How is entropy production rate related to chemical reaction rate?

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Abstract

The entropy production rate is a key quantity in irreversible thermodynamics. In this work, we concentrate on the realization of entropy production rate in chemical reaction systems in terms of the experimentally measurable reaction rate. Both triangular and linear networks have been studied. They attain either thermodynamic equilibrium or a non-equilibrium steady state, under suitable external constraints. We have shown that the entropy production rate is proportional to the square of the reaction velocity only around equilibrium and not any arbitrary non-equilibrium steady state. This feature can act as a guide in revealing the nature of a steady state, very much like the minimum entropy production principle. A discussion on this point has also been presented.

keywords: Entropy production rate, reaction rate, non-equilibrium steady state

1 Introduction

Twentieth century witnessed a paradigm shift in the field of thermodynamics. The focus of the scientific community gradually changed from equilibrium thermodynamics of the previous era to the thermodynamics of irreversible processes [1,2] and of steady states [3]. Starting with the pioneering works of Onsager in the form of reciprocal relations in coupled irreversible processes [1,2], research in non-equilibrium thermodynamics expanded rapidly [1]. The power of the subject to capture real, natural processes ensured its multidisciplinary nature [5] and its applicability to chemistry, physics, biology as well as to various technological aspects [6]. Over the years, the theoretical tools and understanding improved and expanded in various directions [7]. The linear laws of Onsager, applicable to states near thermodynamic equilibrium (TE), were generalized by Prigogine and coworkers giving rise

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to non-linear, irreversible thermodynamics for states far removed from the TE [8, 9]. In the last two decades, the theory has evolved into the thermodynamics of small systems [10]. The fundamental role of fluctuations in governing the properties of these systems has been revealed and the link between microscopic reversibility and macroscopic irreversibility is established in terms of the fluctuation theorems [11, 12]. Chemical reaction systems have also been treated extensively under this field, going beyond the realm of TE [13, 14, 15]. Various analytical and numerical methodologies have emerged to study the non-equilibrium thermodynamics [16] of reactions occurring in bulk as well as at the level of few molecules [17], along with their kinetics [18, 19].

In all these developments, entropy plays the part of the most basic and interesting thermodynamic quantity [20]. A quintessential thermodynamic feature of a system out-of-equilibrium or an open system is the emergence of a non-equilibrium steady state (NESS) [21, 22, 23, 24], with the state of equilibrium being a special case. Whether NESS prevails in a certain situation is characterized by non-vanishing entropy production rate (EPR) [25], measuring the dissipation associated with the process [26]. Still, the measure is a theoretical one and, for complex systems, the connection of EPR with the immediately observable quantities may not be apparent. Therefore, it will be helpful to get an idea about how the EPR of an irreversible process is connected with some ready experimentally observable quantity. In this context, here we study the EPR in relation to chemical reaction rates. We consider a triangular as well as a linear reaction network. The choices are dictated primarily by simplicity, yet exhibiting nontrivial features that permit the emergence of NESS [27, 28]. We particularly focus on the possibility of realization of EPR in these reaction networks in terms of the experimentally measurable velocity of the reaction both near the TE as well as NESS. It is important to note that the reaction velocity \( v(t) \) is not generally equal to the reaction flux, conventionally used in the definition of EPR [4, 29, 30]. This is particularly true for cyclic reaction networks, justifying its choice as a case study. To be specific, here we show that, with \( P, Q, R \) as constants,

(i) EPR = \( P + Qv(t) + Rv^2(t) \), around a NESS,

(ii) EPR = \( Rv^2(t) \), around the TE.

Thus the proportionality of the EPR with square of the reaction rate becomes a hallmark of the TE. This criterion may well be used to distinguish a NESS from the TE. In this issue, mention may be made of the work of Ross et al. [31] that established such a distinction in terms of the minimum entropy
production principle (MEPP) \[5, 8\]. Therefore, we briefly comment on the connection of our findings with the MEPP.

2 Entropy production rate and reaction rate around TE

Let us study the EPR of a triangular reaction network and its linear counterpart around a TE. The relation between the EPR and reaction rate is derived in each of the cases near TE. Here we consider the cyclic system first, because all the results of the simpler linear network would follow as a special case of the former.

2.1 ABC cyclic network

The kinetic scheme of the ABC cyclic network is shown in Fig.1. The kinetic equations of the reaction system are written as

\[
\begin{align*}
\dot{a} &= - (k_1 + k_{-3})a(t) + k_{-1}b(t) + k_3c(t), \\
\dot{b} &= k_1a(t) - (k_{-1} + k_2)b(t) + k_{-2}c(t), \\
\dot{c} &= k_{-3}a(t) + k_2b(t) - (k_{-2} + k_3)c(t),
\end{align*}
\]

Figure 1: Schematic diagram of the ABC cyclic reaction network indicating the forward and backward rate constants of each reaction.
with $a(t), b(t), c(t)$ being the concentrations of species A, B, C, respectively, at time $t$. At the steady state, $\dot{a} = \dot{b} = \dot{c} = 0$. Then one obtains the steady-state solutions as

$$a^* = (k_2k_3 + k_{-1}k_3 + k_{-1}k_{-2})/N_1 = \alpha/N_1,$$

$$b^* = (k_1k_3 + k_{1}k_{-2} + k_{-3}k_{-2})/N_1 = \beta/N_1,$$

$$c^* = (k_1k_2 + k_{2}k_{-3} + k_{-1}k_{-3})/N_1 = \gamma/N_1,$$

with $N_1 = \alpha + \beta + \gamma$.

The EPR $\sigma(t)$ of the cyclic reaction network is expressed in terms of fluxes $J_i$ and the corresponding forces $X_i$ as [4]

$$\sigma(t) = \frac{1}{T} \sum_{i=1}^{3} J_i(t)X_i(t).$$

The fluxes are defined as [4, 29, 30]:

$$J_1(t) = k_1a(t) - k_{-1}b(t),$$

$$J_2(t) = k_2b(t) - k_{-2}c(t),$$

$$J_3(t) = k_3c(t) - k_{-3}a(t).$$

The corresponding forces are

$$X_1(t) = \mu_A - \mu_B = T\ln\frac{k_1a(t)}{k_{-1}b(t)},$$

$$X_2(t) = \mu_B - \mu_C = T\ln\frac{k_2b(t)}{k_{-2}c(t)},$$

$$X_3(t) = \mu_C - \mu_A = T\ln\frac{k_3c(t)}{k_{-3}a(t)}$$

showing

$$X_1(t) + X_2(t) + X_3(t) = 0.$$ 

We have set here (and throughout) the Boltzmann constant $k_B = 1$, and $T$ refers to the local temperature. One can easily see that the reaction velocities are related to the fluxes as

$$\dot{a} = -J_1 + J_3.$$
\[ \dot{b} = J_1 - J_2, \]  
\[ \dot{c} = J_2 - J_3. \]  

So, for the cyclic network, none of the reaction velocities are equal to the fluxes. At steady state, we also have from Eqs. (15-17) that

\[ J_1^* = J_2^* = J_3^* = J_c. \]

Then, from Eq. (7) and Eq. (14), EPR at steady state becomes

\[ T \sigma = J_c(X_1 + X_2 + X_3) = 0. \]

Also, from Eqs. (11)-(13) and Eq. (14), we get

\[ \frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}} = 1. \]

The above relation holds when the system satisfies the condition of detailed balance. This requires the fluxes of each individual reaction to vanish at steady state, i.e.,

\[ J_1^* = J_2^* = J_3^* = J_c = 0. \]

In this case, the reaction system reaches TE. Now, using Eq. (20), it is easy to verify that the steady solutions, Eqs. (4)-(6), do indeed satisfy Eq. (21). So the ABC cyclic network can only reach TE, and no NESS is possible here. This is also indicated by the vanishing \( \sigma(t) \) given in Eq. (19). The TE concentrations are given as

\[ a^e = \frac{k_{-1} k_3}{N_2}, \]
\[ b^e = \frac{k_1 k_3}{N_2}, \]
\[ c^e = \frac{k_{-1} k_{-3}}{N_2}. \]

where \( N_2 = k_1 k_3 + k_{-1} k_3 + k_{-1} k_{-3}. \)

Consider now a situation when the reaction system is close to the TE. The concentrations are taken as

\[ a(t) = a^e + \delta_a, \]
\[ b(t) = b^e + \delta_b, \]
\[ c(t) = c^e + \delta_c. \]
with \( \delta_a + \delta_b + \delta_c = 0 \), because the sum of concentrations of all the species is fixed throughout. It is necessary to find out the relations among \( \delta_a, \delta_b, \delta_c \) to obtain a useful form of EPR close to TE. From definition, it follows that

\[
\dot{\delta}_a = \dot{a} = -(k_1 + k_{-3})\delta_a + k_{-1}\delta_b + k_3\delta_c. \tag{28}
\]

From Eq. (25) and Eq. (28), one can write for an infinitesimal time interval \( \tau \)

\[
(1 + (k_1 + k_{-3})\tau)\delta_a - k_{-1}\tau\delta_b - k_3\tau\delta_c = 0. \tag{29}
\]

Similarly, from the equations of \( \dot{\delta}_b \) and \( \dot{\delta}_c \), one obtains

\[-k_1\delta_a + (1 + (k_{-1} + k_2)\tau)\delta_b - k_{-2}\tau\delta_c = 0 \tag{30}\]

and

\[-k_{-3}\delta_a - k_2\tau\delta_b + (1 + (k_{-2} + k_3)\tau)\delta_c = 0. \tag{31}\]

Using Eqs. (29)-(31), we get

\[
\delta_b = f_1\delta_a, \quad \delta_c = -(\delta_a + \delta_b) = f_2\delta_a, \tag{32}\]

where

\[
f_1 = \frac{k_{-2}(1 + (k_1 + k_{-3})\tau) + k_1k_3\tau}{k_{-1}k_{-2}\tau + k_3(1 + (k_{-1} + k_2)\tau)}; \quad f_2 = -(1 + f_1). \tag{33}\]

It may be pointed out that, in deriving Eq. (32), we do not assume the condition of detailed balance, viz., Eq. (20).

We next obtain the EPR from Eq. (7) near TE, making use of Eq. (32), the TE concentrations, Eqs (22-24) and taking \( \delta_a, \delta_b, \delta_c \) small, as

\[
\sigma(t) = L_1\delta_a^2, \tag{34}\]

where

\[
L_1 = [(k_1 - f_1k_{-1})(1/a^e - f_1/b^e) + (f_1k_2 - f_2k_{-2})(f_1/b^e - f_2/c^e) + \\
(f_2k_3 - k_{-3})(f_2/c^e - 1/a^e)] \\
= \left[ \frac{(k_1 - f_1k_{-1})^2}{k_1} + \frac{(f_2k_3 - k_{-3})^2}{k_{-3}} \right] N_2 \frac{k_3}{k_1k_{-3}}. \tag{35}\]
A good cross check at this juncture would be to examine whether $L_1$ is positive definite. We mention here that the positivity of the last term of Eq.(35), and hence the positivity of $\sigma$, is ensured by the condition of detailed balance. Indeed, one gets from Eq.(20)

$$\frac{f_1 k_{-1} k_{-3}}{f_2 k_1 k_3} = \frac{f_1 k_2}{f_2 k_{-2}},$$

and this guarantees the positivity of $L_1$.

The velocity of the ABC cyclic reaction system, $v(t)$, can be expressed as the rate of change of concentration of any one of the three species. Let us define $v(t) = \dot{a}$. Then, close to TE, we have

$$v(t) = (f_2 k_3 + f_1 k_{-1} - (k_1 + k_{-3})) \delta a = L_2 \delta a. \tag{37}$$

Thus, combining Eq.(34) and Eq.(37), we can write

$$\sigma(t) = \frac{L_1}{L_2^2} v^2(t). \tag{38}$$

Hence, close to TE, EPR is proportional to the square of the reaction velocity. It is easy to see that, defining the reaction velocity as equal to $\dot{b}$ or $\dot{c}$ generates similar type of expression with the same conclusion.

### 2.2 ABC linear network

To emphasize the point expressed in Eq.(38), we take up now the case of the ABC linear reaction network. The reaction scheme is given in Fig.2. The corresponding rate equations and steady state solutions can be obtained from Eqs.(1)-(3) by setting $k_3 = k_{-3} = 0$. Then, one gets the following relations between reaction velocities and fluxes

$$\dot{a} = -J_1, \tag{39}$$

$$\dot{b} = J_1 - J_2, \tag{40}$$

$$\dot{c} = J_2. \tag{41}$$

Unlike the case of ABC cyclic network [see Eqs.(15)- (17)], here the reaction velocities are not all of similar structure. Depending on our choice, it can be equal to the flux or can be different (see below).
Figure 2: Schematic diagram of the ABC linear reaction network indicating the forward and backward rate constants of each reaction.

We note first that, the TE solutions of the linear network are as follows:

\[ a^e = k_{-1}k_{-2}/N_3, \]  
\[ b^e = k_{1}k_{-2}/N_3, \]  
\[ c^e = k_{1}k_{2}/N_3 \]  
\[ \text{with } N_3 = k_{-1}k_{-2} + k_{1}k_{-2} + k_{1}k_{2}. \]

The equivalent of Eq.(32) in this case is

\[ \delta_b = f_1' \delta_a, \quad \delta_c = -(\delta_a + \delta_b) = f_2' \delta_a, \]  
\[ \text{with } \quad f_1' = 1 + k_1\tau, \quad f_2' = -(1 + f_1'), \]  
\[ \text{which follows from Eq.(33) for } k_3 = k_{-3} = 0. \]

Using the above relations along with \( k_3 = k_{-3} = 0 \) in Eq.(34), the EPR of ABC linear reaction network close to TE becomes

\[ \sigma(t) = L_3 \delta_a^2, \]  
\[ \text{where} \]

\[ L_3 = [(k_1 - f_1'k_{-1})(1/a^e - f_1'/b^e) + (f_1'k_2 - f_2'k_{-2})(f_1'/b^e - f_2'/c^e)] \delta_a^2 \]
\[ = \left[ (k_1 - f_1'k_{-1})^2 + (f_1'k_2 - f_2'k_{-2})^2 \frac{k_1k_{-2}}{k_1k_{-2}} \right] \frac{N_3}{k_1k_{-2}}. \]
Note that the positive definite character of $L_3$ is transparent.

Now we define the reaction velocity, say, by $v(t) = \dot{c}$ which is equal to the flux $J_2$. Then close to TE, we have

$$v(t) = (f'_1 k_2 - f'_2 k_{-2}) \delta_a = L_4 \delta_a. \quad (49)$$

Therefore, coupling Eq.(47) and Eq.(49), we can write

$$\sigma(t) = \frac{L_3}{L_4^2} v^2(t). \quad (50)$$

If one chooses to define the velocity as $v(t) = \dot{b}$, which is not equal to any of the fluxes, then close to TE one gets

$$v(t) = (k_1 + f'_2 k_{-2} - f'_1 (k_{-1} + k_2)) \delta_a = L_5 \delta_a. \quad (51)$$

Consequently, the EPR again becomes

$$\sigma(t) = \frac{L_3}{L_5^2} v^2(t). \quad (52)$$

Similar type of quadratic variation follows if one takes $v(t) = \dot{a}$.

### 3 Entropy production rate and reaction rate around NESS

It is now appropriate to take up the cases of chemical reactions that can support a NESS under specified condition. This will allow us to investigate whether the relation between EPR and reaction velocity near TE, derived in Section II, also holds here.

#### 3.1 ABC cyclic network

The ABC cyclic reaction network discussed in Section II.A does not provide any provision for a NESS. So, we consider the triangular network under a special chemiostatic condition, as shown in Fig.3. Here the concentrations of species D and E are externally kept fixed at $d^0$ and $e^0$. The pseudo-first-order rate constants are defined as $k'_1 = k_1 d^0$, $k'_{-1} = k_{-1} e^0$. Then, the fluxes become

$$J_1(t) = k'_1 a(t) - k'_{-1} b(t), \quad (53)$$
Figure 3: Schematic diagram of the ABC cyclic reaction network under chemostatic condition, with the concentrations of D and E held fixed.

\[ J_2(t) = k_2 b(t) - k_{-2} c(t), \quad \text{(54)} \]
\[ J_3(t) = k_3 c(t) - k_{-3} a(t). \quad \text{(55)} \]

The corresponding forces are

\[ X_1(t) = \mu_A + \mu_D - \mu_B - \mu_E = T \ln \frac{k_1' a(t)}{k_{-1} b(t)}, \quad \text{(56)} \]
\[ X_2(t) = \mu_B - \mu_C = T \ln \frac{k_2 b(t)}{k_{-2} c(t)}, \quad \text{(57)} \]
\[ X_3(t) = \mu_C - \mu_A = T \ln \frac{k_3 c(t)}{k_{-3} a(t)}. \quad \text{(58)} \]

The steady state concentrations will now be given still by Eqs.(1)-(3), with \( k_1', k_{-1}' \) replacing \( k_1, k_{-1} \), respectively. At steady state, the fluxes are equal to each other, as was in case of the system discussed in Section II.A. But, an important difference exists. We have here

\[ X_1(t) + X_2(t) + X_3(t) = \mu_D - \mu_E = T \ln \frac{k_1' k_2 k_3}{k_{-1}' k_{-2} k_{-3}}. \quad \text{(59)} \]
Unless the species D and E are in TE, the l.h.s. of Eq. (59) is not zero. This is unlike Eq. (14) of Section II.A. Hence, \( \sigma \) will not vanish at the steady state, establishing the non-equilibrium nature of the latter with broken detailed balance. Only when the l.h.s. of Eq. (59) vanishes, we get
\[
\frac{k'_1 k_2 k_3}{k'_{-1} k_{-2} k_{-3}} = 1, \quad (60)
\]
and the NESS becomes the state of equilibrium satisfying detailed balance Eq. (60), as appropriate here.

Allowing small deviations in concentration, \( \delta_a, \delta_b, \delta_c \) from the steady state, we arrive from Eq. (7) at the general expression of \( \sigma(t) \) close to the NESS in the form
\[
\sigma(t) = (J'_1 + k'_1 \delta_a - k'_{-1} \delta_b) \left( \ln \frac{k'_1 a^s}{k'_{-1} b^s} + (\delta_a/a^s - \delta_b/b^s) \right)
\]
\[
+ (J'_2 + k_2 \delta_b - k_{-2} \delta_c) \left( \ln \frac{k_2 b^s}{k_{-2} c^s} + (\delta_b/b^s - \delta_c/c^s) \right)
\]
\[
+ (J'_3 + k_3 \delta_c - k_{-3} \delta_a) \left( \ln \frac{k_3 c^s}{k_{-3} a^s} + (\delta_c/c^s - \delta_a/a^s) \right) . \quad (61)
\]

We can still use Eq. (32), now containing the pseudo-first-order rate constants, \( k'_1, k'_{-1} \), because its derivation does not require the condition of detailed balance. Then, using Eq. (18) and Eq. (32), we can express Eq. (61) as
\[
\sigma(t) = P_1 + Q_1 \delta_a + R_1 \delta_a^2, \quad (62)
\]
where
\[
P_1 = J'_1 \ln \frac{k'_1 k_2 k_3}{k'_{-1} k_{-2} k_{-3}},
\]
\[
Q_1 = (k'_1 - f_1 k'_{-1}) \ln \frac{k'_1 a^s}{k'_{-1} b^s} + (f_1 k_2 - f_2 k_{-2}) \ln \frac{k_2 b^s}{k_{-2} c^s} + (f_2 k_3 - k_{-3}) \ln \frac{k_3 c^s}{k_{-3} a^s},
\]
\[
R_1 = L'_1.
\]

\( L'_1 \) has the similar mathematical structure as that of \( L_1 \) in Eq. (34) with \( a^e, b^e, c^e \) in Eq. (34) being replaced by \( a^s, b^s, c^s \), now containing the pseudo-first-order rate constants, \( k'_1, k'_{-1} \).
One notes now that the following conditions must hold in order that the EPR becomes proportional to the square of the reaction velocity close to the NESS (see Eq.(38)),

\[ P_1 = 0 = Q_1. \]

However, \( P_1 = 0 \) means either

\[ J_c = 0 \]

and/or

\[ \frac{k'_{1}k_{2}k_{3}}{k'_{-1}k_{-2}k_{-3}} = 1. \]

Actually these two relations are equivalent, both indicating the fulfillment of the detailed balance condition. So, when one relation holds, the other becomes automatic. Under such a restriction, one finds \( Q_1 = 0 \) as \( J_c = 0 \).

So, it follows that \( \sigma \) is proportional to the square of the reaction velocity only near TE, and not around any NESS, the actual relation being already derived in Eq.(33).

### 3.2 ABC linear network

The linear ABC network of Section II.B also reaches TE and not a NESS. This is because, the condition \( \dot{a} = \dot{b} = \dot{c} = 0 \) implies vanishing of all the fluxes at steady state. Therefore, it must be a state of TE as there is no other option for the system but to obey detailed balance. Now, if the species A and C are assumed to act as chemiostats, i.e., their concentrations are kept fixed by connecting with external sources, say, at values \( a^0 \) and \( c^0 \), respectively, then a NESS is possible [31]. The reaction kinetics is described by the rate of change of concentration of B as

\[ \dot{b} = k_1 a^0 + k_{-2} c^0 - (k_{-1} + k_2)b(t). \]  \hspace{1cm} (63)

At steady state, \( \dot{b} = 0 \) with

\[ k_1 a^0 - k_{-1} b^s = k_2 b^s - k_{-2} c^0 = J_t. \]  \hspace{1cm} (64)

The NESS solution is then simply

\[ b^s = \frac{(k_1 a^0 + k_{-2} c^0)}{(k_{-1} + k_2)}. \]  \hspace{1cm} (65)

However, if we further assume that at steady state,

\[ J_t = 0, \]  \hspace{1cm} (66)
then this corresponds to the condition of detailed balance. The system then goes to TE with the concentration

\[ b^e = \frac{k_1a^0}{k_{-1}} = \frac{k_{-2}c^0}{k_2}. \] (67)

This also implies

\[ \frac{k_1k_2a^0}{k_{-1}k_{-2}c^0} = 1. \] (68)

The expression of EPR is given by

\[ \sigma(t) = (k_1a^0 - k_{-1}b(t))\ln \frac{k_1a^0}{k_{-1}b(t)} + (k_2b(t) - k_{-2}c^0)\ln \frac{k_2b(t)}{k_{-2}c^0}. \] (69)

Now, close to the NESS, with \( b(t) = b^s + \delta_b \) as defined earlier, it becomes

\[ \sigma(t) = P_2 + Q_2\delta_b + R_2\delta_b^2, \] (70)

where

\[ P_2 = J_l\ln \frac{k_1k_2a^0}{k_{-1}k_{-2}c^0}, \]

\[ Q_2 = \left( k_2\ln \frac{k_2b^s}{k_{-2}c^0} - k_{-1}\ln \frac{k_1a^0}{k_{-1}b^s} \right), \]

\[ R_2 = \frac{(k_{-1} + k_2)}{b^s}. \]

On the other hand, the reaction velocity, \( v(t) = \dot{b} \) close to the steady state becomes

\[ v(t) = -(k_{-1} + k_2)\delta_b. \] (71)

Therefore, for \( \sigma \) to be proportional to the square of the reaction velocity, one needs

\[ P_2 = 0 = Q_2. \]

Setting \( P_2 = 0 \) means either

\[ J_l = 0 \]

and/or

\[ \frac{k_1k_2a^0}{k_{-1}k_{-2}c^0} = 1. \]

However, as shown above, the first condition implies the second one, and the system satisfies detailed balance. With \( J_l = 0 \), we also find that \( Q_2 = \)
Hence, it is verified that the proportionality between EPR and reaction velocity squared is valid when the reaction system is near TE and not a NESS. The final expression of $\sigma$ in the former case becomes

$$\sigma(t) = (k_{-1} + k_2) \frac{\delta_b^2}{b^e} = \frac{v^2(t)}{b^e(k_{-1} + k_2)}. \quad (72)$$

To summarize the results obtained so far, the EPR is shown to be proportional to the square of the reaction velocity only near TE and not any arbitrary NESS. This feature can act as a measure to distinguish between a TE and a NESS.

4 Link with the minimum entropy production principle

Before concluding, we investigate any possible connection between the behavior of EPR near a NESS and the MEPP. The reasons behind such an endeavour are twofold. The first point is that, recently it has been shown rigorously by Ross and coauthors [31], taking heat flow and chemical reactions as examples of non-equilibrium processes, that MEPP is true if and only if a steady state is the state of TE [32]. So MEPP can theoretically distinguish a NESS from a TE. The second point arises because, the mathematical expressions of EPR in the various cases considered in Section II and Section III are derived by expanding it around TE and a NESS, respectively. Such a type of expansion is also used to find the extremum of the quantity at that point. For non-negative EPR, this extremum is obviously the minimum. Therefore, here we investigate the validity of MEPP using the expressions of EPR in cyclic and linear networks reaching NESS under chemiostatic condition, as discussed in Section III.

First we take the ABC cyclic reaction network under chemiostatic condition, discussed in Section III.A. From the definitions of fluxes and forces (Eqs (53)-(58)), we find at NESS

$$\left( \frac{\partial \sigma}{\partial a} \right)_s = k'_1 \ln \frac{k'_1 a^s}{k'_{-1} b^s} - k_{-3} \ln \frac{k_3 c^s}{k_{-3} a^s}, \quad (73)$$

$$\left( \frac{\partial \sigma}{\partial b} \right)_s = k_2 \ln \frac{k_2 b^s}{k_{-2} c^s} - k'_{-1} \ln \frac{k'_1 a^s}{k'_{-1} b^s}, \quad (74)$$
\[
\left( \frac{\partial \sigma}{\partial c} \right)_s = k_3 \ln \frac{k_3 c^s}{k_{-3} a^s} - k_{-2} \ln \frac{k_2 b^s}{k_{-2} c^s}.
\] 

(75)

Now extremum of \( \sigma \) at NESS [which is obviously the minimum, as \( \sigma \geq 0 \)] requires
\[
\left( \frac{\partial \sigma}{\partial a} \right)_s = \left( \frac{\partial \sigma}{\partial b} \right)_s = \left( \frac{\partial \sigma}{\partial c} \right)_s = 0.
\] 

(76)

Then from Eq.(73) and Eq.(74), we get the condition
\[
\frac{k_1' a^s}{k_{-1}' b^s} = \left( \frac{k_3 c^s}{k_{-3} a^s} \right)^{k_{-3}/k_1'} = \left( \frac{k_2 b^s}{k_{-2} c^s} \right)^{k_2/k_{-1}}.
\]

Hence
\[
\frac{k_3 c^s}{k_{-3} a^s} = \left( \frac{k_2 b^s}{k_{-2} c^s} \right)^{k_2/k_{-1}} k_{-3}.
\] 

(77)

From Eq.(75), one further gets
\[
\frac{k_3 c^s}{k_{-3} a^s} = \left( \frac{k_2 b^s}{k_{-2} c^s} \right)^{k_{-2}/k_3}.
\] 

(78)

Comparing the right hand sides of Eq.(77) and Eq.(78), we get
\[
\frac{k_1' k_2 k_3}{k_{-1}' k_{-2} k_{-3}} = 1.
\]

The above condition is fulfilled when the ABC cyclic reaction network obeys detailed balance. Therefore, it is seen that the NESS must be the state of TE to have minimum EPR, as emphasized by Ross et. al. [31].

Now coming to the ABC linear network, discussed in Section III.B., we obtain from Eq.(69)
\[
\left( \frac{\partial \sigma}{\partial b} \right)_s = k_2 \ln \frac{k_2 b^s}{k_{-2} c^0} - k_{-1} \ln \frac{k_1 a^0}{k_{-1} b^s}.
\] 

(79)

at NESS. Setting \( \left( \frac{\partial \sigma}{\partial b} \right)_s = 0 \), we get
\[
b^s = \left( \frac{k_1 a^0}{k_{-1}} \right)^{k_{-1} + k_2} \left( \frac{k_2 c^0}{k_2} \right)^{k_{-1} + k_2}.
\] 

(80)
Now putting the expression of $b^e$ from Eq. (67) in Eq. (80), one finds

$$b^s = (b^e)^{\frac{k_1+1}{k_1}} (b^e)^{\frac{k_2}{k_1+1}} = b^e.$$  \hfill (81)

Thus, the EPR is again a minimum only at TE.

5 Conclusion

Focusing particularly on chemical reactions, in this endeavor, we have established a connection between the EPR and chemical reaction rate. Both cyclic and linear networks are considered that can attain either a TE or a NESS. We have shown that the EPR in these systems is proportional to the square of the reaction velocity around TE. We have further established that the result is not valid around a NESS. Hence, our result can be used to theoretically differentiate a NESS from a TE. Another way is provided by Ross et al. [31] that relies on the behavior of the MEPP. Thus, the two features, viz., (i) proportionality of EPR to the square of the reaction velocity near a TE and (ii) EPR having its minimum at that TE, have a common thread. Both of them are invalid when the state is a NESS. Our findings should be generalizable to more complex reaction networks and such studies will be reported in due course.

Acknowledgment

K. Banerjee acknowledges the University Grants Commission (UGC), India for Dr. D. S. Kothari Fellowship. The authors are grateful to Prof. D. S. Ray for a thorough discussion.

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Notes

1. The EPR $\sigma(t)$ in Eq.(7) should be written, more precisely, as

$$\sigma(t) = \frac{1}{T} \sum_{i=1}^{3} J_{i}^{\text{kin}}(t) X_{i}(t), \quad (7')$$

$$\sigma^{\text{th}}(t) = \frac{1}{T} \sum_{i=1}^{3} J_{i}^{\text{kin}}(t) X_{i}^{\text{th}}(t), \quad (7a)$$

$$\sigma^{\text{kin}}(t) = \frac{1}{T} \sum_{i=1}^{3} J_{i}^{\text{kin}}(t) X_{i}^{\text{kin}}(t). \quad (7b)$$

$J_{i}$ is always kinetic in nature, as in Eqs (8)-(10). Eq.(11) is more precisely

$$X_{i}^{\text{th}}(t) = \mu_{A} - \mu_{B}, \quad (11a)$$

$$X_{i}^{\text{kin}}(t) = T \ln \frac{k_{1}a(t)}{k_{-1}b(t)}. \quad (11b)$$

Similar definitions apply to Eqs (12)-(13).

The distinctions may be appreciated in view of the following:

(a) $J_{i}$ cannot be written as a linear combination of $X_{i}^{\text{th}}$ near equilibrium. Thus, Onsager linear relations are recovered only when one uses $X_{i}^{\text{kin}}$.

(b) The equality appearing in Eqs (11)-(13) rests on the additional assumption of van’t Hoff: An equilibrium constant between a reactant and a product is expressible as a ratio of forward and backward rate constants.

(c) It is a standard convention to define a steady state (SS) as a state where all time-dependences in observables vanish. Hence, here, fluxes are equal, as in Eq.(15). A TE state, on the other hand, is the one with all forces, $X_{i}^{\text{th}}$, equal to zero.

(d) Note, however, that $\sigma^{\text{th}}(\text{SS}) = 0$ because $\sum_{i} X_{i}^{\text{th}} = 0$ (cf. Eq.(13)) and all fluxes are equal. But, $\sigma^{\text{kin}}(\text{SS})$ is not equal to zero. Its vanishing at SS will be ensured only when detailed balance (DB) is obeyed.

(e) In view of (d), one observes that the role of DB is important only when (b) is assumed a priori.

2. Reaction rate plays a premier role in the present endeavor. Its link with the EPR that we have established is specific to chemical reaction systems. Such a kinship is difficult to obtain in a general way because the
thermodynamic forces may not always be easily expressible in terms of the kinetic ones, as has been accomplished here in Eqs (11)-(13).

3. In going from Eq. (28) to Eq. (29), we have invoked the finite difference approximation to the differential. Thus, $\dot{\delta}_a = \dot{a} \approx \delta_a / \tau$.

4. The quantity $\tau$ in Eq. (29) refers to a time before the attainment of a SS or a TE. Hence, the above association is not in anyway connected to a Taylor expansion. We choose the SS (or TE) at $t = 0$ and consider a time $\tau$ before it (i.e., $t = -\tau$), so that one is close to SS, but not exactly at it. A Taylor expansion around SS is not permissible because no change in observables at any $t > 0$ is allowed.

5. We have actually two independent variables in the cyclic triangular reaction system. But, it will be unwise to conclude on the basis of Eq. (32) that $\delta_b$ and $\delta_a$ are dependent. Indeed, they are independent. The connection via $f_1$ shows only that $\delta_b$ cannot be arbitrary for some given $\delta_a$. Note that $f_1$ contains the characteristic reaction constants plus the time gap $\tau$. At a different $\tau$, $f_1$ will change, thus altering $\delta_b$, even if $\delta_a$ is held fixed.

As an example, consider the triangular system with all rate constants ($k_1$ to $k_{-3}$) equal to unity. The conventional solutions (initial condition at $t = 0$) read as

$$a(t) = (1/3) - (1/3)(1 - 3a_0) \exp [-3t]$$
$$b(t) = (1/3) - (1/3)(1 - 3b_0) \exp [-3t].$$

The variables $a(t)$ and $b(t)$ are independent. However, after a time $\tau$, one will find that

$$a(\tau) = a_0 + \tau(1 - 3a_0)$$
$$b(\tau) = b_0 + \tau(1 - 3b_0).$$

Therefore, one can write that

$$b(\tau) = f_1 a(\tau)$$

with

$$f_1 = (b_0 + \tau(1 - 3b_0))/(a_0 + \tau(1 - 3a_0)).$$

We thus see that $f_1$ merely links the changes of two independent variables. It should not be confused with a proportionality constant.

6. The present work is not an application of the MEPP. Rather, it provides an alternative characterization of NESS vs. TE. The MEPP also distinguishes these two kinds of states. So we explored any possible connection of our endeavor with the MEPP.