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A quantized solution for the nucleation model in gas–solid reactions

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Abstract

A quantized technique has been suggested for the solution of coupled partial differential equations of gas–solid non-catalytic reactions. The application of this method to the nucleation model, which is important in metals production, is presented. This procedure provides a rapid prediction of conversion–time behaviour and an estimation of the kinetic parameters from the experimental data. The results of this method are compared with the numerical and approximate solutions, and show good accuracy. © 1997 Published by Elsevier Science S.A.

Keywords: Quantized solution technique; Nucleation model; Gas–solid reactions

1. Introduction

Gas–solid reactions are important in many chemical and metallurgical processes. Nucleation effects are often significant, for example in the reduction of metallic oxides. The conversion–time behaviour of these systems at low temperatures shows periods of induction, acceleration, and decay [1], e.g. in the reduction of nickel oxide with hydrogen [2].

Most gas–solid reactions start with the formation of nuclei at the solid surface. As the reaction progresses, these nuclei increase in size, overlap one another and cover the surface. When the temperature is high or the surface/volume ratio is small, the induction time is negligible and nucleation is not important. However for the reaction of very fine solid grains in a porous pellet, nucleation is important and sigmoidal curves of the conversion–time behaviour are obtained. A rate equation, in the absence of pore diffusion, has been developed for the interpretation of experimental conversion–time data showing sigmoidal trends [3].

A more general problem has been presented for isothermal and non-isothermal cases [4]. The effect of pore diffusion in the nucleation model has been analysed by Sohn [5]. A numerical solution and an approximate relation between the conversion and time have also been presented. In Ref. [6], the population balance approach was applied to the cuprous iodide oxidation system. In Ref. [7], the cumulative gas concentration was defined and the orthogonal collocation method was applied to solve the nucleation model equations. The results of Ref. [7] are in good agreement with the numerical solution of Sohn [5]. Finally, Shieh and Lee [8] incorporated induction time in the shrinking core model equations using the surface activation concept.

In this work, a mathematical method [9,10] is applied to solve the nucleation model equations. The results of this method are compared with the numerical and approximate solutions, and show acceptable accuracy. This method is very simple to handle on small calculators, and gives an analytical expression for gas and solid concentrations.

2. Mathematical model

A general gas–solid reaction can be given as

$$A(g) + \nu_B B(s) \rightarrow C(g) + \nu_D D(s) \quad (1)$$

For a single porous pellet, the following assumptions can be made.

1. The system is isothermal.
2. The pellet size and its porosity do not change during the reaction. Thus we have a constant effective diffusivity.
3. The reaction is irreversible and first order with respect to the gaseous reactant.
4. The pseudo-steady-state approximation is valid.
5. There is equimolar counter-diffusion.
6. The external mass transfer resistance is negligible.

The general dimensionless conservation equations of gas and solid, based on nucleation growth kinetics [5], are

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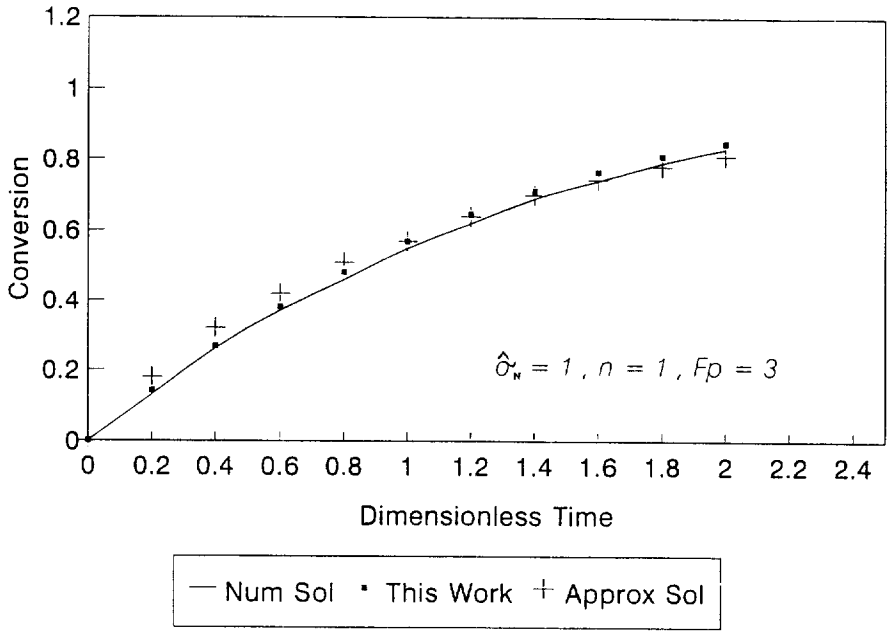

Fig. 1. Comparison of this work with numerical and approximate solutions of Sohn [5], for $n=1$ and spherical pellets (small modulus).

$$\frac{\partial^2 a}{\partial y^2}+\frac{F_p-1}{y}\frac{\partial a}{\partial y}=-2F_p\hat{\sigma}_N^2\frac{a}{f'(b)} \quad (2)$$

$$\frac{\partial b}{\partial \theta}=\frac{a}{f'(b)} \quad (3)$$

with the initial and boundary conditions

$$\theta=0 \quad b=1 \quad (4)$$

$$y=0 \quad \frac{\partial a}{\partial y}=0 \quad (5)$$

$$y=1 \quad a=1 \quad (6)$$

where the dimensionless quantities are defined in the notation, and

$$f'(b)=\frac{\partial f(b)}{\partial b} \quad (7)$$

$$f(b)=[-\ln(b)]^{1/n} \quad (8)$$

These coupled partial differential equations must be solved numerically. An approximate solution based on the law of addition of the reaction and diffusion times has also been presented [5].

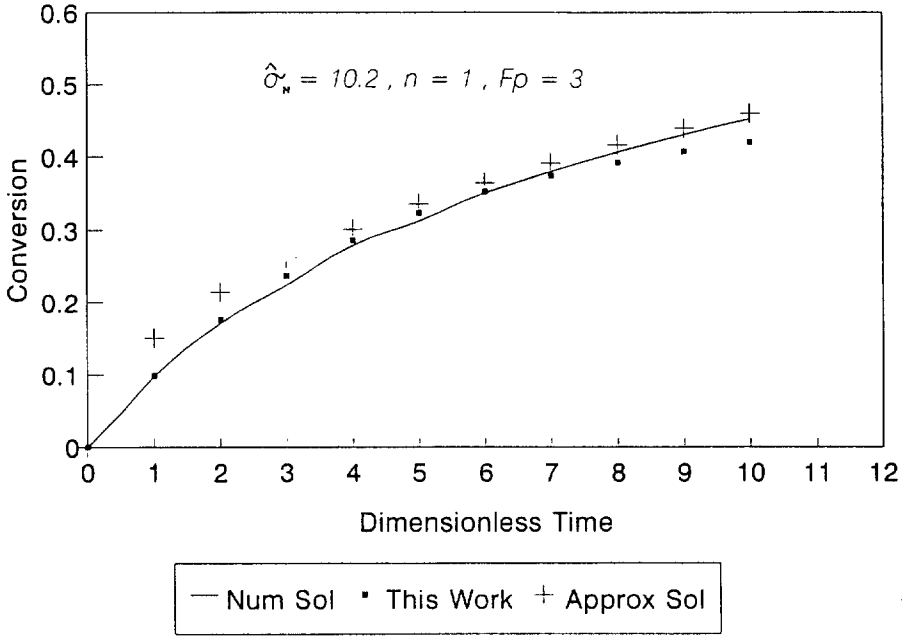

Fig. 2. Comparison of this work with numerical solution of Dudukovic and Lamba [11] and approximate solution of Sohn [5], for $n=1$ and spherical pellets (large modulus).

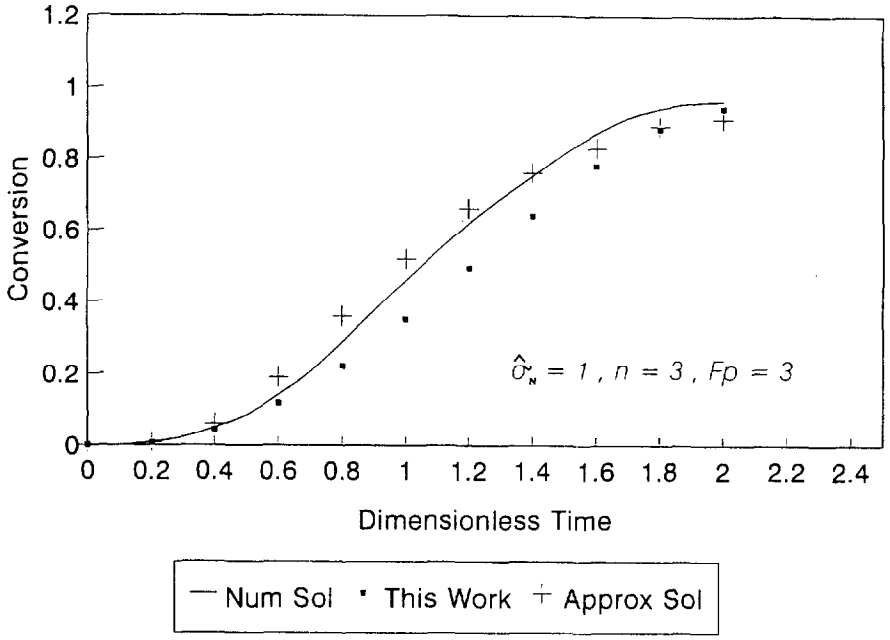

Fig. 3. Comparison of this work with numerical and approximate solutions of Sohn [5], for $n=3$ and spherical pellets (small modulus).

3. Quantized solution technique

3.1. Case 1: $n=1$

Assuming $n=1$, Eqs. (7) and (8) give

$$f'(b) = -\frac{1}{b} \tag{9}$$

and Eqs. (2) and (3) can be written as

$$\frac{\partial^2 a(j,i)}{\partial y(i)^2} + \frac{F_p - 1}{y(i)} \frac{\partial a(j,i)}{\partial y(i)} = 2F_p \hat{\sigma}_N^2 b(j,i) a(j,i) \tag{10}$$

$$\frac{\partial b(j,i)}{\partial \theta(j)} = -b(j,i) a(j,i) \tag{11}$$

where j and i are the time and position indices respectively.

The numerical solution for the above coupled partial differential equations leads to a large set of coupled linear equations. In these linear equations, $a(j,i)$, $a(j,i+1)$, $a(j,i-1)$, $b(j,i)$, $b(j-1,i)$,... are related to each other. Therefore much computational effort is needed to obtain the final results.

In this work, in contrast to the numerical solution, it is assumed that $a(j,i)$ and $b(j,i)$ are independent of $a(j,i\pm1)$, $b(j\pm1,i)$, $y(i\pm1)$ and $\theta(j\pm1)$. In other words the variables a, b, θ and y are related only by their (j,i) states. They are independent in terms of their $(j-1,i)$ or $(j,i-1)$ states.

In this technique, $a(j,i)$ and $b(j,i)$ react with each other at jth time and ith space. Thus there is no reaction between $a(j,i)$ and $b(j-1,i)$.

If we use $b(j-1,i)$ instead of $b(j,i)$ in Eq. (10) as an approximation, certain errors of computation are expected. In the following section, it is shown that this error is small. Using this approximation, we have

$$\frac{\partial^2 a(j,i)}{\partial y(i)^2} + \frac{F_p - 1}{y(i)} \frac{\partial a(j,i)}{\partial y(i)} = 2F_p \hat{\sigma}_N^2 b(j-1,i) a(j,i) \tag{12}$$

$$\frac{\partial b(j,i)}{\partial \theta(j)} = -b(j,i) a(j,i) \tag{13}$$

According to the quantized assumption, $b(j-1,i)$ can be treated as a constant in Eq. (12). With this assumption, on the right-hand side of Eq. (12), $a(j,i)$ is the only variable, and the other terms can be treated as a constant. Therefore a new modified Thiele modulus is defined as

$$M_1(j,i) = \sqrt{2F_p \hat{\sigma}_N^2 b(j-1,i)} \tag{14}$$

By inserting Eq. (14) into Eq. (12), we obtain

$$\frac{\partial^2 a}{\partial y^2} + \frac{F_p - 1}{y} \frac{\partial a}{\partial y} = M_1^2 a \tag{15}$$

Using the above assumption, Eq. (15) will be independent of Eq. (13), and we can integrate Eq. (15) with boundary conditions Eqs. (5) and (6); thus for slab pellets ($Fp=1$)

$$a(j,i) = \frac{\cosh(M_1 y)}{\cosh(M_1)} \tag{16}$$

and for spherical pellets ($Fp=3$)

$$a(j,i) = \frac{\sinh(M_1 y)}{y \sinh(M_1)} \tag{17}$$

By inserting Eqs. (16) or (17) into Eq. (13), and integrating with the initial condition Eq. (4), we obtain the solid concentration. For example, for spherical pellets, we have

$$b(j,i) = \exp\left[-\frac{\sinh(M_1 y)}{y \sinh M_1} \theta \right] \tag{18}$$

In this integration, according to quantization, M_1, which is a function of $b(j-1,i)$, is independent of $b(j,i)$ and $\theta(j)$. Eq.

Table 1
Errors of this work and approximate solution with respect to numerical solution of Sohn [5], for $n=1$ and spherical geometry (small modulus) [a]

$\theta\downarrow$	Numerical solution of Sohn [5]	Approximate solution of Sohn [5]		This work	
	Result	Result	Error %	Result	Error %
0.2	0.130	0.180	38.5	0.141	8.5
0.4	0.260	0.320	23.1	0.267	2.7
0.6	0.370	0.420	13.5	0.381	3.0
0.8	0.460	0.510	10.9	0.482	4.8
1.0	0.550	0.570	3.6	0.570	3.6
1.2	0.620	0.640	3.2	0.646	4.2
1.4	0.690	0.700	1.4	0.711	3.0
1.6	0.740	0.744	0.5	0.765	3.4
1.8	0.790	0.780	−1.3	0.809	2.4
2.0	0.830	0.810	−2.4	0.846	1.9

[a] $\hat{\sigma}_N=1$, $n=1$, $F_p=3$.

(18) seems to be implicit. However, in the quantized method, b in the expression for M_1 is constant between two small time increments. Therefore M_1 is calculated using $b(j-1,i)$.

Eqs. (16)–(18) show the concentration profiles of gas and solid, and from these we can compute b at each time and position. Then, from Eq. (14), we can compute the new M_1 from b at the same position, but at the previous time increment. Conversion of the solid at each time can be calculated for slab pellets

$$X(j)=1-\int_0^1 b(j,i)\,dy \tag{19}$$

and for spherical pellets

$$X(j)=1-3\int_0^1 b(j,i)y^2\,dy \tag{20}$$

3.2. Case 2: $n=3$

In this case, from Eqs. (7) and (8) we have

$$f'(b)=-\frac{1}{3b[-\ln(b)]^{2/3}} \tag{21}$$

Thus the model equations are

$$\frac{\partial^2 a}{\partial y^2}+\frac{F_p-1}{y}\frac{\partial a}{\partial y}=6F_p\hat{\sigma}_N^2 b[-\ln(b)]^{2/3}a \tag{22}$$

$$\frac{\partial b}{\partial \theta}=-3b[-\ln(b)]^{2/3}a \tag{23}$$

We can define the modified Thiele modulus for $n=3$ as

$$M_3(j,i)=\sqrt{6F_p\hat{\sigma}_N^2 b(j-1,i)\{-\ln[b(j-1,i)]\}^{2/3}} \tag{24}$$

By applying the quantized method, the concentration profiles and conversion for $n=3$ can be calculated. For example, the final results for spherical pellets are

$$a(j,i)=\frac{\sinh(M_3 y)}{y\sinh(M_3)} \tag{25}$$

$$b(j,i)=\exp\{-[a(j,i)\theta]^3\} \tag{26}$$

$$X(j)=1-3\int_0^1 b(j,i)y^2\,dy \tag{27}$$

Table 2
Errors of this work and approximate solution of Sohn [5] with respect to numerical solution of Dudukovic and Lamba [11], for $n=1$ and spherical geometry (large modulus) [a]

$\theta\downarrow$	Numerical solution of Dudukovic and Lamba [11]	Approximate solution of Sohn [5]		This work	
	Result	Result	Error %	Result	Error %
1	0.098	0.151	54.1	0.099	1.0
2	0.171	0.214	25.1	0.176	2.9
3	0.224	0.262	17.0	0.237	5.8
4	0.279	0.301	7.9	0.286	2.5
5	0.312	0.335	7.4	0.323	3.5
6	0.350	0.364	4.0	0.352	0.6
7	0.380	0.391	2.9	0.374	−1.6
8	0.401	0.416	3.7	0.392	−2.2
9	0.430	0.439	2.1	0.407	−5.3
10	0.452	0.460	1.8	0.420	−7.1

[a] $\hat{\sigma}_N=10.2$, $n=1$, $F_p=3$.

Table 3
Errors of this work and approximate solution with respect to numerical solution of Sohn [5], for $n=3$ and spherical geometry (small modulus) [a]

$\theta\downarrow$	Numerical solution of Sohn [5]	Approximate solution of Sohn [5]		This work	
	Result	Result	Error %	Result	Error %
0.4	0.050	0.060	20.0	0.044	−12.0
0.6	0.140	0.190	35.7	0.117	−16.4
0.8	0.290	0.360	24.1	0.222	−23.4
1.0	0.460	0.520	13.0	0.351	−23.7
1.2	0.620	0.660	6.5	0.494	−20.3
1.4	0.750	0.760	1.3	0.640	−14.7
1.6	0.870	0.830	−4.6	0.779	−10.5
1.8	0.940	0.890	−5.3	0.882	−6.2
2.0	0.960	0.910	−5.2	0.940	−2.1

[a] $\hat{\sigma}_N=1$, $n=3$, $F_p=3$.

4. Conclusions

In this work, we propose a quantized analytical solution directly applicable to the coupled partial differential equations of the nucleation model. The predicted conversion–time behaviour from the above equations is compared with the numerical and approximate solutions of Sohn [5]. The approximate solution of Sohn [5] is a relation between conversion and time. For example, for spherical pellets, it is

$$\theta \simeq [-\ln(1-X)]^{1/n}+\hat{\sigma}_N^2[1-3(1-X)^{2/3}+2(1-X)] \quad (28)$$

Fig. 1 shows a comparison of our work with the numerical and approximate solutions of Sohn [5] for $n=1$, $F_p=3$ and small modulus. For $n=1$, the induction time is not available. Fig. 2 shows a comparison of our work with the approximate solutions of Sohn [5] and the numerical solutions of Dudukovic and Lamba [11] for $n=1$, $F_p=3$ and large modulus. Fig. 3 shows a comparison of our work with the numerical and approximate solutions of Sohn [5] for $n=3$ and low modulus. For $n=3$ and large modulus, no numerical solution is available for comparison.

As shown in Figs. 1–3, the agreement between our work and the numerical solution is excellent for $n=1$, and good for $n=3$, at small modulus. For large modulus and small and intermediate dimensionless times, our method is more accurate than Sohn's approximate solution (see Fig. 2). However, for large modulus and large dimensionless times, Sohn's approximate solution gives better results. Tables 1–3 show a comparison of our work accuracy with the approximate solution of Sohn [5].

This method provides simple mathematical expressions which can be used for the rapid prediction of the conversion–time behaviour of the nucleation model, and considerably reduces the computational effort required.

Appendix A. Nomenclature

$a=C_A/C_{Ag}$	dimensionless gas concentration
$b=C_B/C_{B0}$	dimensionless solid concentration
C_A	gas concentration in the pellet
C_{Ag}	bulk gas concentration
C_B	solid concentration
C_{B0}	initial solid concentration
D_e	effective diffusivity of gas A in the pellet
$f(b)$	$[-\ln(b)]^{1/n}$
$f'(b)$	$[\partial f(b)/\partial b]$
F_p	shape factor of the pellet
i	position index
j	time index
k	reaction rate constant
M_1	modified Thiele modulus defined by Eq. (14)
M_3	modified Thiele modulus defined by Eq. (24)
n	a positive integer in Eq. (8)
r	distance from the centre of the pellet
R	characteristic pellet length
t	time
X	solid conversion
$y=r/R$	dimensionless position
ϵ	pellet porosity
$\theta=\nu_B k C_{Ag} t$	dimensionless time
ν_N	stoichiometric coefficient of N
ρ_B	true molar density of solid reactant B
$\hat{\sigma}_N=\frac{k\rho_B(1-\epsilon)}{2D_eF_p}$	Thiele modulus for nucleation model

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