat plate. In regard to the reaction time, the discrepancies from the P. S. S. approximation become more remarkable with increase in \( r_m \) and \( X \) for the sphere than for the flat plate in Fig. 1.

Fig. 2 shows the profiles for the concentration of reactant gas component A or the temperature within the product layer for \( r_m = 0, 0.1, 1, \) and 3, and for \( r_e^* = 0.8, 0.5, \) and 0.2. In this Figure, the reciprocal of the dimensionless radius, \( 1/r_e^* \), is taken as the abscissa to give solid straight lines for the P. S. S. profiles. Within the range where \( r_m \) is less than 0.1, the profiles by the exact solution are almost as straight as the P. S. S. profiles; thus the P. S. S. approximation may be considered to be valid in this range. However, for the range where \( r_m \) is greater than 0.1, the profiles deviate gradually from the straight lines of P. S. S. profiles. The reaction rate per unit area of reacting core surface is just proportional to the slope of the curves at \( Ca^* = 0 \) in Fig. 2.

The ratio of the reaction rate computed by the present method to that of the P. S. S. solution calculated by Eq. (13) is shown in Fig. 3 at the same conversion \( X \). For the flat plate and for the sphere at \( X = 0 \), the curve is exactly the same as that shown in Fig. 1. However, the ratio in Fig. 3 for the sphere for \( X > 0 \) is less than that of the reaction time in Fig. 1. Accordingly, the validity of the P. S. S. approximation in regard to the reaction rate is more narrowly restricted than that to the reaction time in Fig. 1. The P. S. S. approximation should, therefore, be applied more carefully where the reaction rate is a very important factor.

Fig. 4 shows the reaction rate per unit area of reacting core surface as a function of conversion \( X \). This unit reaction rate has a minimum value at the conversion of 0.875 (corresponding to \( r_e^* = 0.5 \)) for the case where the P. S. S. approximation is valid. However, as the value of \( r_m \) increases and the unit reaction rate decreases, the conversion \( X \) which gives the minimum unit reaction rate is shifting close to \( X = 1.0 \). Hence, the geometrically unstable region with the criterion of \( d(\text{d}r_e^*/\text{d}t^*)/\text{d}X > 0 \) is extremely narrowed at the last stage of the reaction.

Fig. 5 shows the ratio of conversion \( X \) computed in this study to that calculated by the P. S. S. approximation at the same reaction time, \( t \). Recently, Wen \(^{12} \) presented a similar diagram in his Fig. A2 based upon the calculated results by Tao \(^{10} \). The ratios in Fig. 5 are greater than those in Figs. 1 and 3. Moreover, the ratio for the sphere is closer to unity than that for the flat plate. This means that in regard to the conversion, the P. S. S. approximation can be applied more widely for spheres than for the flat plate.
Figs. 1, 3 and 5 show that the applicability of the P. S. S. approximation depends on the viewpoint of what is to be compared or checked. For calculation of the reaction time, for example, the validity of the P. S. S. approximation can be checked by Fig. 1. On the other hand, for reaction rate and conversion, the validity must be checked by Fig. 3 and Fig. 5, respectively.

As described so far, in testing whether the P. S. S. approximation is valid or not, it must first be elucidated which is the most important factor – the reaction time, the reaction rate, or the conversion – to find the corresponding figure adequately.

4. Discussion

Fig. 6 shows the comparison of the result in this study which is already shown in Fig. 1 with those of Bischoff and Tao. The solution by Bischoff's perturbation method, represented by dotted lines, gives nearly the same values as those in this study over the range where the value of $\gamma_m$ is less than 0.1 and $r_c/R$ is greater than 0.5. As the value of $\gamma_m$ increases or that $r_c/R$ decreases, however, the error becomes drastic due to the limit of the perturbation method.

On the other hand, Tao's result, represented by chain lines in Fig. 6, approaches the solution of the present study where the value of $\gamma_m$ is greater than about unity, except at the early stages of reaction. The curve for $r_c/R = 0.9$ is quite different from the others and is about ten percent less than the value in this study at $\gamma_m = 0.1 \sim 0.2$. The grid size with which Tao computed was $\Delta r_c = 0.025$, and this grid size might perhaps be too wide to follow the abrupt change of the reaction rate at the initial stage of reaction.

In Table 1, the calculated results by the present method of $\gamma_m$ for the diffusion and $\gamma_h$ for the heat transfer are illustrated from the data in previous literature on moving boundary problems such as solid-gas reaction, freezing and drying of water, and thermal decomposition of CaCO$_3$.

In regard to the problem of gas diffusion, the greatest of the estimated values of $\gamma_m$ is $1.4 \times 10^{-3}$ even for the regeneration of coke-deposited catalyst, where solid component, i.e., coke, is very diluted (1~5 wt. %) and the P. S. S. approximation can be concluded to be sufficiently valid.

On the other hand, for the problems of heat transfer, most of the estimated values of $\gamma_h$ are situated in the region where the approximation is not perfectly valid. The values of $\gamma_h$ are as great as 0.12 for ice formation.
Table 1 Estimated values for $r_m$ and $r_k$ in previous works

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Reaction</th>
<th>$r_m$</th>
<th>Investigators</th>
<th>System</th>
<th>$T_0 - T_c$ [°C]</th>
<th>$r_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3) Cannon</td>
<td>Oxidation of zinc sulphide</td>
<td>$1.1 \times 10^{-4}$</td>
<td>8) Seban</td>
<td>Freezing of London water or foods</td>
<td>18~19</td>
<td>0.10</td>
</tr>
<tr>
<td>Denbigh</td>
<td>~$8.1 \times 10^{-5}$</td>
<td></td>
<td>1) Bell</td>
<td>Drying of Nissan woolen beebin</td>
<td>37</td>
<td>0.027</td>
</tr>
<tr>
<td>6) Kawasaki</td>
<td>Reduction of hematite</td>
<td>$3.9 \times 10^{-3}$</td>
<td></td>
<td></td>
<td>~0.12</td>
<td></td>
</tr>
<tr>
<td>Walsh</td>
<td>~$1.2 \times 10^{-1}$</td>
<td></td>
<td>9) Satterfield</td>
<td>Thermal decomposition of CaCO$_3$</td>
<td>22~121</td>
<td>0.013</td>
</tr>
<tr>
<td>11) Weisz</td>
<td>Regeneration of carbon-deposited catalysts</td>
<td>$2.5 \times 10^{-4}$</td>
<td>Goodwin</td>
<td></td>
<td>~0.073</td>
<td></td>
</tr>
</tbody>
</table>

by Seban and London$^8$, and for the drying of wool bobbin by Nissan$^1$. Those values of $r_k$ are situated at the region where the curves in Figs. 1, 3, and 5 just begin to deviate remarkably from unity.

In brief, the P. S. S. approximation is sufficiently correct for gas diffusion, but may introduce some errors for heat transfer. It is necessary, therefore, to examine by one of the Figs. 1, 3, and 5, whether the approximation may be applicable or not.

Conclusion

The partial differential equation for the sphere for moving boundary problems in unsteady state is transformed to an ordinary differential equation, solved numerically, and applied to check the solution by the P. S. S. approximation, in Fig. 1 as to the reaction time, in Fig. 3 as to the reaction rate, and in Fig. 5 as to the conversion. For the former two cases, the P. S. S. solution deviates from the present exact solution gradually with increase in conversion and in $r_m$. On the contrary, as to the conversion, its deviation gradually decreases as the conversion increases.

The distinction between the P. S. S. approximation and the present solution can be determined by $r_m$ or $r_k$. The calculated values of $r_m$ and $r_k$ from the literature data showed that the P. S. S. approximation is sufficiently valid for gas diffusion. For heat transfer, however, some experimental ranges in literature data were found to be beyond the limit of the P. S. S. approximation. For such cases, Figs. 1, 3, and 5 can be applied to analyse those experimental data.

Appendix 1

At first, $y^*$ is defined as

$$y^* = y C_A*$$  \(\text{(A1-1)}\)

Substitution of (A1-1) into Eqs. (7) and (8) gives

$$r_m \frac{\partial y^*}{\partial t} = \frac{\partial y^*}{\partial r^*} \left( \frac{\partial}{\partial r^*} \right)$$  \(\text{(A1-2)}\)

$$y^* = 1 \quad \text{at} \quad r^* = 1 \quad \text{at} \quad r^* = r_c^*$$  \(\text{(A1-3)}\)

Anticipating that a solution can be found of the form $y^* = \phi(t)$, in which $\phi$ is a dimensionless variable ($1-r_c^*$/4$\phi$/$r_m$), and in terms of the new variables, we get,

$$\frac{\partial \phi}{\partial t} + 2 \phi \frac{\partial \phi}{\partial r} = 0$$  \(\text{(A1-4)}\)

where

$$\phi = 1 \quad \text{at} \quad \lambda = 0$$

$$\phi = 0 \quad \text{at} \quad \lambda = \lambda_c$$

Then integration of Eq. (A1-4) and application of the boundary conditions (A1-5) give

$$\phi = y^* = 1 - e^{-\lambda} e^{\lambda_c}$$  \(\text{(A1-7)}\)

The above Eq. (A1-7) can be reduced to Eq. (10).

Appendix 2

If the product layer is very thin, i.e., $r_c^* R$, $r^*$ is also very close to unity. Then by Eq. (A1-1), $y^* C_A*$. Substituting the above relation into Eq. (A1-2),

$$r_m (\partial C_A^* / \partial t) = \partial C_A^* / \partial r^*$$

This is exactly identical with the equation for a flat plate.

Acknowledgement

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Nomenclature

- $a =$ stoichiometric coefficient
- $C_A =$ molar concentration of reactant gas $A$, $C_{A0};$ in bulk stream; Mol/L$^3$
- $C_{A*} =$ dimensionless molar concentration of gas component $A$ ($=C_A/C_{A0}$)
- $C_{S0} =$ concentration of solid component $S$ to be reacted within particle; Mol/L$^3$
- $C_T =$ moles of solid product $T$ per unit volume; Mol/L$^3$
- $C_p =$ molar heat capacity of solid $T$; H/(Mol)T
- $D_{Ae} =$ effective diffusivity of reactant gas $A$ within product layer; $1/\theta$
- $h_H =$ molar latent heat of melting of solid $S$; H/Mol
- $K_e =$ effective thermal conductivity of product layer; H/L$\theta$T
- $R =$ radius of spherical particle; L
- $r^* =$ dimensionless radius ($= r/R), r_c^*$: of unreacted core; L
- $T =$ temperature, $T_0$: of bulk stream, $T_c$: at reacting core surface; L
- $T^* =$ dimensionless temperature ($= T-T_c/(T_0-T_c)$)
- $t =$ time; L
- $t^* =$ dimensionless time defined by Eq. (5)
- $X =$ conversion ($= 1-r_c^* R$)
- $r_m =$ $C_{A0} / C_{S0} dC_A^* (dH_A)$
- $r_m =$ $C_{A0} dC_A^* (dH_A)$
- $\varepsilon =$ void fraction in product layer
- $\lambda_c =$ ($1-r_c^* R$) /4$\phi$/$r_m$

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PREFERENTIAL ION TRANSPORT THROUGH ION EXCHANGE MEMBRANES BY ELECTRODIALYSIS*  

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The preferential transport of a certain ionic species to others through an ion exchange membrane has been investigated. It was found from some experimental data that the preferential ion transport, \( S_{\text{K}^+}/S_{\text{Na}^+} \), should be closely related to an operating parameter \( \xi \), where \( S_{\text{K}^+} \) for example, is defined as the ratio of the Sherwood number concerning the transfer rate of \( \text{K}^+ \) to that of \( \text{Na}^+ \), and \( \xi \) is defined as \( \left( \frac{\Delta \phi}{2 \pi F D V} \right) \). The Stanton number \( St = (1/F)/C^\circ V \) defined as the ratio of the total ionic flux in the direction to the membrane to that in the direction of the bulk flow, was also a function of \( \xi \). These factors, \( \Delta \phi \), \( F \), \( D \), \( V \), \( I \), and \( C^\circ \) are the equivalent conductivity, the effective applied voltage to a single desalting compartment, the Faraday constant, the channel thickness, the linear flow velocity, the current density and the total equivalent concentration, respectively.

Under the operating condition of \( \xi > 10^{-3} \), no ion exchange membrane will serve to transport a certain ion preferentially. If \( \xi \leq 10^{-4} \), however, the membrane will fully reveal its own ability for selecting a certain ionic species, because the concentration ratio of two ionic species at the membrane surface will approach that in the equilibrium state.

Introduction

When an electrodialytic separation is applied to a multicomponent system, the transfer rate for each ionic species through a membrane varies according to the operating condition and hence it changes the composition of the penetrated solution.

This process is sometimes hindered by a few ionic species which make scale deposit on the surface of the membranes.

To counteract scale formation is one of the most important problems in operating an electrodialyzer. The critical scale for membranes may be caused by such kinds of species as calcium sulfate, various metal hydroxides or calcium carbonate.

Calcium sulfate may deposit in an anion exchange membrane and in a concentrated compartment, when \( \text{SO}_4^{2-} \) ion is highly concentrated. Another possibility to form calcium sulfate scale is the conversion of calcium carbonate to calcium sulfate. To prevent the deposit of calcium sulfate scale, the ionic concentration of the concentrated stream should be kept less than the solubility of calcium sulfate.

When \( \text{HCO}_3^- \) ion is too highly concentrated in the concentrated compartment, \( \text{CaCO}_3 \) may also deposit in the anion exchange membrane and in the concentrated compartment. Therefore, acid must be added to the concentrated stream to keep the concentration of \( \text{HCO}_3^- \) low enough to prevent the deposit of carbonate scale.

When neutrality disturbance takes place in the desalting stream due to insufficient turbulence or excessive voltage, \( \text{H}^+ \) or \( \text{OH}^- \) ion penetrates the membranes. \( \text{OH}^- \) ion has a tendency to form scale of carbonates or metal hydroxides in the anion exchange membrane or in the concentrated stream.

Generally there is no tendency to form carbonate and hydroxide scale in the cation exchange membrane, because of the strong Donnan repulsion force for \( \text{HCO}_3^- \) and \( \text{SO}_4^{2-} \) in the cation exchange membrane\(^{13,19} \).

There are three typical groups of studies so far reported of preferential ion transport through a membrane.

(1) The preferential characteristics to a certain ionic species were expressed by Peers\(^{11,15} \) in a simple relation between the current density, the boundary layer thickness and the concentration in the bulk flow, etc. A similar relation was also obtained by Yawataya\(^{19} \) and Seno et al.\(^{11} \).