

Optimal experimental protocol for identification of dissolution and kinetics parameters in the presence of fast reaction

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Abstract

To model the reactive solid phase contribution, knowledge of the solubility and mass transfer should be extracted from empirical measurements. Often unknown factors may complicate the interpretation of the data. In this paper we consider an example and present a practical procedure that allows one to avoid the difficulties. A simplified model is derived for the mass transfer and kinetics. This model provides a straightforward way for estimation of the parameters of interest.

Keywords: Parameter estimation, mass transfer and kinetics, asymptotic methods.

Introduction

Several organic liquid phase reactions are carried in the presence of a sparingly soluble reactive solid phase, which is gradually dissolved during the course of the reaction. To model the reactive solid phase contribution, knowledge of the solubility and mass transfer should be extracted from empirical measurements. However, this may not be possible by the kinetic data alone – the model typically becomes loaded with too many confounded parameters for both the complex kinetics and mass transfer. It would be advantageous

to estimate the mass transfer parameters from separate experiments. But such measurements may, again, introduce unknown factors that complicate the interpretation of the data. In this paper we consider such an example and present a practical procedure that allows one to avoid the difficulties. A simplified model is derived for the mass transfer and kinetics. This model provides a straightforward way for estimation of the parameters of interest.

The example studied in [1] concerns the Claisen condensation between an ester (C) and ketone (A). The kinetics consists of four basic reaction steps, carried out with chlorobenzene (MCB) as the solvent. The reaction is initiated by a proton removal from the ketone (A) with methoxide (B), originally introduced in the system as solid particles. The reaction leads to a formation of carbanion (A_1) and methanol (E). In the second step the carbanion attacks the carbonyl group of the ester, forming an intermediate. The last two steps involve methoxide elimination of the intermediate and charge distribution between the tautomeric keto- and enol- forms yielding the product diketone (D) and methanol. More details are found in [1].

In addition to the above scenario, some side reactions take place. Methoxide is very hygroscopic and prone to adsorb moisture from the air. The water present in the reaction system reacts with methoxide and produces hydroxide (S_{12}) and methanol (E). The hydroxide (S_{12}) saponifies the ester (C), producing carboxylic ion (S_{21}) and methanol (E). The ester (C) reacts also with methoxide (B) yielding carboxylic ion (S_{21}) and dimethyl ether (S_{31}). Methoxide as well as hydroxide are sparingly soluble in chlorobenzene, but their solubilities are enhanced markedly by methanol formed in the reactions.

The equilibrium solubility of sodium methoxide (B) in chlorobenzene-methanol solution as a function of methanol (E) was determined in [1]. An empirical power-law function was introduced to describe the dependence of the methoxide solubility into chlorobenzene as a function of methanol concentration. The resulting curve is reproduced in Figure 1. The temperature had practically no effect on the solubility compared to the effect of methanol concentration in the measured temperature range of 45-85 C° . The saturation law given in Figure 1 was applied in kinetic data fitting to calculate approximate non-mass transfer limited equilibrium solubility for methoxide.

Additional series of experiments were carried out to study the transient behavior of mass transfer. Also, the solubility of sodium methoxide (B) was studied in solutions where the ester C was added in the MCB-solution together with various amounts of methanol. The reaction between B and C produces carboxylic acid (S_{21}) that could be empirically observed. In

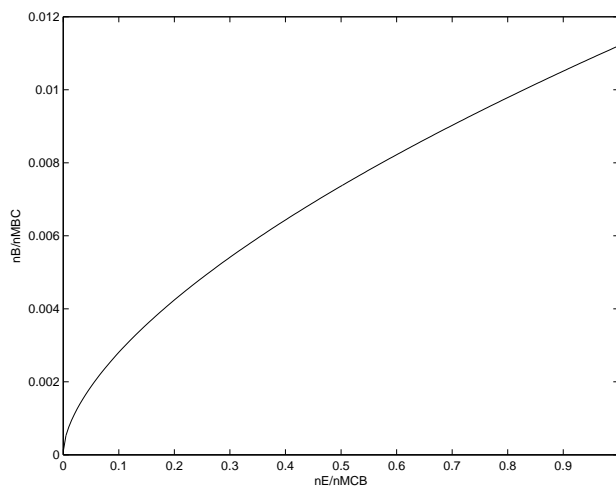
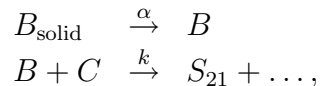


Figure 1: The solubility of methoxide (B) into chlorobenzene-methanol solution, in relative units of the molar amounts of nE , $nMCB$ and nB , $nMBC$.

the experiments, a given amount of solid methoxide was added to various mixtures of ester-MCB and methanol. It was demonstrated that the addition of methanol had a substantial effect on the formation of carboxylic acid (S_{21}). Figure 2 exhibits typical experimental results.

However, as methoxide is very hygroscopic it adsorbs various amounts of moisture from the air, depending on the humidity of the handling environment. Absorbed water reacts with methoxide (B) and produces hydroxide (S_{12}) and methanol (E) so the solid sodium methoxide particles may initially contain sodium hydroxide, free methanol and water on the surface. When these solid particles are added to the mixture of ester-MCB and methanol, the solubility of methoxide and hydroxide as well as water into the MCB-solution is enhanced by methanol. A fast initial formation of carboxylic acid takes place by the reaction between the ester and dissolved hydroxide. The extent of the fast reaction phase depends on the effect of methanol to the initial solubility of reacting species, i.e. the initial concentration of hydroxide in the solution. A further formation of carboxylic acid in the reactions is related to the solubility rate and concentration of methoxide in the reaction medium.

So, the consumption rate of B and C in the reaction



was confounded with other reactions due to an unknown amount of hydroxide in the system. In Figure 2 we see that the production of S_{21} is started with an initial transient – very fast in cases where methanol was added – and followed by a slower production rate. To summarize, the above experimental

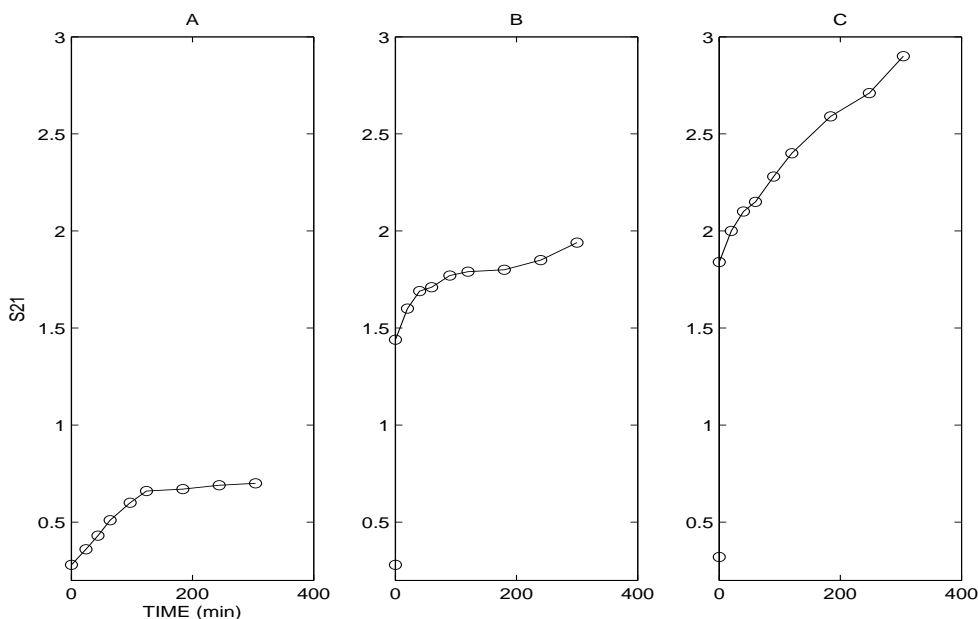


Figure 2: Production of S_{21} as a function of time in a MCB solution with 77 g ester and 700 g methoxide added. Plot A: no methanol added Plot B: 32 g methanol added, Plot C: 64 g methanol added.

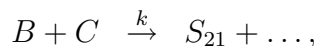
protocol – to add solid particles to various mixtures of solvents – was plagued with the effects of unknown amounts of impurities on the surface the solid phase, resulting in a fast transient in the beginning of the process. For such a situation, we present an alternative protocol: add an excessive amount of the solid particles into the solvent mixture and let it reach a steady state. After this, add an additional amount of the C-solvent mixture. Here we will derive a model and a simplified asymptotic solution for this system. The form of

the solution will immediately reveal the effects of the reaction rate, solubility rate and the saturation concentration on the measurement data. Thus, a combination of modelling and experimentation will guide us to design the experiment in a way that optimally yields the desired results.

1 Statement of the problem and asymptotics

Several unknown factors in the above experimental setup obscure the identification of the model parameters of the system. However, the linear slopes in Figure 2 give an indication for a combination of a fast reaction and slower mass transfer: the reaction transforms the dissolved B into the products as soon as B is dissolved, and the dissolution rate is approximatively constant.

We consider the following chemical reaction scheme:



under assumption that substance B appears due to dissolution process of solid particles. Before the reaction starts the concentration of B in the liquid is equal to a saturation concentration B^* . The reaction starts when an initial amount C_0 of component C is added to the reactor. We assume that in some chosen units of measurement $B^* = O(1)$ and $C_0 \gg B^*$, e.g., $C_0 = O(1/\varepsilon)$, where $0 < \varepsilon \ll 1$ is a small parameter; $k = O(1)$. This means that excessive amount of substance C is introduced in the system.

The system of differential equations describing the dynamics of species concentrations can be written as follows (below we use notation c_B , c_C , and c_S for concentrations of B , C , and S_{12} , respectively):

$$\begin{aligned} \dot{c}_B &= -kc_B c_C + \alpha(B^* - c_B), \\ \dot{c}_C &= -kc_B c_C, \\ \dot{c}_S &= -kc_B c_C. \end{aligned} \tag{1}$$

Here α is the dissolution rate coefficient. The relation that involves α simply states that the concentration of substance B in the liquid in the reactor adjusts to the saturation value B^* via dissolution of solid particles that contain B .

Corresponding initial conditions are:

$$c_B(0) = B^*, \quad c_C(0) = C_0 \gg B^*, \quad c_S(0) = S_0. \tag{2}$$

Let us assume, in addition, that in the chosen units of measurement coefficient $\alpha = O(\varepsilon)$. This means that the dissolution process is slow in comparison with processes associated with the reaction. This assumption is quite natural since usually the dissolution of solid particles occurs on a much longer characteristic time intervals compared with the characteristic times of reactions.

Assuming that the reaction is fast, we can derive the following simplified form for the solution of the above system

$$c_S = S_0 + B^*(1 - e^{-kC_0t}) + \alpha B^*t. \quad (3)$$

(see the Appendix for the technical details)

2 Conclusions following from asymptotic results

The curve c_S given by 3 is plotted, as a function of time, for a few values of B^* in Figure 3. The figure immediately provides rough estimates for all the parameters of interest: B^*, k, α .

The initial jump in the concentration of c_S is related to the saturation value B^* of substance B in the liquid. Due to fast reaction and the fact that the concentration of C introduced into reactor is much greater than corresponding concentration of B , the reaction occurs on a fast time scale. This produces the transition layer captured by Figure 3. The width of the layer is proportional to the value of kC_0t that causes the exponential term $\exp(-kC_0t)$ to vanish; a working estimate for k is obtained by $kC_0t_w = 2$, where C_0 is the known added amount of C and t_w is an approximation of the width of the transition layer.

During the initial reaction, the concentration of B decreases from B^* to values close to zero. So, the height of the initial jump gives, in molar units, an approximation for B^* .

The fact that the concentration of B in the liquid is smaller than saturation concentration B^* leads to dissolution of the solid particles. However, as soon as the "new" molecules of B appear in the liquid they are almost immediately consumed by the reaction with C . Since the dissolution is the slow process, its rate essentially defines the rate of growth of S_{21} as a result

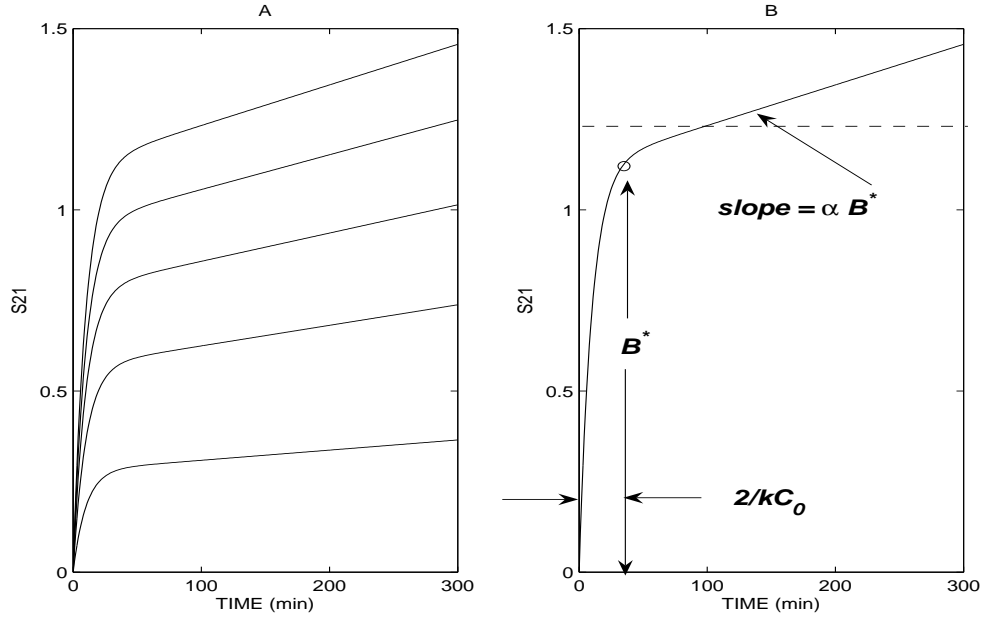


Figure 3: Plot A: Reduced response curves of concentrations of S_{21} for various values of B^* . Plot B: The roles of B^* , kC_0 and αB^* in the shape of the curve.

of reaction (i.e., dissolution of solid particles is a rate limiting step of the whole process). Measuring the slope of the linear part of the experimental c_S curve we can find the coefficient αB^* . Since the saturation concentration B^* is known, we thus define the value of the dissolution coefficient α .

Naturally, all the rough estimates of the parameters, which we directly may extract from the plot, may be further used as initial guesses for a standard least squares parameter estimation procedure, together with proper statistical error analysis. Here we just note that the parameters will be statistically non-correlated, due to the separate effects they have on the data.

It is remarkable that B cannot be detected in this experiment while saturation concentration of B depending on concentration of substance E can be measured experimentally. In fact, B is almost not present in the liquid since it is consumed by the "fast" reaction with C – its concentration cannot reach B^* as long as C is present. However, we can observe the, so-called, new "effective" saturation concentration of B represented by the regular term of the asymptotic expansion of c_B in the second order in ε : $B_{effective}^* =$

$$\varepsilon^2 \tilde{\alpha} B^* / (k C^*) = \alpha B^* / (k C_0) = O(\varepsilon^2).$$

Appendix

We show here how the simplified expression (3) is derived by employing the asymptotic method of boundary layer functions. For more discussion on the methodology, see, e.g., [2], [4].

It immediately follows from (1) that variable c_S can be easily eliminated from the system. Indeed, adding the second and the third equations in (1) and integrating the result, we obtain:

$$c_C(t) + c_S(t) = c_C(0) + c_S(0) = \text{const.}$$

Taking into account the initial conditions, we can write

$$c_S(t) = c_C(0) - c_C(t). \quad (4)$$

Thus, as soon as we find c_C , the function c_S will also be known.

Let us introduce a new rescaled variable and a parameter ε , $0 < \varepsilon \ll 1$:

$$\tilde{c}_C = c_C \varepsilon, \quad \tilde{\alpha} = \alpha / \varepsilon. \quad (5)$$

Here $\tilde{c}_C = O(1)$, $\tilde{\alpha} = O(1)$. Omitting tildes ($\tilde{}$), we can rewrite equations and conditions for c_B and c_C from (1), (2) as follows:

$$\begin{aligned} \varepsilon \dot{c}_B &= -k c_B c_C + \varepsilon^2 \alpha (B^* - c_B), \\ \dot{c}_C &= -k c_B c_C, \end{aligned} \quad (6)$$

and

$$c_B(0) = B^*, \quad c_C(0) = C_0 \varepsilon = C^* = O(1). \quad (7)$$

We seek the uniform asymptotic approximation of the solution of (6), (7) in the form (see [4] for a presentation of the methodology and [2], [3] for earlier applications)

$$c_B = \bar{c}_B^0(t) + \Pi_0 c_B(\tau) + \varepsilon \bar{c}_B^1(t) + \varepsilon \Pi_1 c_B(\tau) + \dots, \quad (8)$$

with similar expression for the other variable. Here, e.g., $\bar{c}_B^0(t)$ is the leading order term of the regular part of the asymptotic expansion describing the

behavior of the solution away from initial transient, and $\Pi_0 c_B(\tau)$ is the, so-called, boundary layer function in the leading order important near the initial instant of time; $\tau = t/\varepsilon$ is the stretched variable. Note that the boundary functions must decay to zero as $\tau \rightarrow \infty$.

Next, we follow the standard procedure to determine the terms of the asymptotic expansion. For regular functions of the leading order, we obtain the equations by setting $\varepsilon = 0$ in (6):

$$\begin{aligned} 0 &= -k\bar{c}_B^0\bar{c}_C^0, \\ \dot{\bar{c}}_C^0 &= -k\bar{c}_B^0\bar{c}_C^0 = 0. \end{aligned} \quad (9)$$

The sum of the regular and boundary functions must satisfy the initial conditions in every order in ε . Thus, in the leading order approximation,

$$\begin{aligned} \bar{c}_B^0(0) + \Pi_0 c_B(0) &= B^*, \\ \bar{c}_C^0(0) + \Pi_0 c_C(0) &= C^*. \end{aligned} \quad (10)$$

The equations for $\Pi_0 c_B$ and $\Pi_0 c_C$ have the form:

$$d(\Pi_0 c_B)/d\tau = -k\bar{c}_C^0(0)(\Pi_0 c_B) - k\bar{c}_B^0(0)(\Pi_0 c_C) - k(\Pi_0 c_C)(\Pi_0 c_B), \quad (11)$$

$$d(\Pi_0 c_C)/d\tau = 0.$$

The equation for $\Pi_0 c_B$ in (11) with condition $\Pi_0 c_B(\infty) = 0$ has solution

$$\Pi_0 c_B \equiv 0.$$

Thus, the initial condition for \bar{c}_C^0 , following from (10), is

$$\bar{c}_C^0(0) = C^*.$$

Taking into account this condition, we obtain from (9):

$$\bar{c}_C^0(t) = C^* = \text{const}. \quad (12)$$

From the first equation in (9) it follows that

$$\bar{c}_B^0(t) \equiv 0. \quad (13)$$

Thus, the problem for the boundary function $\Pi_0 c_B(\tau)$ can now be written in the form:

$$\begin{aligned} d(\Pi_0 c_B)/d\tau &= -kC^*(\Pi_0 c_B), \\ \Pi_0 c_B(0) &= B^*. \end{aligned} \quad (14)$$

Its solution is

$$\Pi_0 c_B(\tau) = B^* \exp(-kC^* \tau). \quad (15)$$

Thus, all the terms of the leading order approximation have been determined. For identification of parameters in the model using experimental data, we need to construct some higher order terms of the asymptotics as well.

In the first order approximation, we obtain the problems:

$$\begin{aligned} 0 &= -k\bar{c}_B^1 \bar{c}_C^0, \\ \dot{\bar{c}}_C^1 &= -k\bar{c}_B^1 \bar{c}_C^0 = 0; \end{aligned} \quad (16)$$

$$d(\Pi_1 c_B)/d\tau = -k\bar{c}_C^0(0)(\Pi_1 c_B) - k\bar{c}_C^1(0)(\Pi_0 c_B) - k(\Pi_1 c_C)(\Pi_0 c_B), \quad (17)$$

$$d(\Pi_1 c_C)/d\tau = -k\bar{c}_C^0(0)(\Pi_0 c_B) = d(\Pi_0 c_B)/d\tau;$$

$$\begin{aligned} \bar{c}_B^1(0) + \Pi_1 c_B(0) &= 0, \\ \bar{c}_C^1(0) + \Pi_1 c_C(0) &= 0, \\ \Pi_1 c_B(\infty) = \Pi_1 c_C(\infty) &= 0. \end{aligned} \quad (18)$$

It follows from the second equation in (17) and the condition at $\tau = \infty$ that

$$\Pi_1 c_C(\tau) = \Pi_0 c_B(\tau) = B^* \exp(-kC^* \tau). \quad (19)$$

Thus, from (18),

$$\bar{c}_C^1(0) = -\Pi_1 c_C(0) = -B^*. \quad (20)$$

Taking into account (20), we obtain from the second equation in (16):

$$\bar{c}_C^1(t) = -B^* = \text{const}. \quad (21)$$

From the first equation of (16) we get

$$\bar{c}_B^1(t) = 0.$$

The problem for the boundary function $\Pi_0 c_B(\tau)$ can now be written in the form:

$$\begin{aligned} d(\Pi_1 c_B)/d\tau &= -kC^*(\Pi_1 c_B) + kB^*(\Pi_0 c_B) - k(\Pi_0 c_B)(\Pi_0 c_B), \\ \Pi_1 c_B(0) &= 0. \end{aligned} \quad (22)$$

Solution of (22) has the form:

$$\Pi_1 c_B(\tau) = \frac{(B^*)^2}{C^*} [-e^{-kC^*\tau} + kC^*\tau e^{-kC^*\tau} + e^{-2kC^*\tau}]. \quad (23)$$

This completes the construction of asymptotics of the first order in ε .

When comparing asymptotic results with the solution of the original model we would want to know approximations for both variables with the same asymptotic accuracy. Here we recall that to return to the original variable c_C we need to divide the approximation for corresponding rescaled variable by ε . This means that to obtain asymptotic expressions for both original variables c_B and c_C with the same order of accuracy (e.g., with the remainder terms of order $O(\varepsilon^2)$) we have to construct the leading and the first order approximations for c_B , and the leading, the first, and the second order approximation for the rescaled c_C .

For the second order approximation, we obtain (here we write the problems for all regular and boundary functions of order $O(\varepsilon^2)$, but we will use only \bar{c}_C^2 and $\Pi_2 c_C$ in the expansion):

$$\begin{aligned} 0 &= -k\bar{c}_B^2 \bar{c}_C^0 + \alpha B^*, \\ \dot{\bar{c}}_C^2 &= -k\bar{c}_B^2 \bar{c}_C^0 = -\alpha B^*; \end{aligned} \quad (24)$$

$$\begin{aligned} d(\Pi_2 c_B)/d\tau &= -k\bar{c}_C^0(0)(\Pi_2 c_B) - k\bar{c}_C^1(0)(\Pi_1 c_B) \\ &\quad - k[(\Pi_1 c_C)(\Pi_1 c_B) + (\Pi_2 c_C)(\Pi_0 c_B)] - \alpha(\Pi_0 c_B), \end{aligned} \quad (25)$$

$$d(\Pi_2 c_C)/d\tau = d(\Pi_1 c_B)/d\tau;$$

$$\begin{aligned} \bar{c}_B^2(0) + \Pi_2 c_B(0) &= 0, \\ \bar{c}_C^2(0) + \Pi_2 c_C(0) &= 0, \\ \Pi_2 c_B(\infty) &= \Pi_2 c_C(\infty) = 0. \end{aligned} \quad (26)$$

From the second equation in (25) and the corresponding condition (26) at $\tau = \infty$, we obtain:

$$\Pi_2 c_C(\tau) = \Pi_1 c_B(\tau). \quad (27)$$

Since $\Pi_2 c_C(0) = \Pi_1 c_B(0) = 0$, we get from (26) that

$$\bar{c}_C^2(0) = 0.$$

Equation for \bar{c}_C^2 in (24) with this initial condition has solution

$$\bar{c}_C^2 = -\alpha B^* t. \quad (28)$$

(We note that it follows from the first equation of (24) that $\bar{c}_B^2 = \alpha B^*/(kC^*) = \text{const}$, and thus, the equation for $\Pi_2 c_B$ in (25) must be solved with the initial condition $\Pi_2 c_B(0) = -\bar{c}_B^2(0) = -\alpha B^*/(kC^*)$. It can be shown that corresponding solution $\Pi_2 c_B(\tau)$ decays exponentially to zero as $\tau \rightarrow \infty$.)

Finally, combining the above results, we can write asymptotic approximation for the original variables (here we only present nontrivial terms of the asymptotics):

$$\begin{aligned} c_B &= \Pi_0 c_B(\tau) + \varepsilon \Pi_1 c_B(\tau) + O(\varepsilon^2) \\ &= B^* e^{-kC^* \tau} + \varepsilon \frac{(B^*)^2}{C^*} [-e^{-kC^* \tau} + kC^* \tau e^{-kC^* \tau} + e^{-2kC^* \tau}] + O(\varepsilon^2), \end{aligned} \quad (29)$$

and

$$\begin{aligned} c_C &= \bar{c}_C^0(t)/\varepsilon + \bar{c}_B^1(t) + \Pi_1 c_B(\tau) + \varepsilon \bar{c}_B^2(\tau) + \varepsilon \Pi_2 c_B(\tau) + O(\varepsilon^2) \\ &= C^*/\varepsilon - B^* + B^* e^{-kC^* \tau} - \varepsilon \tilde{\alpha} B^* t \\ &\quad + \varepsilon \frac{(B^*)^2}{C^*} [-e^{-kC^* \tau} + kC^* \tau e^{-kC^* \tau} + e^{-2kC^* \tau}] + O(\varepsilon^2). \end{aligned} \quad (30)$$

In terms of original parameters, the above expressions can be rewritten as

$$c_B = B^* e^{-kC_0 t} + \frac{(B^*)^2}{C_0} [-e^{-kC_0 t} + kC_0 t e^{-kC_0 t} + e^{-2kC_0 t}] + O(\varepsilon^2), \quad (31)$$

and

$$\begin{aligned} c_C &= C_0 - B^* + B^* e^{-kC_0 t} - \alpha B^* t \\ &\quad + \frac{(B^*)^2}{C_0} [-e^{-kC_0 t} + kC_0 t e^{-kC_0 t} + e^{-2kC_0 t}] + O(\varepsilon^2). \end{aligned} \quad (32)$$

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