The dimensionlessness of chemical kinetic equation

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The techniques of dimensional analysis and scaling of the chemical kinetic equation are investigated in this paper. Along with several examples, the procedure to reduce problems to the dimensionless form is described and a general method about selecting the characteristic scales is given. Our results show that if the difference between the number of the parameters in the dimensional equation and in the dimensionless equation is equal to the rank of dimension matrix plus one, then the selection of scales is suitable and the dimensionless equation is one of the simplest forms.

KEY WORDS: dimensionlessness, scaling, kinetic equation, nonlinear dynamics

1. Introduction

The techniques of dimensional analysis and scaling are very important and useful in nonlinear dynamics. Dimensional analysis permits us to understand the dimensional relationships of the quantities in the equations and the resulting implications of dimensional homogeneity. Scaling can help us understand the magnitude of the terms that appear in the model equations by comparing the quantities to intrinsic reference quantities that appear naturally in the physical situation. Nondimensionalizing the equation can reduce the number of parameters by lumping them together into dimensionless groups. This reduction always simplifies the bifurcation analysis of nonlinear chemical dynamics. There have been many publications devoted to this problem [1–6]. However, how to make out dimensionlessness of a chemical kinetic equation is still a difficult problem existing in kinetics. It is the purpose of this paper to give a general procedure by which chemical kinetic equations can be transformed into the dimensionless forms and present a simple method to decide whether the dimensionless form is the simplest form or not. Before making a formal statement, it is necessary to introduce some definitions.

2. Definitions

It is well known that the basic principle of dimensional analysis and scaling is that equations must be dimensionally homogeneous. According to this principle it is

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generally true that a physical law, such as

$$f(q_1, q_2, \ldots, q_m) = 0 \tag{1}$$

is equivalent to a physical law $F(\lambda_1, \lambda_2, \ldots, \lambda_i) = 0$. Here, $q_1, q_2, \ldots, q_m$ are the dimensioned quantities and $\lambda_1, \lambda_2, \ldots, \lambda_i$ are the dimensionless quantities which can be formed from $q_1, q_2, \ldots, q_m$. In general, the dimensions of q_i, denoted by $[q_i]$, can be written in terms of the fundamental dimensions as $[q_i] = L_1^{a_{1i}} L_2^{a_{2i}} \cdots L_n^{a_{ni}}$ for some choice of exponents $a_{1i}, a_{2i}, \ldots, a_{ni}$, where $L_1, \ldots, L_n$ are fundamental dimensions.

Definition 2.1. If $[q_i] = L_1^{a_{1i}} L_2^{a_{2i}} \cdots L_n^{a_{ni}} = 1$, then q_i is said to be dimensionless.

Definition 2.2. The $n \times m$ matrix

$$D = \begin{pmatrix} a_{11} & \ldots & a_{1m} \\ a_{21} & \ldots & a_{2m} \\ \vdots & & \vdots \\ a_{n1} & \ldots & a_{nm} \end{pmatrix} \tag{2}$$

is called the dimension matrix if the elements in the ith column give the exponents for q_i in terms of the powers of $L_1, \ldots, L_n$.

Any fundamental dimension L_i has the property that its units can be changed upon multiplication by the appropriate conversion factor $\varepsilon_i > 0$ to obtain L_i^* in a new system of units. This means that if $[q] = L_1^{a_1} L_2^{a_2} \cdots L_n^{a_n}$, then $q^* = \varepsilon_1^{a_1} \varepsilon_2^{a_2} \cdots \varepsilon_n^{a_n} q$ gives q in the new system of units. The physical law (1) is said to be independent of the units chosen to express the dimensional quantities $q_1, q_2, \ldots, q_m$, or unit free, if $f(q_1, q_2, \ldots, q_m) = 0$ and $f(q_1^*, q_2^*, \ldots, q_m^*) = 0$ are equivalent physical laws. More formally:

Definition 2.3. The physical law (1) is unit free if for all choices of real numbers $\varepsilon_1, \ldots, \varepsilon_n$, with $\varepsilon_i > 0$, $i = 1, \ldots, n$, we have $f(q_1^*, q_2^*, \ldots, q_m^*) = 0$ if and only if $f(q_1, q_2, \ldots, q_m) = 0$.

It is necessary to distinguish the word "unit" from the word "dimension". By units we mean specific physical units like seconds, hours, days, and years; all of these units have dimensions of time. Similarly, grams, kilograms, etc., are units of the dimension mass. For example, acceleration, as indicated by its typical unit cm/sec^2, has dimension "length/time^2". In simple chemical kinetic equations, time T and concentration C are often taken to be the fundamental dimensions. For instance, the dimension of the second-order rate constant is $C^{-1} T^{-1}$.
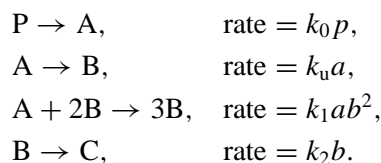
Definition 2.4. Let x be a variable and construct a combination of parameters x_c which has the same dimension as x. If the new variable $\bar{x} = x/x_c$ is a dimensionless variable, x_c is called characteristic scale or intrinsic reference of x.

3.   Theorem

Before giving our general results we first discuss an example: the dimensionless-ness of a simple chemical reaction model. For simplicity our models are all in a thermo-dynamically closed system.

3.1.   Example 1: The two-variable autocatalator model [7–9]

This model considers the conversion of chemical precursor P to a final product C via two reactive intermediates A and B through the sequence of steps

$$
\begin{aligned}
&\text{P} \rightarrow \text{A}, && \text{rate} = k_0 p, \\
&\text{A} \rightarrow \text{B}, && \text{rate} = k_\text{u} a, \\
&\text{A} + 2\text{B} \rightarrow 3\text{B}, && \text{rate} = k_1 a b^2, \\
&\text{B} \rightarrow \text{C}, && \text{rate} = k_2 b.
\end{aligned}
$$

With a constant precursor concentration p_0, the rate equations for the two intermediates are

$$
\begin{aligned}
\frac{\mathrm{d}a}{\mathrm{d}t} &= k_0 p_0 - k_1 a b^2 - k_\text{u} a, \\
\frac{\mathrm{d}b}{\mathrm{d}t} &= k_1 a b^2 + k_\text{u} a - k_2 b.
\end{aligned}
\tag{3}
$$

Equation system (3) involves three variables (a, b, t) and five parameters given by the four rate constants $(k_0, k_\text{u}, k_1, k_2)$ and p_0. To put (3) into a dimensionless form we make following *six-step procedure for nondimensionalization*, which can be used for a large class of chemical kinetic problems.

Step I. Choose fundamental dimensions.   In present instance we choose time T and concentration C as fundamental dimensions.

Step II. List all parameters and variables together with their dimensions in terms of the fundamental dimensions, which is called dimension matrix.   For present problem, we have the following list:

Variables	Dimensions
Dependent variable a, b	C
Independent variable t	T
Parameters	
Constant concentration p_0	C
First-order rate constants k_0, k_u, k_2	T^{-1}
Third-order rate constant k_1	$T^{-1}C^{-2}$

Thus, the dimension matrix is

$$
\begin{array}{c}
\quad t\quad a\quad b\quad p_0\quad k_0\quad\ k_\mathrm{u}\quad\ k_1\quad\ k_2 \\
\begin{array}{c} T \\ C \end{array}
\begin{pmatrix}
1 & 0 & 0 & 0 & -1 & -1 & -1 & -1 \\
0 & 1 & 1 & 1 & 0 & 0 & -2 & 0
\end{pmatrix}.
\end{array}
\tag{4}
$$

Step III. Obtain dimensionless variables. It is obvious to see that the rank r of the dimension matrix (4) is clearly 2. If $\lambda = t^{\alpha_1} a^{\alpha_2} b^{\alpha_3} p_0^{\alpha_4} k_0^{\alpha_5} k_\mathrm{u}^{\alpha_6} k_1^{\alpha_7} k_2^{\alpha_8}$ is a dimensionless variable for some choice of $\alpha_1, \ldots, \alpha_8$ then

$$
[\lambda] = T^{\alpha_1} C^{\alpha_2} C^{\alpha_3} C^{\alpha_4} T^{-\alpha_5} T^{-\alpha_6} \left(T^{-1}C^{-2}\right)^{\alpha_7} T^{-\alpha_8} = T^{\alpha_1-\alpha_5-\alpha_6-\alpha_7-\alpha_8} C^{\alpha_2+\alpha_3+\alpha_4-2\alpha_7} = 1.
$$

Therefore the exponents must vanish and we obtain two homogeneous linear equations for $\alpha_1, \ldots, \alpha_8$, namely

$$
\begin{aligned}
\alpha_1 - \alpha_5 - \alpha_6 - \alpha_7 - \alpha_8 &= 0, \\
\alpha_2 + \alpha_3 + \alpha_4 - 2\alpha_7 &= 0.
\end{aligned}
\tag{5}
$$

The coefficient matrix of linear equation system (5) is just the dimension matrix (4). From elementary matrix theory, the number of independent solutions equals the number of unknowns minus the rank of the matrix. Each independent solution of (5) will give rise to a dimensionless variable. Therefore there are six dimensionless variables that can be formed from $t, a, b, p_0, k_0, k_\mathrm{u}, k_1$ and k_2. We can choose $\alpha_3, \alpha_4, \ldots, \alpha_8$ arbitrarily and write

$$
\begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \\ \alpha_5 \\ \alpha_6 \\ \alpha_7 \\ \alpha_8 \end{pmatrix}
= \alpha_3 \begin{pmatrix} 0 \\ -1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}
+ \alpha_4 \begin{pmatrix} 0 \\ -1 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}
+ \alpha_5 \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}
+ \alpha_6 \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}
+ \alpha_7 \begin{pmatrix} 1 \\ 2 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}
+ \alpha_8 \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}
$$

which have six independent solutions given as

$$
\lambda_1 = \frac{b}{a}, \quad \lambda_2 = \frac{p_0}{a}, \quad \lambda_3 = tk_0, \quad \lambda_4 = tk_\mathrm{u}, \quad \lambda_5 = ta^2 k_1, \quad \lambda_6 = tk_2.
\tag{6}
$$

Step IV. Obtain characteristic scales. According to definition 2.1 and noting that characteristic scales could only be the parameters or their combinations we can obtain the possible characteristic scales directly from the λ_i ($i = 1, \ldots, 6$). From (6) it is easy to obtain the possible characteristic time scales (t_c): $1/k_0$, $1/k_\mathrm{u}$ and $1/k_2$, and the possible concentration scale (x_c): p_0. Characteristic scales can be obtained not only from λ_i directly but also from their combinations indirectly. Hence, the possible concentration scales can also be: $(k_0/k_1)^{1/2}$, $(k_\mathrm{u}/k_1)^{1/2}$ and $(k_2/k_1)^{1/2}$, which are obtained from λ_5/λ_3, λ_5/λ_4 and λ_5/λ_6, respectively.

Step V. Obtain dimensionless equation. Using Greek letters for dimensionless variables we have $\alpha = a/x_c$, $\beta = b/x_c$ and $\tau = t/t_c$. If we select $t_c = 1/k_0$, $x_c = (k_0/k_1)^{1/2}$ and substitute them into dimensional equation system (3), then (3) can be cast as follows:

$$\frac{d\alpha}{d\tau} = \mu - \alpha\beta^2 - \frac{k_u}{k_0}\alpha,$$
$$\frac{d\beta}{d\tau} = \alpha\beta^2 + \frac{k_u}{k_0}\alpha - \frac{k_2}{k_0}\beta \tag{7}$$

where $\mu = (k_1/k_0)^{1/2}p_0$. The ratios, k_2/k_0 and k_u/k_0 are dimensionless because k_2, k_u and k_0 are all first-order rate constants. By setting $k_2/k_0 = C_1$ and $k_u/k_0 = C_2$, equation system (7) becomes:

$$\frac{d\alpha}{d\tau} = \mu - \alpha\beta^2 - C_2\alpha,$$
$$\frac{d\beta}{d\tau} = \alpha\beta^2 + C_2\alpha - C_1\beta. \tag{8}$$

Equation system (8) involves three variables, α, β and τ, and three parameters, C_1, C_2 and μ. This is at least a more economical representation than the full dimensional forms where we have five parameters – the rate constants and p_0. Some of the dimensionless forms of the rate equation for the different selections of x_c and t_c are listed in table 1.

Here the symbol Δ denotes the difference between the number of parameters in dimensional equation and in the dimensionless equations. The actual expressions of μ and C_i in the table are not the same for the different scales though their letters are the same in form. From table 1 it can be found that the maximum of Δ is equal to $r+1$. The dimensionless form is said to be one of the simplest forms if its number of parameters is the least, which means that its Δ is the biggest. Parameters in the dimensionless equation are all dimensionless quantities. This is another advantage of the present method because we need not carry out dimensional analysis to them.

Step VI. Check whether the equality $\Delta = r + 1$ is satisfied or not. If it is satisfied then the choice of characteristic scales is said to be suitable for the dimensionlessness of the equation and the dimensionless form is one of the simplest forms. If $\Delta = r + 1$ does not hold, we should select new characteristic scales. In other words, we should return to Step IV and start from it to continue the procedure. We generalize these results as following theorem.

3.2. Theorem

The dimensionless kinetic equation of a chemical reaction system is one of the simplest dimensionless forms if the equality $\Delta = r + 1$ holds.

Proof. The kinetic equation of a chemical reaction system can be generally written as

$$\frac{dx}{dt} = k_0x_0 + k_1x + k_2x^2 + k_3x^3, \tag{9}$$

Table 1
Dimensionless rate equation of the two-variable autocatalator.

No.	t_c	x_c	Dimensionless form	Δ
1	$1/k_0$	$(k_0/k_1)^{1/2}$	$d\alpha/d\tau = \mu - \alpha\beta^2 - C_1\alpha$	
			$d\beta/d\tau = \alpha\beta^2 + C_1\alpha - C_2\beta$	2
2	$1/k_0$	$(k_u/k_1)^{1/2}$	$d\alpha/d\tau = \mu - C_1\alpha\beta^2 - C_1\alpha$	2
			$d\beta/d\tau = C_1\alpha\beta^2 + C_1\alpha - C_2\beta$	
3	$1/k_0$	$(k_2/k_1)^{1/2}$	$d\alpha/d\tau = \mu - C_1\alpha\beta^2 - C_2\alpha$	2
			$d\beta/d\tau = C_1\alpha\beta^2 + C_2\alpha - C_1\beta$	
4	$1/k_u$	$(k_0/k_1)^{1/2}$	$d\alpha/d\tau = \mu - C_1\alpha\beta^2 - \alpha$	2
			$d\beta/d\tau = C_1\alpha\beta^2 + \alpha - C_2\beta$	
5	$1/k_u$	$(k_u/k_1)^{1/2}$	$d\alpha/d\tau = \mu - \alpha\beta^2 - \alpha$	3
			$d\beta/d\tau = \alpha\beta^2 + \alpha - C_1\beta$	
6	$1/k_u$	$(k_2/k_1)^{1/2}$	$d\alpha/d\tau = \mu - C_1\alpha\beta^2 - \alpha$	3
			$d\beta/d\tau = C_1\alpha\beta^2 + \alpha - C_1\beta$	
7	$1/k_2$	$(k_0/k_1)^{1/2}$	$d\alpha/d\tau = \mu - C_1\alpha\beta^2 - C_2\alpha$	2
			$d\beta/d\tau = C_1\alpha\beta^2 + C_2\alpha - \beta$	
8	$1/k_2$	$(k_u/k_1)^{1/2}$	$d\alpha/d\tau = \mu - C_1\alpha\beta^2 - C_1\alpha$	3
			$d\beta/d\tau = C_1\alpha\beta^2 + C_1\alpha - \beta$	
9	$1/k_2$	$(k_2/k_1)^{1/2}$	$d\alpha/d\tau = \mu - \alpha\beta^2 - C_1\alpha$	3
			$d\beta/d\tau = \alpha\beta^2 + C_1\alpha - \beta$	
10	$1/k_0$	$\left(\dfrac{k_0 k_u}{k_1 k_2}\right)^{1/2}$	$d\alpha/d\tau = \mu - C_1\alpha\beta^2 - C_2\alpha$	1
			$d\beta/d\tau = C_1\alpha\beta^2 + C_2\alpha - C_3\beta$	

where x_0 is a constant concentration, k_i $(i = 0, \ldots, 3)$ are the rate constants. Equation (9) is unit free and can be expressed in the form

$$f(q_1, q_2, \ldots, q_m) = 0, \quad m = 7. \tag{10}$$

If we select concentration C and time T as fundamental dimensions, then

$$[q_j] = L_1^{a_{1j}} L_2^{a_{2j}}, \quad j = 1, 2, \ldots, 7, \tag{11}$$

where L_1 and L_2 are the fundamental dimensions. The dimension matrix is

$$D = \begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} & a_{17} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} & a_{27} \end{pmatrix}, \quad \text{rank } D = r = 2, \tag{12}$$

from which we can construct a set of equations

$$Dy = 0. \tag{13}$$

Obviously, equation system (13) has $m - r = 5$ linearly independent solutions:

$$y_s = (y_{s1}, y_{s2}, \ldots, y_{sm})^T, \quad s = 1, 2, \ldots, 5, \ m = 7. \tag{14}$$

At first we prove that $\lambda_s = \prod_{j=1}^m q_j^{y_{sj}}$ $(s = 1, \ldots, 5)$ are independent dimensionless quantities. By the use of equations (11) we have

$$[\lambda_s] = \prod_{j=1}^m [q_j]^{y_{sj}} = \prod_{j=1}^m \left(\prod_{i=1}^2 L_i^{a_{ij}}\right)^{y_{sj}} = \prod_{i=1}^2 L_i^{\sum_{j=1}^m a_{ij} y_{sj}}. \tag{15}$$

From (13) and (14), we obtain

$$\sum_{j=1}^m a_{ij} y_{sj} = 0, \quad i = 1, 2, \ s = 1, 2, \ldots, 5. \tag{16}$$

Substituting (16) into (15) gives

$$[\lambda_s] = \prod_{i=1}^2 L_i^0 = 1, \quad s = 1, 2, \ldots, 5.$$

Therefore λ_s $(s = 1, 2, \ldots, 5)$ are independent dimensionless quantities according to definition 2.1.

Secondly, we prove that equation (10) is equivalent to the dimensionless equation

$$F(\lambda_1, \lambda_2, \ldots, \lambda_5) = 0. \tag{17}$$

We know that equation system (13) has 5 independent solutions. Without loss of any generality, we assume the first two columns of D are linearly independent. Then these 5 independent solutions can be expressed as

$$\begin{cases} y_1 = (a_1, a_2, 1, 0, 0, 0, 0), \\ y_2 = (b_1, b_2, 0, 1, 0, 0, 0), \\ y_3 = (c_1, c_2, 0, 0, 1, 0, 0), \\ y_3 = (d_1, d_2, 0, 0, 0, 1, 0), \\ y_4 = (e_1, e_2, 0, 0, 0, 0, 1). \end{cases} \tag{18}$$

It has been proved that

$$\begin{cases} \lambda_1 = q_1^{a_1} q_2^{a_2} q_3, \\ \lambda_2 = q_1^{b_1} q_2^{b_2} q_4, \\ \lambda_3 = q_1^{c_1} q_2^{c_2} q_5, \\ \lambda_4 = q_1^{d_1} q_2^{d_2} q_6, \\ \lambda_5 = q_1^{e_1} q_2^{e_2} q_7 \end{cases} \tag{19}$$

are independent dimensionless quantities. From (19) we can obtain

$$q_3 = \lambda_1 q_1^{-a_1} q_2^{-a_2}, \quad q_4 = \lambda_2 q_1^{-b_1} q_2^{-b_2}, \quad q_5 = \lambda_3 q_1^{-c_1} q_2^{-c_2}, \tag{20}$$
$$q_6 = \lambda_4 q_1^{-d_1} q_2^{-d_2}, \quad q_7 = \lambda_5 q_1^{-e_1} q_2^{-e_2}.$$

Substituting (20) into (10) and defining

$$
\begin{aligned}
& g(q_1, q_2, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5) \\
& \quad \equiv f\left(q_1, q_2, \lambda_1 q_1^{-a_1} q_2^{-a_2}, \lambda_2 q_1^{-b_1} q_2^{-b_2}, \lambda_3 q_1^{-c_1} q_2^{-c_2}, \lambda_4 q_1^{-d_1} q_2^{-d_2}, \lambda_5 q_1^{-e_1} q_2^{-e_2}\right) \quad (21)
\end{aligned}
$$

we have that

$$
g(q_1, q_2, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5) = 0 \tag{22}
$$

is equivalent to (10). Since (10) is unit free, it easily follows that (22) is unit free. Therefore, according to definition 2.3 and noting that $\lambda_i^* = \lambda_i$ ($i = 1, 2, \ldots, 5$) under any change of units, we have

$$
g\left(q_1^*, q_2^*, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5\right) = 0, \tag{23}
$$

where

$$
q_1^* = \varepsilon_1^{a_{11}} \varepsilon_2^{a_{21}} q_1, \quad q_2^* = \varepsilon_1^{a_{11}} \varepsilon_2^{a_{21}} q_2 \tag{24}
$$

for every choice of the conversion factors $\varepsilon_1, \varepsilon_2 > 0$. Equation system (24) is equivalent to (22). The factors $\varepsilon_1, \varepsilon_2$ can be selected so that $q_1^* = q_2^* = 1$. We are able to make this choice because

$$
1 = \varepsilon_1^{a_{11}} \varepsilon_2^{a_{21}} q_1, \quad 1 = \varepsilon_1^{a_{11}} \varepsilon_2^{a_{21}} q_2 \tag{25}
$$

implies

$$
\begin{cases}
a_{11} \ln \varepsilon_1 + a_{21} \ln \varepsilon_2 = -\ln q_1, \\
a_{12} \ln \varepsilon_1 + a_{22} \ln \varepsilon_2 = -\ln q_2.
\end{cases} \tag{26}
$$

Since we have assumed that the first two columns of the dimension matrix D are linearly independent, the system (26) has a unique solution $\ln \varepsilon_1$ and $\ln \varepsilon_2$, from which ε_1 and ε_2 can be determined to satisfy (25). Therefore, equation (23) gives

$$
g(1, 1, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5) = 0. \tag{27}
$$

If we define

$$
F(\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5) \equiv g(1, 1, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5) \tag{28}
$$

then $F(\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5) = 0$ is equivalent to (10): $f(q_1, q_2, q_3, q_4, q_5, q_6, q_7) = 0$. By selecting x_c and t_c as the characteristic scales of concentration and time, respectively, the chemical reaction kinetic equation (9) can be transformed into following dimensionless form:

$$
\frac{d\alpha}{d\tau} = C_1 + C_2\alpha + C_3\alpha^2 + C_4\alpha^3, \tag{29}
$$

where $\alpha = x/x_c$, $\tau = t/t_c$, $C_1 = t_c k_0 x_0 / x_c$, $C_2 = k_1 t_c$, $C_3 = k_2 t_c x_c$ and $C_4 = k_3 t_c x_c^2$ are all dimensionless quantities. Equation (29) also can be expressed as

$$
G(\alpha, \tau, C_1, C_2, C_3, C_4) = 0. \tag{30}
$$

In order to satisfy the above conclusion, i.e., $f(q_1, q_2, q_3, q_4, q_5, q_6, q_7) = 0$ is equivalent to $F(\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5) = 0$, one of the dimensionless parameters C_i $(i = 1, \ldots, 4)$ in (30) must be equal to unity. The selection of C_i $(i = 1, \ldots, 4) = 1$ can be made arbitrarily. Here, we choose $C_2 = 1$ and define

$$g(\alpha, \tau, C_1, C_3, C_4) \equiv G(\alpha, \tau, C_1, 1, C_3, C_4). \tag{31}$$

Thus $g(\alpha, \tau, C_1, C_3, C_4) = 0$ is equivalent to $f(q_1, q_2, q_3, q_4, q_5, q_6, q_7) = 0$. Further simplification of equation (31) can be made for some special selections of C_i. Here we select $C_3 = 1$. (We can also choose $C_1 = 1$ or $C_4 = 1$, which does not affect our final conclusion.) By solving simultaneous equations

$$\begin{cases} C_2 = 1 = k_1 t_c, \\ C_3 = 1 = k_2 t_c x_c \end{cases}$$

we can obtain

$$\begin{cases} t_c = \dfrac{1}{k_1}, \\ x_c = \dfrac{k_1}{k_2}. \end{cases}$$
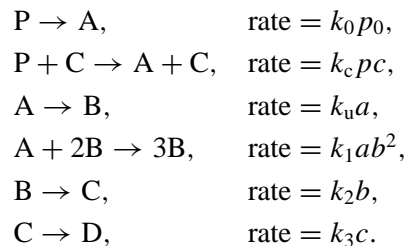
In this case equation (29) becomes

$$\frac{d\alpha}{d\tau} = C_1 + \alpha + \alpha^2 + C_4 \alpha^3. \tag{32}$$

It can be seen that the number of parameters has been reduced from five $(x_0, k_0, k_1, k_2, k_3)$ to two (C_1, C_2). Parameters in (32) cannot be further decreased, so equation (32) is one of the simplest forms. The difference between the number of parameters in the dimensional equation (9) and in the dimensionless equation (32) satisfies the equality $\Delta = r + 1$, where $\Delta = 5 - 2 = 3$ and $r = 2$. The proof of the theorem is complete. $\square$

4. Applications

4.1. Example 2:The three-variable autocatalator model [11]

This model considers the conversion of chemical precursor P to final product D via three intermediates A, B and C. The reaction model is as follows:

$$\begin{array}{lll} P \rightarrow A, & \text{rate} = k_0 p_0, \\ P + C \rightarrow A + C, & \text{rate} = k_c pc, \\ A \rightarrow B, & \text{rate} = k_u a, \\ A + 2B \rightarrow 3B, & \text{rate} = k_1 ab^2, \\ B \rightarrow C, & \text{rate} = k_2 b, \\ C \rightarrow D, & \text{rate} = k_3 c. \end{array}$$

With a constant precursor concentration p_0, the rate equations for the three intermediates are:

$$
\begin{aligned}
\frac{da}{dt} &= k_0 p_0 + k_c p_0 c - k_u a - k_1 a b^2, \\
\frac{db}{dt} &= k_u a + k_1 a b^2 - k_2 b, \\
\frac{dc}{dt} &= k_2 b - k_3 c.
\end{aligned}
\tag{33}
$$

The process of obtaining suitable dimensionless forms for the present model is similar to the example 1. The dimension matrix is

$$
\begin{array}{c c}
 & \begin{array}{c c c c c c c c c c c} t & a & b & c & p_0 & k_0 & k_c & k_u & k_1 & k_2 & k_3 \end{array} \\
\begin{array}{c} T \\ C \end{array} & \left(\begin{array}{c c c c c c c c c c c}
1 & 0 & 0 & 0 & 0 & -1 & -1 & -1 & -1 & -1 & -1 \\
0 & 1 & 1 & 1 & 1 & 0 & -1 & 0 & -2 & 0 & 0
\end{array} \right)
\end{array}
$$

whose rank $r = 2$. So there are nine dimensionless variables:

$$
\begin{aligned}
&\lambda_1 = a^{-1} b, \quad \lambda_2 = a^{-1} c, \quad \lambda_3 = a^{-1} p_0, \quad \lambda_4 = t k_0, \quad \lambda_5 = t a k_c, \\
&\lambda_6 = t k_u, \quad \lambda_7 = t a^2 k_1, \quad \lambda_8 = t k_2, \quad \lambda_9 = t k_3.
\end{aligned}
$$

If we select $x_c = (k_u/k_1)^{1/2}$ which is obtained from (λ_6/λ_5) and $t_c = 1/k_u$ which is from λ_6, then the dimensionless form of the equation system (33) becomes

$$
\begin{aligned}
\frac{d\alpha}{d\tau} &= \mu + C_1 \gamma - \alpha \beta^2 - \alpha, \\
\frac{d\beta}{d\tau} &= \alpha + \alpha \beta^2 - C_2 \beta, \\
\frac{d\gamma}{d\tau} &= C_2 \beta - C_3 \gamma,
\end{aligned}
\tag{34}
$$

where $\mu = (k_0^2 k_1/k_u^3)^{1/2} p_0$, $C_1 = k_c p_0/k_u$, $C_2 = k_2/k_u$, $C_3 = k_3/k_u$.

The parameters have been reduced from seven (p_0 and six rate constants) to four. The difference between dimensional parameters and dimensionless parameters is three which is just equal to $r + 1$. So the selection of scales are reasonable in terms of the previous section. Our results can also be found in other reactions such as the parallel and consecutive autocatalator system [12], the surface reaction system [13] and nonautocatalytic reaction system [14]. It should be indicated that the selection of characteristic scale can be different for different quantities that have the same dimension. For example, we still select time scale as $t_c = 1/k_u$ while the concentration scales are selected as follows: $x_{c(A)} = (k_2/k_1)^{1/2}$, $x_{c(B)} = (k_u/k_1)^{1/2}$, $x_{c(C)} = (k_u k_2^2/k_1 k_3^2)^{1/2}$ which are ob-
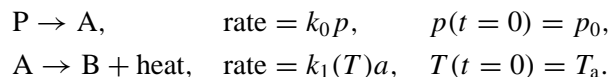
tained from $\lambda_6\lambda_5/\lambda_7^2$, λ_6/λ_5 and $\lambda_8^2\lambda_6/\lambda_7^2\lambda_5$, respectively. Then the dimensionless form of the rate equation system (33) with this selection is given:

$$\frac{d\alpha}{d\tau} = C_1 + C_2\gamma - \alpha\beta^2 - \alpha,$$

$$C_3\frac{d\beta}{d\tau} = \alpha + \alpha\beta^2 - \beta, \tag{35}$$

$$C_4\frac{d\gamma}{d\tau} = \beta - \gamma,$$

where $C_1 = (k_0^2 k_1/k_2^2 k_u)^{1/2} p_0$, $C_2 = k_c p_0/k_3$, $C_3 = k_u/k_2$ and $C_4 = k_u/k_3$. Equation system (35) is the same form as the Peng's [15]. It is required to point out here that the selection of characteristic scale may be different but scales must come from the dimensionless variables λ_i or their combination, such as $\lambda_6\lambda_5/\lambda_7^2$.

4.2. Example 3: Salnikov model [16–18]

Before making dimensional analysis we will at first give some basic descriptions about this model. The Salnikov scheme consists of only two steps and both of these are first order:

$$P \rightarrow A, \qquad \text{rate} = k_0 p, \qquad p(t=0) = p_0,$$

$$A \rightarrow B + \text{heat}, \quad \text{rate} = k_1(T)a, \quad T(t=0) = T_a.$$

The first step involves a pool chemical reactant whose concentration is regarded as constant. This step is also assumed to be virtually thermoneutral so k_0 does not vary with temperature. The second step is exothermic and its rate constant has an Arrhenius form. The equations for mass balance and energy conservation for this system are

$$\frac{da}{dt} = k_0 p_0 e^{-k_0 t} - k_1(T)a \qquad \text{(mass balance)}, \tag{36}$$

$$V\omega\frac{dT}{dt} = QVk_1(T)a - S\chi(T - T_a) \quad \text{(energy balance)}. \tag{37}$$

Here ω is the heat capacity per unit volume, S the surface area, Q the reaction exothermicity, χ the surface heat transfer coefficient and V the volume of a well-stirred closed vessel sitting in a heat bath which has a temperature T_a. For practical purpose we usually take $\Delta T = T - T_a$ as our variable instead of T so the energy balance equation can be written as

$$V\omega\frac{d\Delta T}{dt} = QVk_1(\Delta T)a - S\chi\Delta T. \tag{38}$$

Step I. Choose fundamental dimensions. Time (t), length (L), temperature (Θ) and energy (e) are selected as fundamental dimensions.

Step II. The dimension matrix is

$$
\begin{array}{c}
\\
t\ (time) \\
L\ (length) \\
\Theta\ (temp.) \\
e\ (energy)
\end{array}
\begin{array}{c}
\chi\quad S\quad T\quad T_a\quad E\quad Q\quad V\quad k_1\quad a\quad t\quad \Delta T\quad R\quad \omega \\
\left(
\begin{array}{ccccccccccccc}
-1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 \\
-2 & 2 & 0 & 0 & 0 & 0 & 3 & 0 & -3 & 0 & 0 & 0 & -3 \\
-1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & -1 \\
1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 1
\end{array}
\right)
\end{array} \tag{39}
$$

where $m = 13$, $r = 4$.

Step III. Obtain dimensionless variables. Because the rank $r = 4$ so there are nine ($m - r = 9$) dimensionless quantities. The practical calculations are similar to the example 1:

$$
\lambda_1 = \chi E^{-1} a^{-2/3} t (\Delta T), \quad \lambda_2 = S a^{2/3}, \quad \lambda_3 = T(\Delta T)^{-1}, \quad \lambda_4 = T_a (\Delta T)^{-1},
$$

$$
\lambda_5 = E^{-1} Q, \quad \lambda_6 = V a, \quad \lambda_7 = kt, \quad \lambda_8 = E^{-1}(\Delta T) R, \quad \lambda_9 = E^{-1} a^{-1}(\Delta T) \omega. \tag{40}
$$

Step IV. Obtain characteristic scales. In terms of the equations (40), the characteristic scales of variables can be selected as follows:

(1) time scales $t_c = \omega V / \chi S$ (which is obtained from $\lambda_1 \lambda_2 / \lambda_6 \lambda_9$);

(2) concentration scales $x_c = \chi S R T_a^2 / (E Q V k_1(T_a))$ (obtained from $\lambda_1 \lambda_2 \lambda_4^2 \lambda_8 / (\lambda_5 \lambda_6 \lambda_7)$);

(3) temperature scale $T_c = E/R$ (from $\lambda_3 \lambda_8$ or $\lambda_4 \lambda_8$);

(4) temperature rise scale $(\Delta T)_c = R T_a^2 E^{-1}$ (from $\lambda_4^2 \lambda_8$).

Step V. Obtain dimensionless equations. At first we carry out dimensionlessness of the Arrhenius rate law. It is well known that $k_1(T) = A \exp(-E/RT)$ and $k_1(T_a) = A \exp(-E/RT_a)$. Using Greek letter θ as dimensionless temperature rise and γ as dimensionless temperature we have

$$
\theta = \frac{\Delta T}{(\Delta T)_c} = \frac{E(T - T_a)}{R T_a^2} \quad \text{and} \quad \gamma = \frac{R T_a}{E}.
$$

Then $k_1(T)$ can be expressed as

$$
k_1(T) = k_1(T_a) \exp\left[\frac{\theta}{1 + \gamma \theta}\right]. \tag{41}
$$

Substitution of $\alpha = a/x_c$, $\tau = t/t_c$ and equation (41) into (36) and (38) gives

$$
\frac{d\alpha}{d\tau} = C_1 \exp(-C_2 \tau) - C_3 \alpha \exp\left[\frac{\theta}{1 + \gamma \theta}\right],
$$

$$
\frac{d\theta}{d\tau} = \alpha \exp\left[\frac{\theta}{1 + \gamma \theta}\right] - \theta. \tag{42}
$$

Here

$$C_1 = \frac{k_0 \omega E Q k_1(T_a) V^2}{R(\chi S T_a)^2}, \quad C_2 = \frac{k_0 \omega V}{\chi S} \quad \text{and} \quad C_3 = \frac{k_1(T_a)\omega V}{\chi S}.$$

Step VI. Check if the equality $\Delta = r + 1$ is satisfied or not. Equation system (42) involves three variables as well as four parameters C_1, C_2, C_3 and γ. The number of parameters has been decreased from nine $(\chi, S, T_a, Q, V, k_1, k_0, p_0, \omega)$ to four. The difference Δ is five which is just equal to $r + 1$ (here $r = 4$). Therefore the selection of the characteristic scales is reasonable and (42) is one of the simplest dimensionless forms.

5. Conclusion

The main purpose of transforming a dimensional equation into an equivalent dimensionless form is to decrease the numbers of parameters in the equation and drastically simplify the mathematical models. Thus the dynamical behaviour of the reaction equation is not determined primarily by the absolute values of all the rate constants, but only by one or more ratios of them. This reduction of parameters is particularly important in the studying of nonlinear chemical dynamics. In present paper we have demonstrated the process of dimensional analysis and have given a general method to nondimensionalize the kinetic equation of a chemical reaction system. The key to the transforming a dimensional equation into dimensionless form lies in selecting characteristic scales. The scales can be obtained not only from the dimensionless quantities but also from their combinations. Whether the selections of scales are suitable or not depend on the difference Δ. We have proved that if the equality $\Delta = r + 1$ holds the selections of characteristic scales is said to be reasonable and the dimensionless equation is one of the simplest forms. Therefore the equality $\Delta = r + 1$ can be taken as a necessary condition for selecting characteristic scales. Our result is not only available in chemical systems but also available in the other fields, for example, the dimensionlessness of the ecological model [19].

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