Effects of surface rates for the series reaction *A* → *B* → *C* on successive separated spherical sites.

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# Introduction

The steady - state reaction of the chemical species *A* on the surface of a sphere 1 of radius *a1* with a first order irreversible reaction rate constant *kA*and diffusivity *DA* to form the intermediate species *B*, followed subsequently by the reaction of *B* on the surface of a sphere 2 of radius *a2* with a first order irreversible reaction rate constant *kB* and diffusivity *DB* to form the series reaction product *C*, occurs on two spherical sites a center – to – center distance *d* apart. The reaction model provides a means to examine the effects of a number of physical chemical rate changes of interest and importance. All else being equal, i.e., equal sphere sizes, is the series reaction rate more influenced by an increase in the first reaction site kinetic rate, *kA/DA*, or the second site rate, *kB/DB*, and what are the respective quantitative increases? If the reactive site kinetic rate parameters are held equal at both sites, how can one compare changes in geometry versus surface kinetics on the series reaction rate? Suppose the spherical site 1 surface reaction is very fast, how will the site 2 finite rates and the sphere geometries control the series reaction rate? Are the changes different for reaction control at site 1? In a previous paper paper [1] on the two – sites, steady - state series reaction when both of site reactions were diffusion controlled, a maximum in the series reaction rate was obtained at an optimum sphere separation. Will this maximum still occur at finite surface rates?

 The reaction model proposed above may be important to understand aspects of a number of physical chemical kinetic processes, the sequential coupling of metabolic reactions [2,3], the biophysics of cellular mutualisms [4,5], industrial composited polystep catalysis for the reforming of hydrocarbons [6], as well as, the effects of transport in dispersed phase and bifunctional surface catalysts [7]. In these applications, the spheres 1 and 2 represent, respectively, different enzymatic species participating in a metabolic reaction chain [2,3], several biological cells , the first which provides nutrients for the other [4,5], a simple mechanical mixture of several polysteps catalytic component particles [6], or solid dispersed nanoparticles and a reactive support [7].

 In section 2, the sequential series reaction model for first order reactions on the surfaces of successive spheres, along with transport equations and associated boundary conditions, is presented. The twin spherical harmonic method is applied in section 3 to obtain the necessary coefficient equations. The Neumann iterative solution of the coefficient equations in section 4 generates solutions for the series reaction rate as an expansion in the reciprocal center – to – center separation distance between the reactive spherical sates. Section 5 discusses the evaluation of the expansion form. Various plots of the series reaction rate versus the center – to – center sphere separation are used to examine the relative importance of the two site reaction rates, site geometry versus site kinetics, reaction control by either site 1 or site 2, and the onset of the series reaction rate maximum. An application to the isomerization of n-pentane is discussed in section 6.

# Series reaction model and equations

The steady - state series reaction requires simultaneous models both for the first *A* → *B*, and the second reaction *B* → *C.* Since a steady state is assumed, the first series reactant *A* must be continuously supplied from the bulk solution, and its concentration *cA*, far from the spheres 1 and 2, is a constant equal to the bulk concentration *cO*.

*cA* = *cO* (outer boundary). (1)

The species *A* reacts with an irreversible, first order reaction on the surface of spherical site 1, the boundary condition is

***ν*1•** *DA* ∇ *cA* = *kA cA* (***r*** on sphere 1) , (2)

where ***ν*1** is the normal unit vector pointing locally outward at the point ***r*** on the sphere 1 surface, *DA* is the *A* molecular diffusivity and *kA* is the first order rate constant of *A* on sphere 1. The species *A* does not react on sphere 2, and a reflecting boundary condition applies.

***ν*2**• *DA* ∇ *cA* = 0 (***r*** on sphere 2), (3)

where **ν2** is normal unit vector outward from any point ***r*** on sphere 2.

The *A* reactant concentration distribution is governed the Laplace equation

*DA* ∇2 c*A* = 0 . (4)

At large distances from the spheres, we assume the concentration *cB* of the intermediate *B* is zero, supposing either scavenger molecules consume the *B* that is not reacted by sphere 2 or that it escapes from the system [8].

*cB* = 0 (outer boundary) , (5)

From the selection of the bulk concentration of the intermediate to vanish the only *B* present must come for the reaction of *A* on sphere 1. Then any *B* reacting on sphere 2 must come from the reaction on sphere 1, and this allows us to trace the effects of diffusion and geometry along the reaction path of the series reaction *A* → *B* → *C*. Later on, one can easily introduce separately a non-zero bulk concentration of *B*\*, have it reflect from sphere 1 and react on sphere 2, and sum the reaction rate of *B* and *B*\* for more general results. The problem solution for the reaction *B*\* is available in Ref. [8].

 The chemical reaction rate *A* → *B* provides the source of the series reaction intermediate species *B*. A flux balance between the reactant *A* flux onto the surface of sphere 1 and the resulting intermediate *B* production flux is required locally at any point ***r*** on sphere 1

 (***r*** on sphere 1), (6)

where *DB* is the Fickian diffusion coefficient of *B*. Subsequently, the reaction *B* → *C* on a surface point ***r*** of sphere 2 is irreversible, first order with a rate constant *kB*.

 (***r*** on sphere 2) . (7)

Elsewhere, the intermediate *B* concentration is determined by the Laplace equation

 (8)

The reaction rate of *B* → *C* on the surface s2 of sphere 2, given in terms of a surface integral over s2, provides the net series dimensionless reaction rate formation of a product *C*

 . (9)

The reactions rate in Eq. (9) is made nondimensional with the division by the diffusion - controlled Smoluchowski rate of reaction *A* on isolated sphere 1. The dimensionless *R* of Eq. (9) will never exceed unity. The division in Eq. (9) removes any explicit mention of *c*0, *DA* and from the series reaction rate result, and allows *R* to be expressed solely in terms of the dimensionless inverse surface reaction rate coefficients λ*A*

 (10)

of reaction *A* → *B* on the sphere 1 surface, the dimensionless inverse surface rate coefficient λ*B*

 (11)

of *B* → *C* on sphere 2, the radius ratio *γ*

, (12)

the dimensionless center – to – center intersphere distance

 , (13)

and the diffusivity ratio

 . (14)

# **Twin spherical expansion**

An exact, steady - state analytical solution for the rate of series reaction on two successive spherical sites could be attempted in various ways. The two reactive spheres problem with a single reaction has been done using bispherical coordinates [9] with a Gaussian elimination solution of coefficient equations [10]. The Hobson’s translational reexpansion formulae [11–13] for solid harmonics in the case of axial symmetry allows the general solutions to the Laplace equation to be written in terms of the local coordinate systems connected to both spheres in order to satisfy the boundary conditions imposed on each sphere. This approach leads to infinite sets of linear equations with respect to the unknown coefficients to determine the concentration fields and the desired series reaction rate. A brief title is needed to refer to this method and to avoid confusion with the alternative “bispherical coordinate methods”, the term “twin spherical expansion” will be used. The twin spherical expansion method with a Neumann iterative treatment of the coefficient equations has been presented by Traytak [12] and Tsao [13]. Traytak has developed an irreducible tensor method [14] for many arbitrary distributed spheres. The twin spherical expansion with Neumann iteration has also been applied to the two spheres problem of a single reactant with different reaction at each sphere [8,15], a parallel reaction. The series reaction case under consideration requires the solution of two simultaneous equations respectively, for *cA* and *cB*, coupled by a demanding flux balance condition [6], for which last mentioned method is better suited.

 The coordinates for the twin spherical expansion are generated from a two sphere system separated by a vector distance from sphere 1 center to the sphere 2 center. Position vectors ***r1*** of magnitude *r1* and ***r2***of magnitude *r2* run, respectively, from the centers of sphere 1 and sphere 2 to a single point ***r*** in space. The angle *θ1* is the smaller angle between ***r1*** and the center – to – center vector ***d*** measured positive counter – clockwise. The angle *θ2* is also the smaller angle between ***r2*** and ***d*** (or the line between the two sphere centers) measured positive counter – clockwise.

 The solution of the Laplace equations (4) and (8) can be written in terms of twin spherical expansion coordinates and the Legendre functions, [16] *Pn* of order *n*, the twin spherical expansion

 (15)

where

 *i* = *A* or *B*,

 is the Kronecker delta function and *i1n* and *i2n* are the coefficients of the series (15) (*A*1*n*, *A*2*n*, *B*1*n*, *B*2*n*) to be determined by the conditions (2), (3), (6), (7) on the sphere surfaces. The boundary conditions can only be applied with the aid of the shift formula [1,8,11–13,15].

for rk-3<*d* , (16)

*k*=1,2 ,

where for *k*=1 Eq. (16) eliminates *θ*1 and *r*1 on sphere 2 for *r*2 and *θ*2, or for k=2 Eq. (16) eliminates *θ*2 and *r*2 in Eq. (15) on sphere 1 for *r*1 and *θ*1.

 To derive the *cA* coefficient equations for *A*1*n* and *A*2*n*, we substitute the series (15) for *i*=*A* with the shift formula (16) for *k*=2 into the reaction boundary condition (2), apply the orthogonality of the Legendre polynomials [16], and rearrange the series. We have

 (17)

with

, (18)

and

 , (19)

where

 *i* = *A* or *B .*

Substituting the shift formula (16) for *k*=1 into the twin spherical expansion (15) for *i* = *A*, using the no flux boundary condition (3) on the resulting *cA* form, employing the orthogonality integral for *Pn*, and applying straight forward algebra, gives us the second coefficient *A*2n for the concentration *cA* of Eq. (15)

 . (20)

The above equations (17), (18), (19) and (20) provide the basis for the determination of the coefficients *A*1*n* and *A*2*n*.

 To generate the *cB*coefficient equations for *B*1n and *B*2n, the shift formula (16) for *k*=1 is substituted into the twin spherical expansion (15) for the case *i* = *B*. Then with boundary condition (7) evaluated on sphere 2, along with the orthogonality condition [16] of *P*n we obtain

 . (21)

The twin spherical expansion forms (15) for *i* = *A* and *i* = *B* are used, respectively, on the left - hand side and right - hand side of the matching flux boundary condition (6) on sphere 1, along with the shift formula (15) for *k* = 2. After application of the Legendre orthogonality condition [16], we find

 (22)

 The surface integral (9) with the concentration equation (15) for *i* = *B* and shift formula (16) for *k* = 1 are applied on sphere 2 to generate an expansion form for the dimensionless series reaction rate defined by equation (9). As the surface integral of equation (9) includes an integration over *θ*2, the Legendre orthogonality property [16] reduces this expansion to the simple result

 (23)

where α and γ are given, respectively, by equations (12) and (14).

# Infinite series solution for *R*

 The twin spherical expression with Neumann iterative solution of the coefficient equations generates analytical forms for the reaction rates as a series in powers of the dimensionless inverse center-to-center distance, . Note the *B*20 of Eq. (23) for *R* is expressed in terms of the full set of coefficients {*B*1*m*} through Eq. (21), each of the *B*1*n* coefficients are given in terms of the full sets of coefficients {*B*2*m*} and {*A*2*m*} from Eq. (23), the *A*2*n* coefficients depend on the full set {*A*1*n*} in Eq. (20), and the solution for the *A*1*n* coefficients will require the use of Eq. (17). To derive the series reaction rate *R*, we will need the simultaneous solution for Eqs. (17), (20), (21) and (22) followed by the substitution into the rate equation (23). A procedure to generate the rate equation follows.

 To obtain the coefficients {*A*1*n*} the coefficient equation (20) for *A*2*n* is substituted into the coefficient equation (17) for *A*1*n*, we have

 (24)

where

 (25)

The iterative Neumann expansion of Eq. (24) in the kernels of Eq. (25) provides the coefficient *A*1*n* in the form

 (26)

where *k* is any positive integer. We note from Eq. (18) and the definition (13) that *Qmn* depends on as , but as the first term in the sum (25) vanishes, has a form times a power series in . Using this information and the Neumann expansion (26) we find that the series for contains first a negative Kronecker delta plus an infinite sum of *k* type terms each of the form times a power series in , where *k* is the full set of positive integers. To calculate *cA* from Eq. (15) with *i*=*A*, we need to sum *n* over all non negative integer values, even, zero or odd. For *n* even, *A*1*n* will be a series of even powers of , while *A*2*n* from Eqs. (18) and (20) will have only odd powers of . For an *n* of zero *A*10 will be a power series in and *A*20 vanishes. For *n* odd the *A*1*n* will have odd powers of , and *A*2*n* will have even powers.

 To derive the equations for the second set of coefficients {*B*2*n*}, we combine Eq’s. (20),(21),(22) and (25)

 , (27)

where

 (28)

and

 . (29)

The Neumann expansion of Eq. (27) in the kernels yields

 (30)

The summation expansion (28) for together with the definition (18) of *Qmn* can be combined to demonstrate that the kernel of Eq. (27) is of the form of a factor

times a power series in . The series nature of the En term in Eq. (27) for *B*2*n* is clarified, when the series form (26) of *A*1*n*/*c*0 is substituted into Eq. (29).

 . (31)

From Eq’s (18), (19), (25), and (28), the leading terms in the series (31) for *En* is a single contribution of order , then the sum skips to times a power series in . In turn, the expression (30) for *B*2*n* contains the *En* above as its first element followed by another series of the form times a power series in .

To calculate *cB* from Eq. (15) with *i=B* for *n* even or zero *B*2*n* will be a sum over odd powers of , while for *n* odd *B*2*n* must sum over even powers of . From Eq’s. (18) and (22), for even or zero *n* the coefficients *B1n* will sum only even powers of , but for the case of *n* odd *B1n* will sum odd powers of .

 The engineering parameter of interest is the dimensionless reaction rate *R* defined by Eq. (9) and given in terms of the twin spherical expansion coefficients by Eq. (23). We seek to evaluate, from the expressions (18), (19), (25), (28), (30), and (31), the case, as a series of odd powers of , including all terms up to order , i.e.,

 (32a)

where

 (32b)

 (32c)

 (32d)

 (32e)

 (32f)

 Five possible dimensionless parameters, two kinetic , one geometric radius ratio , a dimensionless center – to – center separation distance , and a diffusivity ratio are defined, respectively, by Eq’s. (10) - (19). While the coefficients of the reciprocal expansion (32b) – (32f) of *R* depend on , they do not depend explicitly on . For the steady state solution, the coefficients for *cA* from Eq’s. (17) – (20) depend on and , but not explicitly on the *D*A diffusion coefficient of reactant *A*. The matching flux condition (22) on sphere 1 equates the Fickian flux of *A* reactant onto sphere 1 with factor of *D*A to the efflux of intermediate product *B* away from sphere with factor of *D*B. Hence the concentration coefficients of *c*B, , must contain the factor . Then the Fickian flux of *B* onto sphere 2, the series reaction rate, must include the *B* diffusion coefficient *D*B times from the *B* concentration gradient. As the *R* dimensionless series reaction rate (9) is divided by *D*A, then the cancels out of *R*.

# Results and discussion

The series expansion (32a) - (32f) provides values for *R*, the steady-state production of *C* on sphere 2 from the series reaction *A*→*B*→*C* on two successive spheres, made dimensionless with the division by 4π *D*A*c*0*a*1. It is expressed in increasing odd powers of the inverse dimensionless center-to-enter sphere separation, starts with a leading term of order , skips down to and finally neglects terms of order and smaller. The C*i* coefficients (32b) - (32f) contain the effects of finite reaction rates at spheres 1 and 2 using Eq. (19) with the respective dimensionless inverse reaction rates , and their excluded volumes geometry with the radius ratio . In the limit of very fast reactions and , the C*i* coefficients reduce to the diffusion-controlled values, Eq.’s (29b) - (29f) of the earlier Reference 1.

It is interesting to note that the first term in the expansion from Eq.’s (19), (32a) and (32b) has the form

 . (33)

This monopole form of Eq. (32) can be derived directly from the physical model, Eq.’s (1) - (9), for the two reactive spheres located a large distance apart. This first term in the R series, slowly decays harmonically with separation as , the second term drops much more rapidly as and the next term decreases even faster as , etc.. Eq. (33) not only represents the analytical solution at larger , but as the leading term in an expansion of rapidly decreasing correction terms, will still dominate the *R* values even for moderate values not far from unity. It also appears for a fixed set of values for the three parameters , the asymptotic monopole *R* form (33) will be unchanged for any exchanges of the , and parameter values. Then if the first term of the *R* series dominates the sum at modest to large , the resulting *R* versus curves will coincide for any permutation of except very near a of unity. Note, for convenience in discussions and Figure curves, the notation order will be used to assign the parameters for the various cases considered.

To examine the characteristics of the *R* reaction series solution, we need to construct *R* versus plots from Eq.’s (32a) - (32f). The *R* plots generally require an accuracy of two significant figures or more from the series expansion. The expansion (32a)-(32f) of *R* in inverse powers include only positive, odd terms starting with and neglecting terms of order and smaller. For the values considered, this decrease in value of the neglected term, by a factor of more than compared to the R partial sum, along with the natural asymptotic decrease in the C*i* coefficient values for the higher order terms, provides sufficiently accurate *R* values even when the spheres are close. We find that either the last term is negligible by itself when compared to the partial *R* sum, or it is small enough that we can argue that the next term can be neglected compared to *R*. The convergence of the asymptotic series (32a)-(32f), whose coefficients depend on the parameters may vary within the three-dimensional region. Convergence difficulties in the neighborhood of a center-to-center distance of unity have been found [1] for smaller , and may also occur for larger . The inverse kinetics can be taken to be large or small without losing the convergence limit.

Consider the situation where the sphere sizes are equal, i.e. , but the finite dimensionless inverse rates, of the first reaction *A*→*B* on sphere 1 or of the second reaction *B*→*C* on sphere 2, are varied in the same fashion. We start with a base line case of moderate and inverse reaction rate values of unity, and plot the *R* curve for (1, 1, 1) versus the dimensionless center-to-center distance from 1 to 10 given as the solid curve in Figure 1.

Figure 1. The dimensionless series reaction rate *R* of Eq.’s (9) and (32a) - (32f) versus the dimensionless center-to-center distance for equal size spheres , and various values of the spherical site inverse reaction rates and in the combination . The base case for moderate reaction rates (1, 1, 1) is shown as a solid curve. The relative *R* increase when the first reaction rate *A*→*B* on sphere 1 is increased from to is given by upper dashed curve (1, 0.5, 1). When instead the second reaction rate *B*→*C* on sphere 2 is increased in a similar manner from to , the results appear as the upper dash-dot values of (1, 1, 0.5). The corresponding decrease of the first spherical site reaction rate for from 1 to 2 generates the lower dashed curve (1, 2, 1), whereas the similar decrease in the second spherical site reaction rate from 1 to 2 gives values for the lower dash-dot curve (1, 1, 2) on the Figure.

Unlike the fast kinetic, diffusion – controlled results of Reference 1, the excluded volume blocking effects of the reactive spheres are diminished at these lower rates. There is no flat region or maximum in the *R* curve near the left-hand axis, and the *R* curve (1, 1, 1) decreases monotonically from maximum of 0.12 at down to ever decreasing values at larger .

 To examine the relative influence of the first and second sphere reaction rates in equivalent geometries on the series reaction rate *R* production of product *C*, we impose from the solid base curve (1, 1, 1) for equal sphere sizes the same rate change first at sphere site 1and then at sphere 2. The rate at sphere 1 of is increased by decreasing the dimensionless inverse rate from to , all else hold constant, i.e. . The new resulting upper dashed *R* rate curve (1, 0.5, 1) lies entirely above the base curve (1, 1, 1). Note the observed increase in the series reaction rate *R* is 33% for this sphere 1 rate increase, when the reactive spheres are nearly touching, i.e., . If instead, the second reaction rate at sphere 2 of is increased in the same manner by reducing the inverse rate of the base curve (1, 1, 1) to , all else held equal, i.e. , , the resulting upper dash – dot *R* rate curve (1, 1, 0.5) in Figure 1 lies above the (1, 1, 1) base curve, but below (1,0.5, 1). The series reaction rate *R* increase is 30% for the equivalent sphere 2 rate change, when the reactive spheres are touching at . For spheres in close proximity increasing the first rate reaction has a greater impact in the series reaction rate than increasing the second. But for larger , e.g. , there is little difference in the two curves (1,0.5, 1) and (1,1, 0.5). This is a case of the insensitivity of the series reaction rate *R* to an interchange in the parameter set discussed in the second paragraph of this section.

 The corresponding decrease in the rate on sphere 1 from the base solid curve (1, 1, 1) is generated by the increase of the dimensionless inverse sphere site kinetics value from to with and . The (1, 2, 1) curve is displayed in Figure 1 as the lower dashed curve, lies entirely below the solid (1, 1, 1) base curve, and the dimensionless series reaction *R* rate has a drop of 33% at . If instead, the same decrease in the rate on sphere 2 from the base case (1, 1, 1) is applied from to with fixed and , the lower dashed – dot *R* curve (1, 1, 2) lies below the base (1, 1, 1) curve, but above the (1, 2, 1) dashed curve with a drop of 32% at . For reactive spheres close by the somewhat larger drop in the *R* series reaction rate value with a change (1,2,1) in the first reaction rate at sphere 1, compared to the equivalent change (1,1,2) in the second reaction rate at sphere site 2 implies, as above, the overall series reaction rate is more impacted by the first reaction the at sphere 1. However, for , the two curves (1,2,1) and (1,1,2) are indistinguishable and the overall series reaction rate is insensitive to the order of the sphere site dimensionless inverse reaction rates.

Figure 2. The dimensionless series reaction rate *R* of Eq’s (32a) – (32f) versus the dimensionless sphere center – to – center distance . The effects of sphere size are simulated for equal molecular sphere kinetics of the two spheres surface reactions. The surface kinetics parameters are set equal with the resulting equality . The value of the first sphere inverse kinetics is set, and the radius ratio is varied. For faster kinetics, the upper two curves in the Figure, and , and for the slower kinetics, the lower curves and . The upper solid curve combination is (1, 0.5, 0.5) and various other curve designations are shown in the Figure legend.

To simulate the impact of sphere size geometry for equivalent molecular kinetics at the two reactive sphere surfaces, the reactive sphere radius ratio is varied for the case of identical molecular kinetics parameters on the two spheres, i.e., . Then, for this discussion of equivalent sphere surface kinetics in Figure 2, we have from Equations (10), (11), and (12).

 (34)

Consider the selection of a faster reaction with equal size spheres, . With Equation (34) for , the dimensionless series reaction rate *R* from Equations (32a) – (32f) is plotted versus the dimensionless center – to – center distance as the upper solid curve (1, 0.5, 0.5) in Figure 2, and decreases monotonically with from a maximum 0.21 at . To examine the effect of sphere size, the first sphere dimensionless kinetics is held fixed at , but the radius of the second sphere *a*2 is cut in half. By Equations (12) and (34), this results in the selection of parameters (2, 0.5, 1), with the series reaction rate curve given as the dashed curve in Figure 2. The series reaction rate *R* is decreased both by a relative reduction of the sphere size of the second sphere [ is larger], as well as an effective decrease in the reaction rate at sphere 2 [ the dimensionless inverse kinetics rate of on sphere 2 is increased] with a drop in *R* of 47% when .

 A slower surface rate reaction at the first sphere of provides some additional insight. For equal size spheres from Equations (12) and (34), we have the parameters (1, 2, 2) and with equations (32a) – (32f) the results are plotted in Figure 2 as the lower solid curve monotonically decreasing from the maximum 0.056 at . Doubling the size of the second sphere reduces both the value and the inverse kinetics, i.e., the second sphere is larger, , with an effectively faster rate of , . This selection generates the dash dot curve (0.5, 2, 1) in Figure 2, which lies entirely above the solid curve (1, 2, 2) with an increase of *R* at of 93%. If instead, the radius *a*2 of the second sphere is cut in half with equal molecular kinetics on the two spheres and , the resulting parameter selection (2, 2, 4) generates the lowest dotted curve in Figure 2. This smaller sphere 2 curve lies entirely below the base curve (1, 2, 2) with a decrease of *R* of 58% at . In general, from the curves in Figure 2, it seems this doubling the sphere 2 size with identical molecular kinetics parameters on the two spheres roughly doubles the dimensionless series reaction rate *R*. The rate *R* curves (0.5, 2, 1) and (2, 2, 4) give an instance where the molecular kinetic parameters on the spheres 1 and 2 are identical with fixed, but sphere 2 has two times the radius of sphere 1 with a higher *R*, or sphere 2 has one-half the radius of sphere 1with a lower *R* curve.

 The faster molecular surface reaction rate on sphere 1, curves, (1, 0.5, 0.5), (2, 0.5, 1) in Figure 2 lie entirely above those of the lower molecular sphere 1 surface rate, curves, (0.5, 2, 1), (1, 2, 2), (2, 2, 4). The lowest of curves (2, 0.5, 1) and the highest of the curves (0.5, 2, 1) are coincident for in Figure 2. This is another example of the invariance of *R* for moderate to larger to a permutation in its parameters , already discussed in the second paragraph of this section. Unlike the case in Figure 1 where the interchange of the dimensionless inverse kinetics and occur, this permutation in Figure 2 involves the sphere size radius ratio γ and . When the spheres are very close and is nearly unity, the curve (2, 0.5, 1) with the larger and lower lies slightly above (3.7%) the (0.5, 2, 1) curve. The faster rate of sphere 1 offsets the larger , smaller size of sphere 2.

Figure 3. The dimensionless series reaction rate *R* of Equations (32a) – (32f) is plotted against the dimensionless center – to – center distance . The second reaction at sphere 2 is assumed to be very fast, , so that the rate is controlled by the first reaction rate and the geometry. The values of the dimensionless inverse kinetics of the first reaction at sphere 1 are and the sphere radius ratios are . There is always a solid curve for , a dashed curve for and a dash – dot curve for . Then for each curve type, i.e. solid, dashed or dash – dot, the upper case is for the fastest kinetics , the mid curve gives and the lower represent the slowest kinetics , as provided in the legend .

 Other interesting examples of the *R* solutions from Equations (32a) – (32f) occur when one of the sphere site reactions is very fast, and the series reaction rate is controlled by the other slower reaction or the geometrical radius ratio. Figure 3 examines some instances where the second reaction at sphere 2 is diffusion-controlled, i.e., , the size parameters are selected to be and the dimensionless inverse kinetics of the first reaction of at sphere 1 are . The upper dashed (1, 0.5, 0), mid dashed (1, 1, 0) and lower dashed (1, 2, 0) curves in Figure 3 provide the series reaction rates for the rate of reaction control by the first reaction of , when the two spheres are the same size, γ = 1. Of course, the solid curves for (0.5, 0.5, 0), (0.5, 1, 0) and (0.5, 2, 0) must lie, respectively, above their counterparts, whereas the cases (2, 0.5, 0), (2,1,0) and (2, 2, 0) must lie below. The possible combinations of provide a matrix, where the three diagonal entries curves in Figure 3 will not overlap, but the other six off – diagonals will generate three pairs of curves. Each pair represents an interchange for , hence they overlap for .

 The left – hand axis intercepts for the diagonal entry curves (0.5, 0.5, 0), (1, 1, 0) and (2, 2, 0) in Figure 3 are, respectively, 0.39, 0.22, and 0.096. Each of the three pairs will overlap for , but separate near the left – hand axis, where the spheres are in close proximity. For each of the three off – diagonal curve pairs, (1, 0.5, 0) – (0.5, 1, 0), (2, 0.5, 0) – (0.5, 2, 0) and (2, 1, 0) – (1, 2, 0), the second entry with the smaller (larger *a*2) gives the larger *R* intercept at . This is true even though the dimensionless inverse rate on sphere 1 is larger (the reaction on sphere 1 is significantly slower) in each of these cases. For the pair of curves (1, 0.5, 0) – (0.5, 1, 0), the intercept of the first curve has a value 0.29 with the second 3.6% larger, for the pair of curves (2, 0.5, 0) – (0.5, 2, 0) the first has an intercept 0.19 with the second 8.2% above it, and for the pair (2, 1, 0) – (1, 2, 0) the first has an intercept 0.14 with the second 4.5% larger. Because in Figure 3 the second reaction occurs at an infinite rate on sphere 2, the *R* intercept is more sensitive to an increase in *a*2 (decrease in ), than an increase in the rate at sphere 1 (decrease in ). Note that this is in contrast to the overlapping pair in Figure 2 where the (2, 0.5, 1) intercept is higher than (0.5, 2, 1). Due to the slower rate of on sphere 2, *R* is less sensitive to the *a*2 value and , and the smaller , faster spherical site 1 reaction, is favored over the smaller .

Figure 4. The dimensionless series reaction rate *R* of Equations (32a) – (32f) is plotted against the dimensionless center – to – center distance . The first reaction at sphere 1 is assumed to be very fast, , so that the rate is controlled by the second reaction rate and the geometry. The values of the dimensionless inverse kinetics of the second reaction at sphere 2 are and 0.2, and the sphere radius ratios are . There is always a solid curve for , a dashed curve for and a dash dot curve for . Then for each curve type, the upper case is a faster kinetics and the lower represents , as provided in Figure 4 legend .

 Also note for any given in Figure 3, e.g., , as the inverse kinetics value decreases from 2 through 1, down to 0.5, an inflection point develops in *R* versus curves. This is a precursor behavior to set up the maximum *R* values that have been found in Reference 1 for the limit at the various values.

 The situation where the first reaction at spherical site 1 is very fast and diffusion-controlled, i.e., , with either the second reaction of finite dimensionless inverse rate at spherical site 2, or geometry based radius ratio control, is shown in Figure 4. The solid, dashed and dash – dot curves represent the radius ratio values, respectively, of . For the slower reaction curves of , i.e. the lower three curves in Figure 4, no inflection is found for and , while a small amount is seen for the solid curve (0.5, 0, 0.5). To generate an enhanced picture of the inflection point development, a somewhat faster reaction rate is included in Figure 4. These three upper curves, (0.5, 0, 0.2), (1, 0, 0.2), (2, 0, 0.2) already for give a small inflection near the left – hand axis intercept. The inflection increases with up to a nearly maximum, horizontal, flat R intercept for the curve.

 A comparison of the *R* curves in Figure 4, where the first reaction rate for on spherical site 1 is very fast () with a limiting finite rate for at spherical site 2, to those of Figure 3 where the second reaction rate for on sphere 2 is diffusion – controlled with an equivalent limiting finite rate for on sphere 1 gives additional information about the role of the individual site reaction rates and radius ratios on the overall series reaction rates. The three curves, (0.5, 0, 0.5), (1, 0, 0.5), and (2, 0, 0.5) from Figure 4, respectively, will each coincide with the three curves, (0.5, 0.5, 0), (1, 0.5, 0), (2, 0.5, 0) from Figure 3 for sphere separations . However, for small sphere separations the Figure 4 curves will lie above the corresponding curve in Figure 3 with intercepts, respectively, 0.9%, 6.4% and 12% larger. It appears for spheres in close proximity that the fast reaction at spherical site 1 produces a greater series reaction rate *R*, than the fast reaction at spherical site 2 for equal dimensionless inverse reaction rate at the opposite site and any equivalent radius ratio. This is consistent with the conclusions from Figure 1. Of course, all three curves (1, 0, 0.5), (0.5, 1, 0), (1, 0.5, 0), the first from Figure 4 and the second and third from Figure 3 will coincide for , but near the associated *R* values will be stacked first case greater than second and second greater than third. Similarly, the three curves (2, 0, 0.5), (0.5, 2, 0), (2, 0.5, 0) will coincide, but near will exhibit the same stacking order.

 The twin spherical expansion method with Neumann iterative solution of the coefficient equations has been used to generate a rigorous analytical rate equation for the series reaction , where occurs on a first spherical site 1 of radius *a*1, and takes place on a second sphere 2 of radius *a*2, a center – to – center distance *d* from sphere1. The inclusion of finite first order surface reaction rate coefficients *k*A and *k*B, respectively, at spheres 1 and 2, and the diffusivities *DA* for the reactive species *A* and *DB* for the intermediate *B*, permits the formulation of certain physical chemical questions about the dimensionless reaction rate *R* in terms of the dimensionless inverse reaction rates , the geometrical radius ratio for various dimensionless center – to – center distances .

 Except when the spheres are in relatively close proximity, the series reaction rate solution *R* is heavily influenced by the first term from the inverse sphere separation expansion series (32a) – (32f). Furthermore, this first term is invariant to any interchange of the parameter set . Any interchanged set of these parameters will generate reaction rate curves (*R* versus ) that coincide for moderate to large values, .

 For equal sized spheres, increasing just the dimensionless reaction rate on site 1 or just on site 2, each by same amount, as seen in Figure 1, will result in the same increase in the overall dimensionless series reaction rate *R* so long as . If the spheres are in close proximity, then the rate increase at site 1 has a stronger impact. The same is true for an equivalent decrease in kinetics at sites 1 or 2. Figure 2 gives results on the effects of sphere size changes for fixed surface kinetics. Comparing (2, 0.5, 1) to (1, 0.5, 0.5); (2, 2, 4) to (1, 2, 2); and (1, 2, 2) to (0.5, 2, 1), we find that doubling the sphere 2 radius a2 for equivalent sphere surface kinetics and fixed roughly doubles the series reaction rate *R*. On the other hand, comparing the curves (2, 0.5, 1) and (0.5, 2, 1) in Figure 2 for a fixed site 2 kinetics , the interchange of values provides overlapping *R* curves for . For nearby spheres, the series reaction rates do favor the first mentioned curve with smaller (faster site 1 kinetics) even though is larger (*a*2 is smaller at site 2). For the dimensionless series reaction rate versus dimensionless center – to – center sphere separation in Figure 3, site 2 is diffusion controlled, , and the series rate is controlled by site 1 kinetics and geometry radius ratio . Of the three cases in Figure 3, where the curves coincide for , the behavior of each is similar enough that only the pair (2, 0.5, 0) and (0 .5, 2, 0) need be discussed. When the spheres are close by, these curves separate and the series reaction rates do favor the second mentioned curve. In direct contrast to the (2, 0.5, 1) - (0 .5, 2, 1) pair discussed in Figure 2 above, the second mentioned curve with smaller (*a*2 larger at site 2) has the faster series rate, even though (the site 1 is slower). The reason why the size of site 2 dominates over the site 1 rate kinetics in Figure 3 is , the much faster reaction at site 2 means sphere 2 site size overrides the slower kinetics at sphere site 1. In Figure 4 where site 1 is diffusion controlled, the diffusion controlled reaction at site 1 always gives the better series rate than diffusion control of the second reaction at site 2, hence, respectively, (0.5, 0, 0.5), (1, 0, 0.5), (2, 0, 0.5) of Figure 4 will lie on or above (0 .5, 0.5, 0), (1, 0.5, 0), (2, 0.5, 0) of Figure 3. For those cases in Figures 3 and 4, where one of the sites is diffusion-controlled, and the alternate sphere site becomes faster, inflection points appear as a precursor to the *R* maximum series reaction rates found in Reference 1.

# Application

 In the absence of site 1- site 1 and site 2 – site 2 competition [8], this model applies to results dilute in site 1 and site 2, nevertheless reaction kinetics insight is available. Consider the reforming reaction [17][18], the isomerization of n-pentane over Pt/Al2O3 catalyst. The accepted mechanism [18] includes adsorption of the n-paraffin on the Pt crystallite site [19], followed by dehydrogenation into a n-olefin, and subsequent desorption; diffusion to an acid site on an Alumina ultimate particle [20] of the support; adsorption of the n-pentene on the site, skeletal rearrangement to isopentene, and desorption; diffusion to a Pt crystallite; adsorption, hydrogenation, and desorption. Hosten and Froment [18] have found that adsorption on the Al2O3 acid site is the slow, rate determining step, and the other steps are presumed to be very rapid.

 In a smaller Pt/Al2O3 catalyst pellet, the first reaction of dehydrogenation can be assumed to be in uniform equilibrium. The A of our model is the olefin, n-pentene. The isomerization reaction has been already treated as irreversible [17] with the reverse reaction neglected because the concentration of the isopentene product is small. The diffusion of B, the isopentene intermediate, and the rapid adsorption, hydrogenation and desorption can be included in the model with the vanishingly small . Typical values of a1, the Alumina ultimate particle radius, and a2, the Pt crystallite radius, suggested respectively in [20] and [19], are a1 = 100 Aº and a2 = 50 Aº with a value from Eq. (12) of 2. Hosten and Froment [18] have measured the uniform kinetic rate constant kA for the n-pentene isomerization on the Alumina sphere 1 as 0.0431 m/hr at 425 ºC and an Alumina Chlorine content of 0.0242 mol%. Their stated surface area and catalyst density suggest a pore size of 172 Aº, and from this a transition diffusivity DA of 0.00473 x 10-4 m2/s has been estimated. With the ultimate Alumina solid particle radius a1 of 100 Aº, the dimensionless inverse kinetic value form Eq. (10) is 3.95 x 106.

 The reaction rate for the Alumina spherical particle 1 in the isolated sphere case, where the reactive spheres 1 and sphere 2 are completely separated, is the well-known Smoluchhowski result . To remove dimensions for convenience in Eq. (9), we have divided the rate by , so the first term in the dimensionless series reaction rate R is , and the second, Q, is the rate site structure factor

 (34)

Q is always less than unity. Q represents the reduction in R from the Smoluchowski rate because of blockage by the Pt crystallite of n-pentene approaching the reactive Alumina particle, which is particularly important when the reactive spheres of Alumina and Pt are in contact. Q also includes the effect that, while some isopentene will be drawn to the sphere 2, Pt crystallite by its shape and reaction, some intermediate will escape.

Figure 5. The site structure factor versus the dimensionless center-to-center distance . The R is obtained from Eq.’s (32a)-(32f) and is defined by Eq. (10). The curve is drawn for the parameter set (2, 3.95 x 106, 0), which characterizes the conditions from Ref. [18] for the hydroforming isomerization of n-pentane to isopentane on an Alumina/Platinum dispersion catalyst at 425 ºC. Material characteristic radius values for the Alumina ultimate particles and Platinum crystallite are suggested by Ref.’s [20] and [19].

 In figure 5, the value of the site structure factor Q is shown versus the dimensionless center-to-center separation distance for the n-pentane isomerization reaction to isopentane on a Pt/ Al2O3 catalyst for the case (2, 3.95 x 106, 0). The first term in Eq. (34) for R, the Smoluchowski reaction rate is rather small, 2.53 x 10-7, due to the very slow rate of adsorption of the n-pentene on the Alumina ultimate particle surface. The initial value of Q at is 0.292 due to the Alumina particle – Pt crystallite excluded volume effects mentioned above when the Pt dispersion crystallite lies on the surface of the active Alumina, excluded volume plays a significant role, and reduces the reaction rate by 70.8 %. This Pt crystallite placement on the Alumina support surface is a common one. If we note that the maximum possible production rate of isopentene from the Aumina ultimate particle is given by the Smoluchowski reaction rate, then the single Platinum crystallite on this Alumina particles’ surface can hydrogenate 29.2% of this product.

 In figure 5, the site structure factor Q drops significantly with increasing center-to-center separation. For example the value of Q at is 0.030, a 90 % reduction from the Q value of 0.292 at . In the case, a Smoluchowski generation rate actually occurs at the Alumina ultimate particle surface for the inverse kinetics , but only 3 out of 100 isopentene olefins emitted from the Alumina particle will be hydrogenated at the Pt crystallite located at , i.e., mμ. While we have considered only the dilute site case, these results suggest that hydrogenation closer to the Alumina source seems more likely.

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**References**

[1] W. Strieder, S. Saddawi, Series reactions A → B → C on successive spheres, Chem. Phys. 473 (2016). doi:10.1016/j.chemphys.2016.04.011.

[2] P.A. Srere, Complexes of Sequential Metabolic Enzymes, Annu. Rev. Biochem. 56 (1987) 89–124. doi:10.1146/annurev.bi.56.070187.000513.

[3] C. Eun, P.M. Kekenes-Huskey, V.T. Metzger, J.A. McCammon, A model study of sequential enzyme reactions and electrostatic channeling, J. Chem. Phys. 140 (2014) 105101. doi:10.1063/1.4867286.

[4] J.E. Bailey, D.F. Ollis, Biochemical Engineering Fundamentals, 1st ed., McGraw-Hill, New York, 1988.

[5] N. McDonald, W. Strieder, Diffusion and reaction for a spherical source and sink, J. Chem. Phys. 118 (2003) 4598–4605. doi:10.1063/1.1543937.

[6] P.B. Weisz, Diffusion and Chemical Transformation: An interdisciplinary excursion, Science (80-. ). 179 (1973) 433–440. doi:10.1126/science.179.4072.433.

[7] B.C. Gates, Catalytic chemistry, Wiley, 1992.

[8] N. McDonald, W. Strieder, Competitive interaction between two different spherical sinks, J. Chem. Phys. 121 (2004) 7966. doi:10.1063/1.1797051.

[9] G. Zoia, W. Strieder, Competitive diffusion into two sinks with a finite surface reaction coefficient, J. Chem. Phys. 108 (1998) 3114–3118. doi:10.1063/1.475708.

[10] W. Strieder, S. Saddawi, Alternative solution for diffusion to two spheres with first-order surface reaction, J. Chem. Phys. 113 (2000) 10818. doi:10.1063/1.1323730.

[11] E.W. Hobson, The Theory of Spherical and Ellipsoidal Harmonics, Cambridge University Press, Cambridge, 1931.

[12] S.D. Traytak, On the time-dependent diffusive interaction between stationary sinks, Chem. Phys. Lett. 453 (2008) 212–216. doi:10.1016/J.CPLETT.2008.01.066.

[13] H.-K. Tsao, Diffusion into a pair of reactive spheres with first-order reaction, J. Chem. Phys. 114 (2001) 10247–10251. doi:10.1063/1.1375138.

[14] S.D. Traytak, The diffusive interaction in diffusion-limited reactions: the steady-state case, Chem. Phys. Lett. 197 (1992) 247–254. doi:10.1016/0009-2614(92)85763-Z.

[15] H.-K. Tsao, Competitive diffusion into two reactive spheres of different reactivity and size, Phys. Rev. E. 66 (2002) 011108. doi:https://doi.org/10.1103/PhysRevE.66.011108.

[16] M. Abramowitz, I.A. Stegun, Handbook of mathematical functions with formulas, graphs, and mathematical tables, U.S. Department of Commerce, National Bureau of Standards, 1964.

[17] J.H. Sinfelt, H. Hurwitz, J.C. Rohrer, Kinetics Of n-Pentene Isomerization Over Pt-Al2O3 Catalyst, J. Phys. Chem. 64 (1960) 892–894. doi:10.1021/j100836a017.

[18] L.H. Hosten, G.F. Froment, Isomerization on n-Pentane, Ind. Eng. Chem. Process Des. Dev. 10 (1971) 280–287. doi:10.1021/i260038a023.

[19] R.L. Moss, The Structure of Supported Platinum Catalysts, Platin. Met. Rev. 11 (1967) 141–145.

[20] M.F.L. Johnson, J. Mooi, The origin and types of pores in some alumina catalysts, J. Catal. 10 (1968) 342–354. doi:10.1016/0021-9517(68)90149-8.