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Entropy production in the reversible Oregonator oscillatory model: The calculation of chemical entropy production rate in the course of a complete oscillation cycle

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Field expanded the five step Oregonator model of the oscillatory Belousov-Zhabotinskii reaction by introducing reversibility into the various steps. The present work involves the calculation of entropy flow ($\phi[S]$) and entropy production ($P[S]$) in a specially designed reversible Oregonator. Entropy flow due to thermostatic temperature control and the osmotic transport of the reactants (A,B) and product (P) into and out of the reactor has been considered. Entropy production (e.p.) due to mixing of the reactants and product, diffusion of the intermediates (X, Y, and Z), and most importantly the chemical reactions has been considered. An attempt has been made to calculate the e.p. of the model using the results obtained by Field by numerical integration of the appropriate stiff kinetic differential equations. The following new results are obtained: (a) Limit cycle traces of e.p. against concentration of the oscillatory intermediates have been constructed. (b) The model resides on the low e.p. branch for about 97% of the total oscillation period and then switches to the high e.p. branch accompanied by about 10^5 -fold increase of the value. (c) The time average of e.p. is obtained for a complete cycle and is compared with the value at the true unstable steady state.

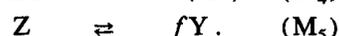
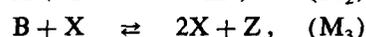
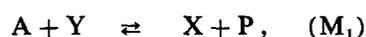
I. INTRODUCTION

The Field, Körös, and Noyes¹ (FKN) mechanism of the Belousov-Zhabotinskii² (BZ) reaction is the most highly developed of those of the several oscillatory chemical reactions understood so far. Field and Noyes³ abstracted a skeletonized version which retains most of the important features of the complete FKN mechanism. They referred to this model as the "Oregonator." Field⁴ considered the case in which the reactions of the Oregonator steps are reversible as it is a more realistic representation of the chemistry involved and increases the confidence about the success of this oscillatory kinetic model.

In the BZ reaction, malonic acid (MA) is oxidized by potassium bromate in the presence of cerium ions in a sulfuric acid medium. The reactions shown in Table I indicate the characteristic features of the overall reaction. Reactions (A₁) and (A₂) are dominant at higher bromide ion concentrations, while reactions (B₁) and (B₂) are dominant at lower bromide ion concentrations. Oscillations occur because

reactions (A₁) and (A₂) consume bromide ion and thus may lead the system to the regime dominated by reactions (B₁) and (B₂); but these latter reactions produce Ce(IV), which liberates bromide ion in reaction (C). The control of the system by reactions (A₁) and (A₂) returns after sufficient release of bromide ions by reaction (C).

The reversible⁴ Oregonator kinetic model is represented by the following five reversible steps:



When compared to cerium catalyzed BZ² reaction, the species identities are $A \equiv B \equiv \text{BrO}_3^-$, $X \equiv \text{HBrO}_2$, $Y \equiv \text{Br}^-$, $Z \equiv 2\text{Ce(IV)}$, and $P \equiv \text{HOBr}$; f denotes a stoichiometric factor. The present work involves the calculation of entropy flow and entropy production in this fascinating, reversible oscillatory model and also correlates chemical entropy pro-

TABLE I. Characteristic reaction steps of the Belousov-Zhabotinskii reaction.

Reactions	k_+ ^a	k_- ^a
(A ₁) $\text{Br}^- + \text{BrO}_3^- + 2\text{H}^+ \rightleftharpoons \text{HOBr} + \text{HBrO}_2$	$2.1 \text{ M}^{-2} \text{ s}^{-1}$	$1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$
(A ₂) $\text{Br}^- + \text{HBrO}_2 + \text{H}^+ \rightleftharpoons 2\text{HOBr}$	$2 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$	$5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$
(B _{1a}) $\text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \rightleftharpoons 2\text{BrO}_2 + \text{H}_2\text{O}$	$1 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$	$2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
(B _{1b}) $2\text{Ce(III)} + 2\text{BrO}_2 + 2\text{H}^+ \rightleftharpoons 2\text{HBrO}_2 + 2\text{Ce(IV)}$
(B ₁) $2\text{Ce(III)} + \text{HBrO}_2 + \text{BrO}_3^- + 3\text{H}^+ \rightleftharpoons 2\text{Ce(IV)} + 2\text{HBrO}_2 + \text{H}_2\text{O}$
(B ₂) $2\text{HBrO}_2 \rightleftharpoons \text{HOBr} + \text{BrO}_3^- + \text{H}^+$	$4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	$2 \times 10^{-10} \text{ M}^{-2} \text{ s}^{-1}$
(C) $\text{Ce(IV)} + \text{BrMA} + \text{MA} \rightleftharpoons f\text{Br}^- + \text{Ce(III)} + \text{other products}$		

^a k_+ and k_- are, respectively, forward and reverse rate constants; MA represents malonic acid and f is a stoichiometric coefficient.

duction rate with the intermediate concentrations X , Y , and Z at different stages in a complete oscillation cycle using numerical results of Field⁴ on the reversible Oregonator.

II. DESIGN AND RATE CONSTANT ASSIGNMENTS

For comparison with experiment, the conditions $[\text{BrO}_3^-] = 0.06 \text{ M}$ and $[\text{H}^+] = 0.8 \text{ M}$ are adopted. The concentrations of A , B , and P are assumed to be maintained at a constant value by flow through a semipermeable membrane or other appropriate device through which X , Y , and Z intermediates cannot pass.

Comparison of steps (M_1), (M_2), and (M_4) with reactions (A_1), (A_2), and (B_2) of Table I leads to the relations

$$\begin{aligned}k_{M_1} &= k_{A_1} [\text{H}^+]^2 = 1.34 \text{ M}^{-1} \text{ s}^{-1}, \\k_{M_2} &= k_{A_2} [\text{H}^+] = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}, \\k_{M_{-1}} &= k_{A_{-1}} = 1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}, \\k_{M_{-2}} &= k_{A_{-2}} = 5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}, \\k_{M_4} &= k_{B_2} = 4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}, \\k_{M_{-4}} &= k_{B_{-2}} = 1.6 \times 10^{-10} \text{ M}^{-2} \text{ s}^{-1}.\end{aligned}$$

The rate constant assignment of steps ($M_{\pm 3}$), and ($M_{\pm 5}$) are taken from the work of Field⁴ as

$$\begin{aligned}k_{M_3} &= k_{B_{1a}} [\text{H}^+] = 8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}, \quad k_{M_5} = 1 \text{ s}^{-1}, \\k_{M_{-3}} &= 4.8 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}, \quad k_{M_{-5}} = 10^{-5} \text{ s}^{-1}.\end{aligned}$$

Step (M_5) corresponds to the reduction of Ce(IV) to Ce(III) by MA and BrMA with the liberation of Br^- ion [reaction (C)]. The value of the stoichiometric coefficient f

corresponds to the overall production of $f \text{ Br}^-$ ions for each two ceric ions consumed. The simple mass action definition of the equilibrium constant for step (M_5) is not applicable. However in the kinetic equation presented in Sec. III, the stoichiometry of the step (M_5) is treated normally. The assigned values of k_{M_5} and $k_{M_{-5}}$ maintain the equilibrium position of step (M_5) far to the right. For a given set of rate constants of the component steps, the values of A , B , and P define the distance from equilibrium.

III. KINETIC STABILITY ANALYSIS

The mass-action rate expressions describing the dynamics of the model are

$$\begin{aligned}\dot{X} &= k_{M_1}AY - k_{M_{-1}}XP - k_{M_2}XY + k_{M_{-2}}P^2 + k_{M_3}BX \\ &\quad - k_{M_{-3}}X^2Z - 2k_{M_4}X^2 + 2k_{M_{-4}}BP,\end{aligned}\quad (1a)$$

$$\begin{aligned}\dot{Y} &= -k_{M_1}AY + k_{M_{-1}}XP - k_{M_2}XY + k_{M_{-2}}P^2 \\ &\quad + fk_{M_5}Z - fk_{M_{-5}}Y,\end{aligned}\quad (1b)$$

$$\dot{Z} = k_{M_3}BX - k_{M_{-3}}X^2Z - k_{M_5}Z + k_{M_{-5}}Y,\quad (1c)$$

where A , B , P , X , Y , and Z refer to the concentrations of the respective species; dot ($\dot{}$) represents differentiation with respect to time. To get the steady state solution, Eqs. (1a)–(1c) may be reduced to a polynomial in X and this may be solved numerically for X_0 (steady state value) using an interval-halving technique.

The stability of the stationary state is determined by the signs of real parts of the eigen values of the Jacobian matrix (\mathbf{J}) evaluated at the stationary state.

$$\begin{aligned}\mathbf{j} &= \frac{\partial(\dot{X}\dot{Y}\dot{Z})}{\partial(X,Y,Z)} \\ &= \begin{bmatrix} -k_{M_{-1}}P - k_{M_2}Y + k_{M_3}B - 2k_{M_{-3}}XZ - 4k_{M_4}X & k_{M_{-1}}P - k_{M_2}Y & k_{M_3}B - 2k_{M_{-3}}XZ \\ k_{M_1}A - k_{M_2}X & -k_{M_1}A - k_{M_2}X - fk_{M_{-5}} & k_{M_{-5}} \\ -k_{M_{-3}}X^2 & fk_{M_5}Z & -2k_{M_{-3}}X^2 - k_{M_5} \end{bmatrix}.\end{aligned}\quad (2)$$

The eigenvalues λ_i ($i = 1 \rightarrow 3$), are the roots of the third order polynomial,

$$\det(\mathbf{J} - \lambda \mathbf{1}) = 0.\quad (3)$$

A positive real part of any eigenvalue of the Jacobian matrix evaluated at the steady state (X_0, Y_0, Z_0) indicates instability of the stationary state.

IV. ENTROPY PRODUCTION

The Prigogine⁵ arguments distinguish entropy production in a system and entropy production associated with any fluxes between the system and its surroundings when the system is open in the thermodynamic sense. We may write for the entropy production per unit time

$$\frac{diS}{dt} = P[S] = \int \sigma[S] dV \geq 0,\quad (4)$$

where $\sigma[S]$ is the entropy production source per unit time

and volume and dV is the volume element.

Likewise, we have for the entropy flow

$$\frac{deS}{dt} = \phi[S] = \int \varphi_n d\Omega,\quad (5)$$

where φ_n is the component of the entropy current along the interior normal n to the boundary surface Ω .

A. Entropy flow in the model

There are two kinds of contribution to the entropy flow in the model described, one due to thermostatic temperature control and one due to fluxes of matter due to osmotic transport through the semipermeable membrane.

The five component reaction steps are supposed to take place inside the open isothermal reactor, and each reaction is assumed to have a known heat of reaction value. Therefore, the flow of heat between the reactor and the thermostat through the isothermal wall contributes to the flow of en-

TABLE II. Reaction rates and affinities of the different steps of the Oregonator.^a

i	Reactions (M_i)	Reaction rate (w_i)	Exp (A_i/RT)
1	(M_1)	$k_{M_1}AY - k_{M_{-1}}XP$	$(k_{M_1}AY/k_{M_{-1}}XP)$
2	(M_2)	$k_{M_2}XY - k_{M_{-2}}P^2$	$(k_{M_2}XY/k_{M_{-2}}P^2)$
3	(M_3)	$k_{M_3}BX - k_{M_{-3}}X^2Z$	$(k_{M_3}B/k_{M_{-3}}XZ)$
4	(M_4)	$2k_{M_4}X^2 - 2k_{M_{-4}}BP$	$(k_{M_4}X^2/k_{M_{-4}}BP)$
5	(M_5)	$k_{M_5}Z - k_{M_{-5}}Y$	$(k_{M_5}Z/k_{M_{-5}}Y)$

^a $k_{M_{\pm i}}$ are the rate constants for the reactions $M_{\pm i}$; A_i is the affinity of the reaction M_i and $A, B, P, X, Y,$ and Z are the concentrations of the reactants, product, and intermediates, respectively; w_i is the rate of reaction i .

ropy, whose value⁵ [φ_n (thms)] per unit area of the surface Ω is given by

$$\varphi_n \text{ (thms)} = w_j T_{,j}^{-1}, \quad (6)$$

where w_j is the heat flow along the geometrical coordinate j , T is the absolute temperature, and the subscript j is used for the derivation symbol $\partial/\partial x_j$ with respect to coordinate x_j .

The components A and B are coming in and the product P is going out of the model system by osmotic flow through the semipermeable membrane. Osmotic force per unit area can be expressed in terms of the concentration difference (ΔC_S) of the solute (S) across the membrane⁶ by $\sigma \Delta C_S RT$, where σ is the nonideality factor of the semipermeable membrane, R is the gas constant, and T is the absolute temperature. Therefore, the entropy flow $\varphi_{n(\text{osm})}$ per unit area due to osmotic transport of the components A, B, and P is given by

$$\varphi_{n(\text{osm})} = T^{-1} \sigma^2 (RT)^2 (L_A \Delta C_A^2 + L_B \Delta C_B^2 - L_P \Delta C_P^2), \quad (7)$$

where L_i is the phenomenological coefficient applicable to the osmotic transport of the component i ($i = A, B, P$, respectively).

Therefore, the total entropy flow $\phi[S]$ is given by

$$\begin{aligned} \phi[S] &= \int \varphi_n d\Omega \\ &= WT^{-1} + T^{-1} (RT)^2 \sigma^2 \Omega (L_A \Delta C_A^2 \\ &\quad + L_B \Delta C_B^2 - L_P \Delta C_P^2). \end{aligned} \quad (8)$$

B. Entropy production $\mathcal{P}[S]$ in the model

There are three kinds of contribution to the entropy production in the described model. One due to mixing of the chemical species, the second due to diffusion of the intermediates X, Y, Z whose concentrations vary excepting at the steady state, and third and most importantly the contribution due to chemical reaction.

The entropy of mixing⁷ when 1 mol of i is introduced into a system is given by

$$S_{\text{mix}} = - \ln x_i \quad (9)$$

when x_i is the mole fraction of the component i . Since it is assumed that A, B, and P are kept constant, there are necessarily rates of entropy production due to the entropy of mixing of the in and outflow of A, B, and P. These rates per unit volume (σ_{mix}) are expressed with the help of Table II as

$$\begin{aligned} \sigma_{\text{mix}} &= -w_1 \ln(A/N) + w_1 \ln(P/N) + 2w_2 \ln(P/N) \\ &\quad - w_3 \ln(B/N) + w_4 \ln(P/N) + w_4 \ln(B/N) \\ &= \ln \left[\left(\frac{P}{A} \right)^{(k_{M_1}AY - k_{M_{-1}}XP)} \cdot \left(\frac{P}{N} \right)^{2(k_{M_2}XY - k_{M_{-2}}P^2)} \right. \\ &\quad \left. \cdot \left(\frac{N}{B} \right)^{(k_{M_3}BX - k_{M_{-3}}X^2Z)} \cdot \left(\frac{PB}{N^2} \right)^{(2k_{M_4}X^2 - 2k_{M_{-4}}BP)} \right], \end{aligned} \quad (10)$$

where N is the total molar concentration.

The entropy production⁸ (σ_{diff}) due to diffusion of the components X, Y, and Z is given by the expression

$$\sigma_{\text{diff}} = -T^{-1} \sum_{i=1}^3 J_i (\text{grad } \mu_i)_T, \quad (11)$$

where

$$J_i = \rho_i (v_i - v), \quad (12)$$

$i = 1, 2, 3$ and corresponds to X, Y, Z species, respectively, and v is the barycentric velocity defined by

$$v = \sum_{i=1}^3 \rho_i v_i \rho^{-1}, \quad (13)$$

where ρ is the total density defined by

$$\rho = \sum_{i=1}^3 \rho_i. \quad (14)$$

However, we can neglect this contribution if the reaction mixture is assumed to be stirred uniformly. In that case we would also have to consider entropy production due to stirring.

The rate of entropy production due to chemical reaction⁷ (σ_{chem}) is given by the expression

$$\sigma_{\text{chem}} = T^{-1} \sum_{i=1}^5 w_i A_i, \quad (15)$$

where w_i and A_i are velocity and affinity of the i th reaction, respectively. Substituting the values of the velocities and affinities from Table II, and then applying simple algebra, one obtains

$$\begin{aligned} \sigma_{\text{chem}} &= T^{-1} \left[(k_{M_1}AY - k_{M_{-1}}XP) RT \ln \frac{k_{M_1}AY}{k_{M_{-1}}XP} \right. \\ &\quad + (k_{M_2}XY - k_{M_{-2}}P^2) RT \ln \frac{k_{M_2}XY}{k_{M_{-2}}P^2} \\ &\quad \left. + (k_{M_3}BX - k_{M_{-3}}X^2Z) RT \ln \frac{k_{M_3}B}{k_{M_{-3}}XZ} \right] \end{aligned}$$

TABLE III. Data from the work of Field (Ref. 4) on the reversible Oregonator model.

Observation (i)	Time in s (t_i)	$\log X^a$	$\log Y^a$	$\log Z^a$	$(5 + \log \sigma_{\text{chem}})_i$	$\bar{\sigma}_{\text{chem}}^b$ (e.u. s $^{-1}$)
1	~0	-5.50	-7.90	-7.00	3.838	
2	0.5	-5.50	-6.50	-3.50	4.091	
3	1.0	-6.00	-4.00	-3.50	5.924	
4	1.25	-10.25	-4.00	-3.50	2.925	
5	2.50	-10.25	-3.70	-4.40	2.254	
6	5.00	-10.25	-3.80	-5.50	1.927	
7	7.50	-10.25	-4.00	-6.75	1.690	
8	10.00	-10.25	-4.20	-7.30	1.678	
9	12.50	-10.25	-4.30	-7.50	1.373	
10	15.00	-10.25	-4.40	-7.60	1.262	
11	17.50	-10.25	-4.50	-7.60	1.155	7.268×10^{-5}
12	20.00	-10.25	-4.70	-7.60	0.936	
13	22.50	-10.25	-4.90	-7.60	0.730	
14	25.00	-10.25	-5.20	-7.60	0.415	
15	27.50	-10.25	-5.30	-7.60	0.312	
16	30.00	-10.25	-5.40	-7.60	0.205	
17	32.50	-10.25	-5.50	-7.60	0.177	
18	35.00	-10.15	-5.60	-7.60	0.083	
19	37.50	-10.10	-6.00	-7.60	0.214	
20	40.00	-10.00	-6.25	-7.50	0.309	
21	42.00	-9.50	-6.50	-7.00	0.050	
22	42.80	-5.50	-7.90	-7.00	3.838	

$X_0 = 2.3 \times 10^{-3}$ (M), $Y_0 = 2.8 \times 10^{-7}$ (M), $Z_0 = 1.03 \times 10^{-6}$ (M); subscript "0" indicates the value at the steady state.

$${}^b (5 + \log \sigma_{\text{chem}}) = \frac{\sum_i t_i (5 + \log \sigma_{\text{chem}})_i}{\sum_i t_i} = 0.8614; (\sigma_{\text{chem}})_0 = 5.946 \times 10^{-3} \text{ e.u. s}^{-1}.$$

$$+ (2k_{M_4}X^2 - 2k_{M_{-4}}BP)RT \ln \frac{k_{M_4}X^2}{k_{M_{-4}}BP} + (k_{M_5}Z - k_{M_{-5}}Y)RT \ln \frac{k_{M_5}Z}{k_{M_{-5}}Y} \quad (16)$$

V. RESULTS AND DISCUSSION

Substituting the assigned values of A , B , and the $k_{M_{\pm i}}$'s ($i = 1 \rightarrow 5$) as has been discussed in Sec. II, one can formulate an expression for σ_{chem} for different sets of concentrations of the intermediates X , Y , and Z in terms of the stoichiometric factor f and the product concentration P . The ratio A/P measures the position of the Oregonator steady state with respect to equilibrium. The steady state may be maintained far from equilibrium by increasing the ratio A/P .

Field⁴ discussed in detail the stability of the reversible Oregonator steady state as a function of the stoichiometric factor f , the concentration of the product P , and the assumed value of k_{M_5} . In the same paper he numerically integrated the kinetic equations (1a)–(1c) for the reversible Oregonator using a BASIC version of the Gear algorithm for numerical integration of stiff differential equations. Limit cycle oscillations of a form very similar to those seen in the Belousov–Zhabotinskii reaction were found (*vide* Figs. 3 and 4 of Ref. 4) assuming $f = 1$ and $P = 10^{-4}$ M. The oscillation period was found to be about 42.8 s. The values of different sets of concentrations of X , Y , and Z obtained from this paper have been listed in Table III at different stages in a complete oscillation cycle. Here, in addition to the assigned values discussed in Sec. II, let us further assign $P = 10^{-4}$ M and $f = 1$. Equation (16) then takes the form

$$10^3 \times \sigma_{\text{chem}} = 4.56 \left[(80.4Y - 10^3X) \log \frac{0.0804Y}{X} + (1.6 \times 10^{12}X \cdot Y - 5 \times 10^{-10}) \log (0.32 \times 10^{22}X \cdot Y) + (0.48 \times 10^6X - 4.8 \times 10^{14}X^2Z) \log \frac{10^{-9}}{XZ} + (8 \times 10^{10}X^2 - 0.192 \times 10^{-11}) \log (41.666 \times 10^{21} \cdot X^2) + (10^3Z - 10^{-2}Y) \log \left(\frac{10^5Z}{Y} \right) \right] \quad (17)$$

It is interesting to note that by applying Eq. (17) one can calculate σ_{chem} for each set of values of X , Y , and Z during oscillatory phases of the reversible Oregonator. It should be remembered that the assumptions made during formulation of Eq. (17) are essentially $f = 1$ and $P = 10^{-4}$ M; these were

the assumptions made by Field⁴ during numerical integration of the Oregonator differential equations (1a)–(1c). The entropy production values (σ_{chem}) calculated by Eq. (17) have been listed in a different column in the same table (Table III) for each set of values of X , Y , and Z . σ_{chem} values

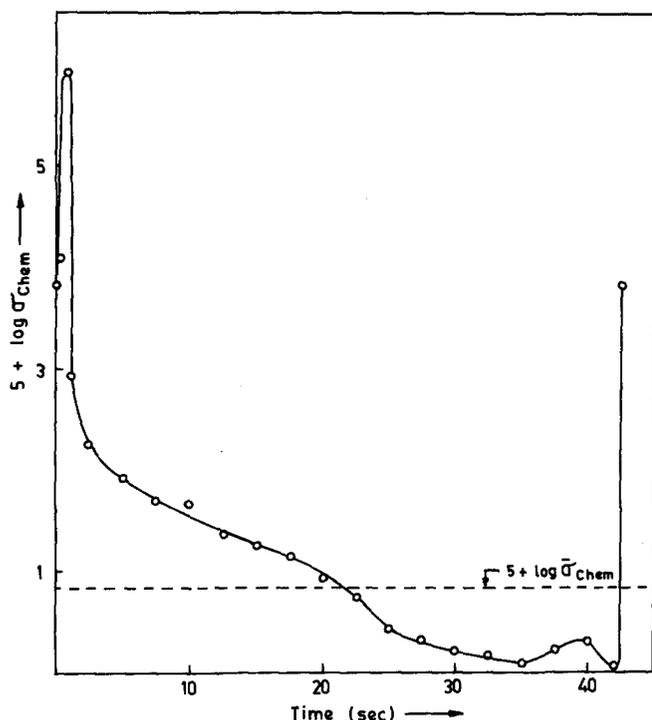


FIG. 1. A plot of σ_{chem} against time in the reversible Oregonator model. The data are from Table III. The dotted line indicates $\bar{\sigma}_{chem}$ in one oscillation cycle.

have been plotted against time (t) in the course of a complete oscillation cycle (Fig. 1). The limit cycle trajectories of σ_{chem} vs X , σ_{chem} vs Y , and σ_{chem} vs Z have been shown in Figs. 2, 3, and 4, respectively. The time average value ($\bar{\sigma}_{chem}$) during the illustrated oscillation cycle has been cal-

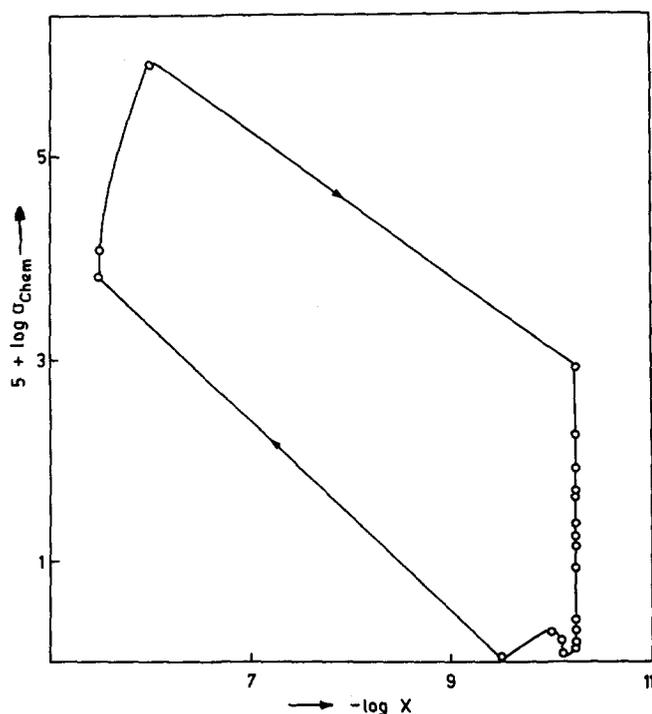


FIG. 2. A limit cycle trace of σ_{chem} against concentration X in the reversible Oregonator model. The data are from Table III.

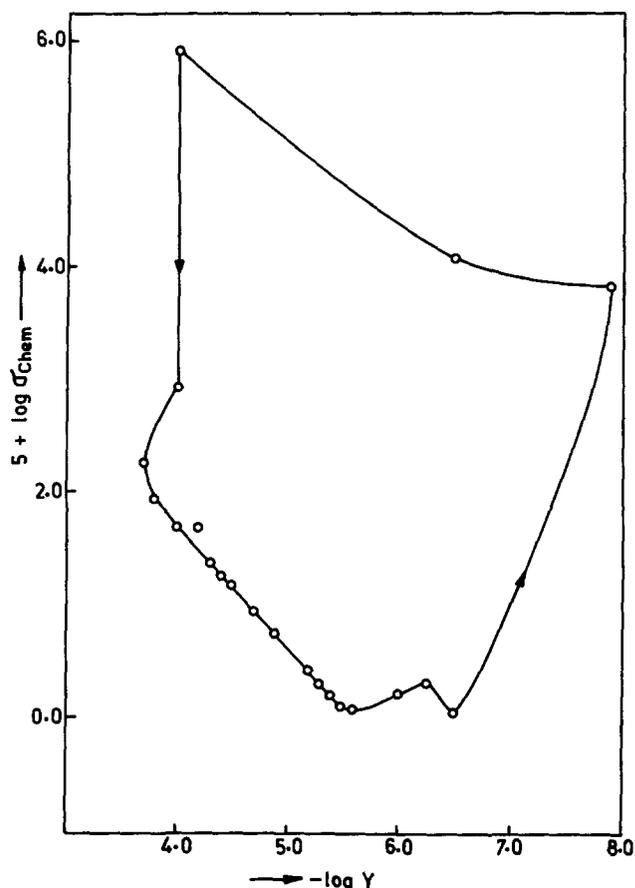


FIG. 3. A limit cycle trace of σ_{chem} against concentration Y in the reversible Oregonator model. The data are from Table III.

culated from Fig. 1 to be 7.268×10^{-5} e.u. s^{-1} and is represented by a dotted line in the same figure. The calculated entropy production [$(\sigma_{chem})_0$] at the true unstable steady state is 5.946×10^{-3} e.u. s^{-1} .

From the limit cycle trajectories of Figs. 2–4, it is clear that oscillation in the reversible Oregonator model of Field⁴ results from the transition between two unstable steady state branches. One steady state branch lies in the high entropy production (e.p.) mode and the other in the low e.p. mode. The transition between these two unstable steady state branches takes place when the required kinetic condition for oscillatory instability is maintained (*vide* Sec. III). It is very interesting to note that for most of the time ($\sim 97\%$) during the illustrated oscillation cycle, the Oregonator remains at the low e.p. steady state branch and there is about 10^5 -fold increase of this value when it switches to high e.p. mode.

VI. CONCLUSION

Chemical oscillation in the B–Z reaction is an example of higher-order time structure accompanied by decrease^{5,9,11} of entropy production rate. This theoretical treatment of reversible Oregonator is an extension of the work of Field⁴ with an effort to investigate the role of chemical entropy production rate in the course of a complete oscillation cycle. The principal objective of this work is to correlate the entropy production with the concentrations of the interme-

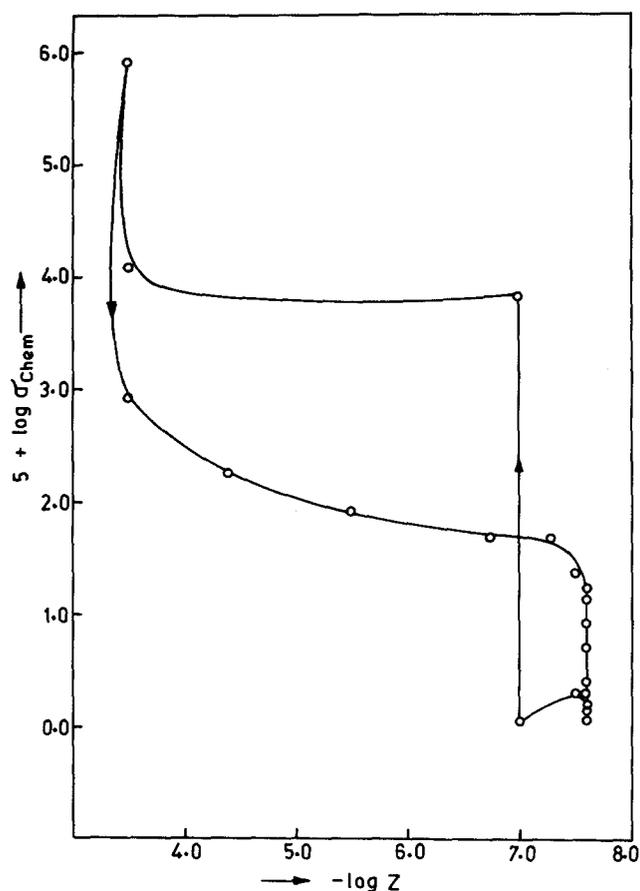


FIG. 4. A limit cycle trace of σ_{chem} against concentration Z in the reversible Oregonator model. The data are from Table III.

diates X , Y , and Z during oscillatory state as well as true unstable steady state in this fascinating oscillatory kinetic model.

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