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## Research paper

## Kinetics of the formation of core–shell structures under transient external conditions

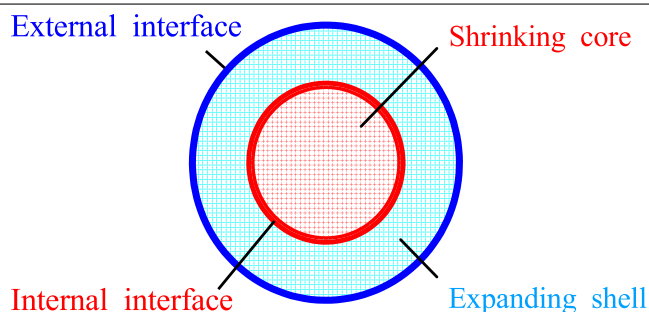
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## HIGHLIGHTS

- The focus is on absorption of molecules by particles.
- The process is described using the core–shell model.
- Concentration of molecules outside is considered to increase.
- The kinetically and diffusion-limited regimes are treated.
- The specifics of the corresponding kinetics are shown.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

The kinetics of absorption of molecules by particles are analyzed using the core–shell model provided the concentration of molecules outside increases continuously from zero up to fixed value. In the kinetically limited case, the dependence of the uptake on time is found to be of the  $S$  shape. In the diffusion-limited case, the uptake is proportional to  $t^{1/2}$  in the beginning and then exhibits slowdown. These features are qualitatively different compared to those predicted by the conventional model implying the concentration of molecules outside to be constant.

## 1. Introduction

Solid and soft-matter particles with the core–shell structure (Fig. 1) often occur in nature. In theoretical studies, this structure is also often implied to be a reasonable approximation in the context of real particles of more complex shapes (e.g., Wulff crystallites). From these perspectives, the core–shell structure is generic in various branches of natural sciences. More specifically, this structure is often accepted as one the key elements of the kinetic models describing various processes occurring in real particles on the length scales from a few nm to a few cm. In physics, good examples are oxidation of and hydride formation in metal particles. In fact, the kinetic core–shell model proposed by Valensi [1] and Carter [2] for diffusion-limited oxidation of metal particles was historically one of the first models of this category. For

more recent models aimed at oxidation and hydride formation, one can, respectively, see e.g. articles [3–6], references therein, and subsequent studies. Nowadays, the interest to these processes is renewed in relation with the rapid development of nanoscience and new directions in the energetics (e.g., storage of hydrogen [5]). In chemistry, the kinetic core–shell model is widely used to describe chemical conversion of particles [7]. One example is coke removal from catalytic porous pellets [8]. In the currently important environmental context [9], this model may be relevant in the case of  $\text{CO}_2$  absorption by solid-state particles. In medical applications, the core–shell model is widely employed to describe the drug release from pellets [10] and can potentially be applied to soft-matter nanocarriers of drugs [11].

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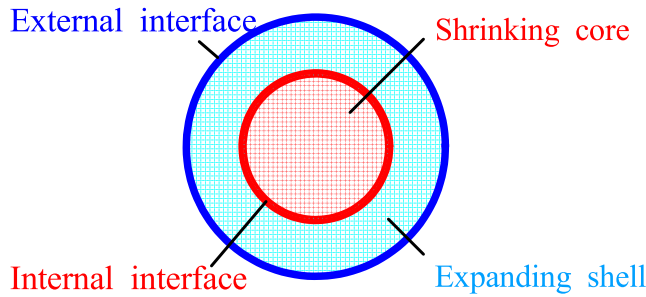


Fig. 1. Core-shell structure.

Referring to the core-shell structure (Fig. 1) in the context of kinetic processes, one usually implies that the core represents the original material whereas the shell is associated with the newly formed material. Geometrically, the core-shell structure is characterized by the radii,  $r_1$  and  $r_2$ , of the internal interface (between the core and shell) and external interface (between the shell and surrounding medium), respectively. The reaction is assumed to occur at the internal interface, i.e., at  $r = r_1$ , and accordingly  $r_1$  decreases with increasing time. At the level of the balance relations, the conversion fraction is given by

$$f = 1 - r_1^3/r_o^3, \quad (1)$$

where  $r_o$  is the initial particle radius. In turn,  $r_1$  and  $r_2$  are expressed via  $f$  as

$$r_1 = r_o(1 - f)^{1/3}, \quad (2)$$

and

$$r_2 = r_o(1 - f + \alpha f)^{1/3}. \quad (3)$$

The reaction kinetics are usually represented in terms of the dependence of  $f$  on time.

The reaction itself implies the reactant transport from or to a particle or, in other words, the presence of reactant outside a particle. In the case of release of molecules from particles, their presence outside can often be neglected. In the case of absorption of molecules by particles, the conversion rate is determined by the concentration of molecules located outside, and accordingly their presence outside is mandatory. In the available kinetic core-shell models aimed at absorption of molecules by particles (see e.g. the references above), this concentration is customarily considered to be constant. In recent applications, this is often not the case. For example, CO<sub>2</sub> absorption by particles can be studied in a fixed bed reactor by observing the propagation of the CO<sub>2</sub>-concentration front [12]. In such experiments, the CO<sub>2</sub> concentration around each particle increases from zero up to some fixed level.

This theoretical study is focused on the situations of the latter category, i.e., the conversion of particles is considered to occur at the internal (core-shell) interface with the reactant supply from the gas or liquid phase to the external interface and subsequent diffusion in the shell towards the former interface. The details of the corresponding treatment depend on whether the conversion is kinetically limited by reaction at the internal interface (Section 2) or limited by reactant diffusion in the shell (Section 3). In both cases, the treatment starts from the conventional equations describing the situations with time-independent reactant concentration outside particles. Then, the treatment is extended to the situations with transient increase of this concentration from zero to fixed value. The whole process is assumed to occur at fixed temperature. The situations with time-dependent temperature are briefly discussed as well (Section 4).

## 2. Kinetically limited regime

In the kinetically limited case, the reactant diffusion in the shell is rapid so that the gradients of the reactant concentration are there considered to be negligible. Physically, this means that there is equilibrium of the reactant inside the shell and outside in the gas or liquid phase. In other words, this means that the internal reactant concentration,  $c$ , is a function of the external concentration,  $\tilde{c}$ . Under such conditions, the radial coordinate of the internal interface is reduced as

$$dr_1/dt = -\kappa, \quad (4)$$

where  $\kappa$  is the corresponding rate (it depends on  $c$  which in turn depends on  $\tilde{c}$ ). In terms of the reaction kinetics, this rate is represented as  $\kappa = wv$ , where  $w$  is the reaction rate per unit area of the internal interface (it depends on  $c$  and can be represented as a function of  $\tilde{c}$ ), and  $v$  is the decrease of the core volume per an elementary reaction act.

In the conventional case,  $\tilde{c}$ ,  $c$ , and  $\kappa$  are constant, and Eq. (4) yields

$$r_1 = r_o - \kappa t, \quad (5)$$

where  $r_o$  is the initial particle radius [as in (1) and (2)]. The conversion kinetics is then determined by substituting (5) into (1),

$$f = 1 - (1 - \kappa t)^3. \quad (6)$$

If  $\tilde{c}$  depends on time,  $c$  and  $\kappa$  depend on time as well, and Eq. (5) can be generalized as

$$r_1 = r_o - \int_0^t \kappa(t') dt'. \quad (7)$$

Below, I use this equation and focus on the transient dependence of  $\tilde{c}$ ,  $c$  and  $\kappa$  on time or, more specifically, on the situations with increase of these parameters from zero to  $\tilde{c}_*$ ,  $c_*$  and  $\kappa_*$ , respectively. In fact, Eq. (7) depends only on  $\kappa(t)$ . The shape of the dependence of this parameter on time can be slightly different, and partly it is determined by the dependence of  $\kappa$  on  $c$  and the dependence of  $c$  on  $\tilde{c}$ .

To keep the treatment general, I use the phenomenological relaxation equation in order to describe the dependence of  $\kappa$  on time,

$$d\kappa(t)/dt = [\kappa_* - \kappa(t)]/\tau, \quad \text{or} \quad (8)$$

$$\kappa(t) = \kappa_*[1 - \exp(-t/\tau)], \quad (9)$$

where  $\tau$  is the timescale characterizing the transition regime. The advantage of Eqs. (8) and (9) is in their applicability to a wide class of the transient kinetics without the specification of the details of the dependence of  $\kappa$  on  $\tilde{c}$ .

Substituting (9) into (7) yields

$$r_1 = r_o - \kappa_*(t + \tau[\exp(-t/\tau) - 1]). \quad (10)$$

Using then this expression in (1) results in

$$f = 1 - \left\{ 1 - A \left[ \frac{t}{\tau} + \exp\left(-\frac{t}{\tau}\right) - 1 \right] \right\}^3, \quad (11)$$

where

$$A = \kappa_*\tau/r_o. \quad (12)$$

If  $A \ll 1$ , Eq. (11) indicates that  $f$  becomes appreciable provided  $t/\tau \gg 1$ . In this case of rapid transition period,  $\exp(-t/\tau) - 1$  can in the square parentheses of (11) be neglected, and (11) is reduced to (6) (with  $\kappa = \kappa_*$ ). In the alternative situations with  $A \gg 1$ ,  $f$  becomes appreciable already at  $t/\tau \ll 1$ . In the latter case, the transition period is relatively slow, the expression in the square parentheses of (11) can be expanded as  $[\dots] \simeq t^2/2\tau^2$ , and (11) is reduced to

$$f = 1 - (1 - At^2/2\tau^2)^3. \quad (13)$$

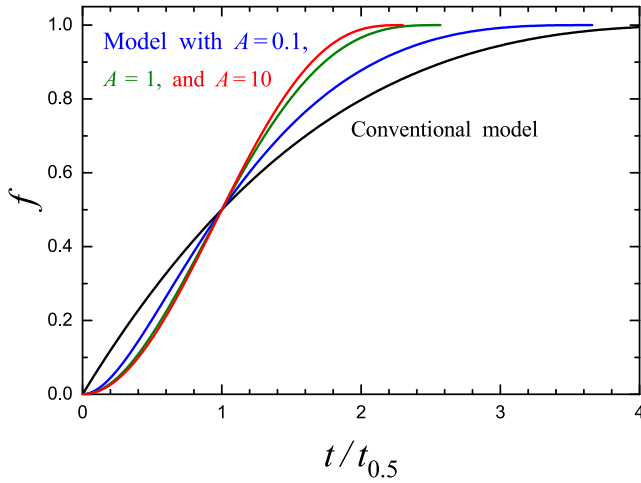


Fig. 2. Kinetically limited conversion of spherical particles to the new phase as a function of the normalized time in the core-shell model in the conventional case with fixed conditions outside [Eq. (6)] and under transient conditions [Eq. (11)] with  $A = 0.1$ , 1 and 10).

To illustrate graphically the shape of the kinetics predicted by Eq. (11) at different values of  $A$ , it is instructive to use dimensionless normalized time. One of the options is to show the kinetics as a function of  $t/\tau$ . In this case, the duration of the kinetics calculated at different  $A$  will, however, be rather different, and the specifics of the kinetics with short duration will be poorly visible. From this perspective, a more convenient way is to exhibit the kinetics as a function of  $t/t_{0.5}$ , where  $t_{0.5}$  is the time needed to reach  $f = 0.5$  (this time depends on  $A$ ). The corresponding kinetics are exhibited in Fig. 2. In the conventional case [Eq. (6)], the conversion first grows linearly and then the growth is slowed down because the area of the internal interface decreases with increasing time and accordingly the reaction rate decreases as well. Under transient conditions [Eq. (11)], the shape of the dependence of the conversion on time is of the  $S$  type with the initial phase with  $f \propto t^2$  [Eq. (13)], and this effect increases with increasing  $A$ .

### 3. Diffusion-limited regime

If the conversion is limited by diffusion of reactant in the shell, its distribution is there not homogeneous and should be specified. The shell itself can, however, be often considered to be homogeneous. Under such conditions, the reactant transport can be described by using the conventional diffusion equation. In addition, one can take into account that the timescale of evolution of the reactant distribution is relatively short, and accordingly the diffusion equation can be solved in the steady-state approximation as

$$c = c_o \left(1 - \frac{r_1}{r}\right) / \left(1 - \frac{r_1}{r_2}\right), \quad (14)$$

where  $r$  is the radial coordinate, and  $c_o$  is the reactant concentration in the shell near the external boundary (it depends on  $\tilde{c}$ ). This expression implies that  $c$  vanishes near the internal interface because at this interface the reaction is rapid. In this diffusion-limited regime, the reaction rate can be identified with the reactant diffusion flux towards the internal interface, i.e.,

$$W = 4\pi r^2 D \frac{\partial c}{\partial r} = 4\pi c_o D r_1 / \left(1 - \frac{r_1}{r_2}\right), \quad (15)$$

where  $D$  is the diffusion coefficient. On the other hand, the reaction rate can be expressed in terms of the radial coordinate of the internal interface,

$$W = -\frac{4\pi r_1^2}{v} \frac{dr_1}{dt}. \quad (16)$$

Using (2), the latter expression can be rewritten in terms of  $f$  as

$$W = \frac{4\pi r_o^3}{3v} \frac{df}{dt}. \quad (17)$$

Equating the rates given by (15) and (17) yields

$$\frac{r_o^3}{3} \left(\frac{1}{r_1} - \frac{1}{r_2}\right) df = v D c_o dt. \quad (18)$$

In this equation,  $r_1$  and  $r_2$  depend on  $f$  according to (2) and (3). With this specification, it can be integrated as

$$\frac{\alpha - (\alpha - 1)(1 - f)^{2/3} - (1 - f + \alpha f)^{2/3}}{2(\alpha - 1)} = \frac{v D}{r_o^2} \int_0^t c_o(t') dt'. \quad (19)$$

The latter equation determines the conversion kinetics for arbitrary dependence of  $c_o$  on time.

In the conventional Valensi–Carter case [1,2],  $\tilde{c}$  and  $c_o$  are independent of time, and Eq. (19) results in

$$\frac{\alpha - (\alpha - 1)(1 - f)^{2/3} - (1 - f + \alpha f)^{2/3}}{2(\alpha - 1)} = \frac{v D c_o}{r_o^2} t. \quad (20)$$

If  $f \ll 1$ , the left-hand part of this equation is proportional to  $f^2$ , and accordingly  $f \propto t^{1/2}$ .

If  $\tilde{c}$  and  $c_o$  depend on time, or, more specifically,  $c_o$  increases from zero up to  $c_*$ , the latter dependence can phenomenologically be described by analogy with (9) as

$$c_o(t) = c_* [1 - \exp(-t/\tau)]. \quad (21)$$

Substituting this expression into (19) yields

$$\frac{\alpha - (\alpha - 1)(1 - f)^{2/3} - (1 - f + \alpha f)^{2/3}}{2(\alpha - 1)} = B \left[ \frac{t}{\tau} + \exp\left(-\frac{t}{\tau}\right) - 1 \right], \quad (22)$$

where

$$B = \tau v D c_* / r_o^2. \quad (23)$$

Expression (22) is reduced to (20) provided  $B \ll 1$  because in this case the conversion takes place primarily at  $t/\tau \gg 1$ . Alternatively (with  $B \gg 1$  and  $t/\tau \ll 1$ ), (22) is reduced to

$$\frac{\alpha - (\alpha - 1)(1 - f)^{2/3} - (1 - f + \alpha f)^{2/3}}{2(\alpha - 1)} = B t^2 / 2\tau^2. \quad (24)$$

As already noticed, the left-hand part of this equation is proportional to  $f^2$  provided  $f \ll 1$ . In this limit, the latter equation yields  $f \propto t$ .

### 4. Conclusion

I have scrutinized the kinetics of absorption of molecules by solid and soft-matter particles in the framework of the core-shell model (Fig. 1). The attention has been focused on the situations when the concentration of molecules outside particles increases continuously from zero to up to fixed value in the fashion described by the phenomenological relaxation equation [Eqs. (8) and (9) or (21)]. The analysis has been performed for the kinetically and diffusion-limited regimes. In both cases, the kinetics predicted under transient external conditions are qualitatively different compared to the conventional kinetics calculated provided the concentration of molecules outside particles is constant. In the kinetically limited case, the conventional kinetics exhibit a linear increase of the conversion fraction with subsequent slowdown, whereas under transient external conditions the dependence of the conversion on time is predicted to be of the  $S$  shape (Fig. 2). In the diffusion-limited case, the conventional expectation is that the conversion fraction is proportional to  $t^{1/2}$  in the beginning with subsequent slowdown, whereas under transient external conditions the conversion fraction is predicted to be linear in the beginning and then its increase is slowed down (Fig. 3).

Finally, I can repeat that the equations presented were derived assuming the concentration of molecules outside particles to depend

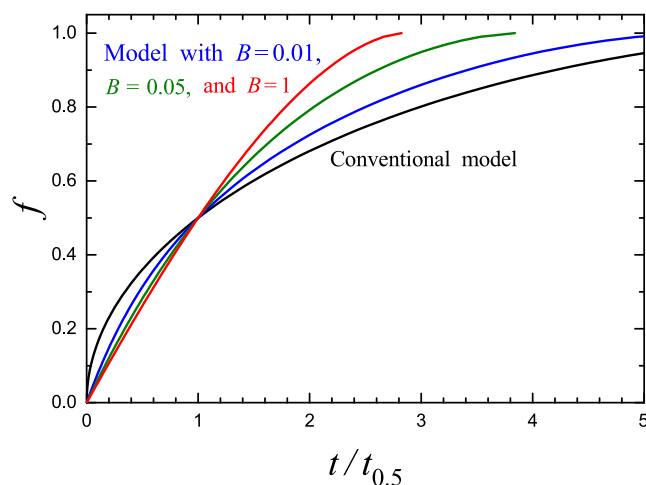


Fig. 3. Diffusion-limited conversion of spherical particles to the new phase as a function of the normalized time in the core-shell model in the conventional case with fixed conditions outside [Eq. (20)] and under transient conditions [Eq. (22) with  $\alpha = 2$  and  $B = 0.01, 0.05$ , and  $1$ ].

on time whereas the temperature to be constant. In real situations, the temperature may depend on time as well. If needed, the equations presented can easily be generalized in order to describe the latter case. In particular, the kinetically limited regime is treated by employing Eq. (7) where the dependence of  $\kappa$  on  $t$  is assumed to be related to the transient increase of the reactant concentration outside particles. One can, however, admit that this dependence is related also to change of temperature, i.e., Eq. (7) and other equations in Section 2 remain to be applicable. The diffusion-limited regime (Section 3) is described by using Eq. (19) implying the dependence of  $c_o$  on  $t$  to be related to the transient increase of the reactant concentration outside. If in addition the temperature depends on time, it will be manifested in the dependence of  $D$  on  $t$ . This factor can be taken into account by replacing  $D \int_0^t c_o(t') dt'$  in Eq. (19) by  $\int_0^t D(t') c_o(t') dt'$  and introducing related modifications into the other equations.

## Declaration of competing interest

I declare that I have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

## Data availability

No data was used for the research described in the article.

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