Entropy production and element conservation in the quasi-steady-state approximation

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1. Introduction

To reduce the number of differential equations that are required to describe complex reacting systems, the quasi-steady-state approximation (QSSA) is frequently employed for some species [1–3]. The species for which QSSA is employed are termed minor species and the remaining species are major species. Keck [4] cast doubt on whether entropy production is always nonnegative (as required by the second law of thermodynamics) when the quasi-steady-state assumption is employed. In his argument, Keck gave an expression for the entropy production for the whole system consisting of both the major and the minor species. And for the whole system, whether the entropy production is always nonnegative is not clear. However, usually when QSSA is invoked we are primarily interested in the major species. In the following, we show that both element conservation and the second law are satisfied if we consider the system consisting only of the major species.

2. Element conservation

In the following, for demonstration, we consider a system with fixed energy $E$ and volume $V$, but the conclusions apply to the general case.

The evolution of a chemically reacting system with fixed $E$ and $V$ can be described using a detailed chemical mechanism involving $n_s$ species and $n_r$ elementary reactions. With $B_j$ denoting the symbol for species $j$, the $k$th elementary reaction can be written

$$
\sum_{j=1}^{n_s} v^+_{jk} B_j \leftrightarrow \sum_{j=1}^{n_s} v^-_{jk} B_j, \quad (1)
$$

where $v^+_{jk}$ and $v^-_{jk}$ are the stoichiometric coefficients for the forward and reverse directions of the elementary reaction $k$. And the phenomenological rate equation for an individual species is

$$
\dot{N}_j = V \sum_{k=1}^{n_r} v_{jk} r_k, \quad (2)
$$

where $N_j$ denotes moles of species $j$, the overall stoichiometric coefficients are given by $v_{jk} = v^-_{jk} - v^+_{jk}$, and the overall reaction rate $r_k (r_k = r^+_{k} - r^-_{k})$ is the net reaction rate per unit volume. The forward and reverse reaction rates are given by the phenomenological expressions

$$
r^+_{k} = k^+_{k} (T, p) \prod_{j=1}^{n_s} [N_j]^{v^+_{jk}} \quad (3)
$$

and

$$
r^-_{k} = k^-_{k} (T, p) \prod_{j=1}^{n_s} [N_j]^{v^-_{jk}} \quad (4)
$$

where $k^+_{k} (T, p)$ and $k^-_{k} (T, p)$ are rate constants for the forward and reverse reactions and $[N_j]$ denotes molar concentration of species $j ([N_j] = N_j / V)$.

Let $a_{ij}$ denote the number of atoms of element $i$ in a molecule of species $j$. Element conservation in chemical reactions forces the relation

$$
\sum_{j=1}^{n_s} a_{ij} v_{jk} = 0, \quad (5)
$$

for all elements $i$ and all elementary reactions $k$. 

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E-mail address: zr26@cornell.edu (Z. Ren).
We consider the quasi-steady-state approximation applied to \( n_p \) species \((1 \leq n_p < n_s)\). Without loss of generality, we order the species so that the \( n_p \) minor species are first in the ordering. The quasi-steady-state approximation is that the net creation rate of the minor species is zero, i.e.,

\[
\sum_{k=1}^{n_s} \nu_{jk} r_k = 0, \quad \text{for } j \leq n_p.
\]  

It is essential to distinguish between the “net creation rate of minor species” (defined as the left-hand side of Eq. (6)) and the “rate of change of minor species” are set to zero) and the “net creation rate of minor species” (defined as \( \dot{N}_j \), for \( j \leq n_p \)). When a detailed kinetics mechanism is used (without QSSA), then these two quantities are equal (see Eq. (2)). But with QSSA, the net creation rates of minor species are set to zero; whereas in general the minor species have nontrivial rates of change, in response to the changes in the major species.

If we consider the elements in the major species only, we have

\[
\frac{d}{dt} \left( \sum_{j=n_p+1}^{n_s} \sum_{k=1}^{n_s} a_{ij} \nu_{jk} r_k \right) = \sum_{j=n_p+1}^{n_s} a_{ij} \dot{N}_j
\]

\[
= V \sum_{j=n_p+1}^{n_s} a_{ij} \sum_{k=1}^{n_s} \nu_{jk} r_k
\]

\[
= V \sum_{j=n_p+1}^{n_s} a_{ij} \sum_{k=1}^{n_s} \nu_{jk} r_k + V \sum_{j=1}^{n_p} a_{ij} \sum_{k=1}^{n_s} \nu_{jk} r_k
\]

\[
= V \sum_{j=1}^{n_s} a_{ij} \sum_{k=1}^{n_s} \nu_{jk} r_k = V \sum_{j=1}^{n_s} a_{ij} \sum_{k=1}^{n_s} \nu_{jk} r_k
\]

\[
= 0,
\]

where the third step follows from Eq. (6) (the “net creation rate of minor species” are set to zero) and the last step follows from Eq. (5). Thus, Eq. (7) establishes that for the major species alone element conservation is satisfied for all elements \( i \).

However if we consider both the major species and the minor species, we have

\[
\frac{d}{dt} \left( \sum_{j=1}^{n_s} a_{ij} \dot{N}_j \right) = \sum_{j=1}^{n_s} a_{ij} \dot{N}_j
\]

\[
= \sum_{j=n_p+1}^{n_s} a_{ij} \dot{N}_j + \sum_{j=1}^{n_p} a_{ij} \dot{N}_j
\]

\[
= \sum_{j=n_p+1}^{n_s} a_{ij} \dot{N}_j + \sum_{j=1}^{n_p} a_{ij} \dot{N}_j.
\]

where the last step follows from Eq. (7). The minor species in QSSA are solved from the nonlinear algebraic equations (Eq. (6)) in terms of the major species. If we differentiate Eq. (6) with respect to time, we can see that the minor species evolve with the major species and their rate of change \( \dot{N}_j \), for \( j = 1, \ldots, n_p \), is usually nonzero. So element conservation is not guaranteed if we consider the system of both the major and the minor species.

3. Entropy production

In conventional thermodynamics, for a system with energy \( E \), volume \( V \), and moles of species \( N_j \), the governing equation for entropy production is given by the Gibbs equation

\[
T \frac{dS}{dt} = dE + p dV - \sum_{j=1}^{n_s} \mu_j dN_j,
\]

where \( T \) is the temperature, \( S \) is the entropy, \( p \) is the pressure, and \( \mu_j \) is the chemical potential of species \( j \). So from the Gibbs equation (Eq. (9)), it can be seen that the entropy production due to chemical reactions is

\[
\sigma_R = - \sum_{j=1}^{n_s} \mu_j \dot{N}_j / T,
\]

and indeed this is the total entropy production for a system of constant \( E \) and \( V \). A consequence of the second law is that \( \sigma_R \) is nonnegative. The entropy production given by Eq. (10) can be decomposed into two parts

\[
\sigma_R = \sigma_R^{\text{major}} + \sigma_R^{\text{minor}},
\]

with

\[
T \sigma_R^{\text{major}} = - \sum_{j=n_p+1}^{n_s} \mu_j \dot{N}_j,
\]

\[
T \sigma_R^{\text{minor}} = - \sum_{j=1}^{n_p} \mu_j \dot{N}_j,
\]

where \( \sigma_R^{\text{major}} \) accounts for the entropy production from the major species and \( \sigma_R^{\text{minor}} \) accounts for the entropy production from the minor species. Keck [4] derived an expression for the entropy production when QSSA is employed,

\[
T \sigma_R = - \sum_{j=1}^{n_p} \mu_j \dot{N}_j + k_B T V \sum_{k=1}^{n_r} (r_k^+ - r_k^-) \ln(r_k^+ / r_k^-),
\]

where \( k_B \) is the Boltzmann constant. The second term on the right-hand side is positive semidefinite, but the first term can be positive or negative. On this basis
Keck argued that it is not clear that the entropy production is always nonnegative when the quasi-steady-state approximation is employed. However, if we consider the entropy production for the major species alone, from Eqs. (11), (12), and (13), we readily obtain

\[
T \sigma_{R}^{\text{major}} = k_B T V \sum_{k=1}^{n_c} \left( r_k^+ - r_k^- \right) \ln \left( \frac{r_k^+}{r_k^-} \right) \geq 0. \tag{14}
\]

Moreover, if we solve the energy equation for the reacting system based solely on the major species, then energy conservation is also guaranteed.

To demonstrate the satisfaction of element conservation and the first and second laws of thermodynamics if only the major species are considered, we take as a test case the adiabatic autoignition of methane. The initial composition (stoichiometric methane–air) is taken to be (in relative volume units) N₂ (79), O₂ (21), and CH₄ (10.5); the initial temperature is 1500 K; and the pressure is atmospheric throughout. The GRI2.11 detailed mechanism is employed, and the major species are selected identically to those in the augmented reduced mechanism [3]. The QSSA assumption is applied to the remaining (i.e., minor) species. The corresponding differential algebraic equations are solved by the DDASAC code (Caracotsios and Stewart, 1985). Figure 1 shows the element moles, enthalpy, and entropy versus time (based both on the major species and on all species). As may be seen, when based on the major species (dashed lines) the element moles and enthalpy remain constant, whereas the entropy increases. In contrast, when based on all species, the element moles and enthalpy vary, and at times (around t = 1.2 ms) the entropy decreases.

4. Conclusion

In summary, when the quasi-steady-state approximation is used, the system is best regarded as consisting solely of the major species. For then, element conservation and the first and second laws of thermodynamics are satisfied. The minor species determined from QSSA affect only the reaction rates. In contrast, if the system is considered to consist of all species, then neither element conservation nor the second law is guaranteed to be satisfied as the system evolves through chemical reactions.

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References


