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Instabilities and oscillations in "The Reversible Oregonator Model": A thermodynamic approach to calculate the excess entropy production ($\delta_m P$) and the corresponding antisymmetric function ($\delta_m II$)

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Near equilibrium thermodynamic analysis of the reversible "Oregonator kinetic model" has been done using the entropy production technique of Prigogine in the range of the validity of the Onsager relations. Expressions for the excess entropy production ($\delta_m P$) and the corresponding antisymmetric function ($\delta_m II$) have been derived in terms of the rate constants of the steps, the concentrations of the reactants and products, steady state concentrations of the intermediates, and the coefficients of the real and imaginary parts of the complex differentials δX , δY , and δZ , which represent, respectively, the fluctuations from the steady state concentrations of the intermediates X , Y , and Z . Factors destabilizing the steady states have been determined and steps other than autocatalytic and cross catalytic are also found to be involved.

INTRODUCTION

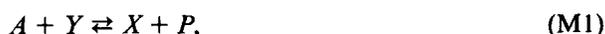
Prigogine and co-workers^{1,2} proposed a chemical scheme exhibiting limit cycle behavior. This scheme has been called the "Brusselator" by Tyson³ and is comprised of four steps. Two reactants A and B react giving two products D and E through two intermediates X and Y . Prigogine analyzed the thermodynamic stability of the Brusselator by an entropy production technique to find the point beyond which instability of the steady states sets in. This scheme is useful as an ideal oscillating model due to its extreme simplicity. But a basic defect is that the autocatalytic step involved is termolecular, which is not expected in a chemical reaction taking place under normal conditions.

In 1974, Field and Noyes⁴ proposed the "Oregonator" kinetic model composed of five steps, two reactants, two products, and three intermediates to model the essential features of the mechanism of the Belousov-Zhabotinskii reaction,⁵ the metal-ion catalyzed oscillatory bromate oxidation of malonic acid. They formed this scheme by replacing the autocatalytic termolecular step of the Brusselator by two bimolecular steps. This scheme is rather complicated compared to the Brusselator, but its difficulty is not so great as to overwhelm its attractiveness as a model of a real oscillating system.

It seems well established that instabilities and chemical oscillations are far from equilibrium phenomena, and the Oregonator model proposed by Field and Noyes⁴ meets this requirement by assuming irreversibility of the steps. Field⁷ in 1975 took into account reversibility of the various steps to propose a reversible Oregonator as it would become a more realistic representation of the chemistry occurring in the Belousov-Zhabotinskii reaction.⁵

DESIGN OF THE MODEL

The reversible Oregonator⁷ is written



when compared to the cerium catalyzed Belousov-Zhabotinskii reaction $A = B = \text{BrO}_3^-$, $X = \text{HBrO}_2$, $Y = \text{Br}^-$, $Z = 2 \text{Ce(IV)}$, and $P = \text{HOBr}$; f denotes a stoichiometric factor. Species A and B are consumed and P is produced through the intermediates X , Y , and Z . The simplest stoichiometric combination of the steps (M1)–(M5) such that there is no change in the concentrations of the intermediates is $fM_1 + fM_2 + 2M_3 + M_4 + 2M_5$ and this corresponds to the overall stoichiometry



Other appropriate linear combinations of the stoichiometries of the component equations have been formulated by Noyes.⁶ Regarding design of the scheme, it may be considered that the reactants A and B are fed from outside continuously at the same rate as they are being consumed, and P is taken out of the model system at the rate it is being formed. Thus the open system approximation keeps the concentrations of A , B , and P constant.

THERMODYNAMIC ASPECTS

To understand the thermodynamic background, one should consider the behavior of a dissipative system^{1,2} in

the neighborhood of a steady state (for a single normal mode of complex frequency λ). This is guided by the relations

$$\lambda_r^2 \delta^2 S = \lambda_r \delta_m P \leq 0 \quad (1)$$

and

$$\lambda_i^2 \delta^2 S = \lambda_i S_{\delta m \pi} \leq 0, \quad (2)$$

where $\lambda = \lambda_r + i\lambda_i$ (subscripts r and i indicate real and imaginary parts, respectively); $\delta^2 S$ is the excess entropy and $\delta_m P$, $\delta_m \pi$ are defined, respectively, as

$$\delta_m P = \frac{1}{2} \int dV \sum_{\rho} (\delta \omega_{\rho}^* \delta A_{\rho} + \delta \omega_{\rho} \delta A_{\rho}^*), \quad (3)$$

which is the excess entropy production in the case of a single normal mode and its complex conjugate. The quantity

$$\delta_m \pi = \frac{i}{2} \int dV (\delta \omega_{\rho}^* \delta A_{\rho} - \delta \omega_{\rho} \delta A_{\rho}^*) \quad (4)$$

represents an antisymmetric function consisting of velocity (ω_i) and affinity (A_i) terms associated with the component chemical reaction steps ($i = 1, 2, \dots, \rho$), dV being the volume element.

The first relation (1) gives the stability criterion for a single normal mode ($\delta_m P > 0$ as $\lambda_r < 0$) and the second relation (2) shows that the sign of $\delta_m \pi$ is opposite to that of λ_i . One may therefore define two thermodynamic transition points. One is

$$\delta_m P = 0, \quad (5)$$

where there exists nontrivial normal modes with $\lambda_r = 0$ and the system is at (or around) a marginally stable steady state. The second transition point satisfies the condition

$$\delta_m \pi = 0 \quad (6)$$

and represents a critical state where $\lambda_i = 0$ and the steady state is aperiodic. Oscillation is therefore expected to take place when either the condition (6) for aperiodical¹ motion or the stability condition $\delta_m P \geq 0$ is violated.

ANALYSIS OF THE KINETIC MODEL

The kinetic behavior of the model system may be represented by

$$\frac{dX}{dt} = k_1 AY - k_{-1} XP - k_2 XY + k_{-2} P^2 + k_3 BX - k_{-3} X^2 Z - 2k_4 X^2 + 2k_{-4} BP \dots, \quad (a)$$

$$\frac{dY}{dt} = -k_1 AY + k_{-1} XP - k_2 XY + k_{-2} P^2 + f k_5 Z - f k_{-5} Y, \quad (b)$$

$$\frac{dZ}{dt} = k_3 BX - k_{-3} X^2 Z - k_5 Z + k_{-5} Y, \quad (c)$$

where k_i and k_{-i} are rate constants of the steps M_i and M_{-i} , respectively. From the set of kinetic equations (a)–(c), at the steady state ($\dot{X} = \dot{Y} = \dot{Z} = 0$) one gets nontrivial steady state solutions X_0 , Y_0 , and Z_0 from the known values of the rate constants⁴ and the concentrations of A , B , and P with the simplified assumption that the stoichiometric factor $f = 1$ (criterion of maximum sensitivity to oscillations discussed by Field and Noyes⁴).

As presented earlier in Eq. (3), the excess entropy production^{1,8,9} for a single normal mode and its complex conjugate in the neighborhood of the steady state of our kinetic model is given by

$$\delta_m P = \frac{1}{2} \int dV \sum_{\rho=1}^5 (\delta \omega_{\rho}^* \delta A_{\rho} + \delta \omega_{\rho} \delta A_{\rho}^*). \quad (7)$$

Substituting the velocity values ω_i ($i = 1, 2, \dots, 5$) and the chemical affinity values A_i ($i = 1, 2, \dots, 5$) defined by

$$A_i = RT \log(K_i/Q), \quad (8)$$

where K_i is the equilibrium constant for the i th reaction and $Q = [\text{product}]/[\text{reactant}]$, one gets

$$\begin{aligned} \delta_m P &= \frac{1}{2} \int dV [(\delta \omega_1^* \delta A_1 + \delta \omega_1 \delta A_1^*) + (\delta \omega_2^* \delta A_2 + \delta \omega_2 \delta A_2^*) + (\delta \omega_3^* \delta A_3 \\ &\quad + \delta \omega_3 \delta A_3^*) + (\delta \omega_4^* \delta A_4 + \delta \omega_4 \delta A_4^*) + (\delta \omega_5^* \delta A_5 + \delta \omega_5 \delta A_5^*)] \\ &= \frac{1}{2} \int dV \left[\delta(k_1 AY^* - k_{-1} X^* P) \delta \left(RT \log \frac{K_1 AY}{XP} \right) + \delta(k_1 AY - k_{-1} XP) \delta \left(RT \log \frac{K_1 AY^*}{X^* P} \right) \right. \\ &\quad + \delta(k_2 X^* Y^* - k_{-2} P^2) \delta \left(RT \log \frac{K_2 XY}{P^2} \right) + \delta(k_2 XY - k_{-2} P^2) \delta \left(RT \log \frac{K_2 X^* Y^*}{P^2} \right) \\ &\quad + \delta(k_3 BX^* - k_{-3} X^{*2} Z^*) \delta \left(RT \log \frac{K_3 B}{XZ} \right) + \delta(k_3 BX - k_{-3} X^2 Z) \delta \left(RT \log \frac{K_3 B}{X^* Z^*} \right) \\ &\quad + \delta(2k_4 X^{*2} - 2k_{-4} BP) \delta \left(RT \log \frac{K_4 X^2}{BP} \right) + \delta(2k_4 X^2 - 2k_{-4} BP) \delta \left(RT \log \frac{K_4 X^{*2}}{BP} \right) \\ &\quad \left. + \delta(k_5 Z^* - k_{-5} Y^*) \delta \left(RT \log \frac{K_5 Z}{Y} \right) + \delta(k_5 Z - k_{-5} Y) \delta \left(RT \log \frac{K_5 Z^*}{Y^*} \right) \right]. \end{aligned}$$

Considering A , B , P , and K constant throughout, one gets

$$\begin{aligned} \delta_m P = & \frac{RT}{2} \int dV \left[(k_{1A} \delta Y^* - k_{-1P} \delta X^*) \left(\frac{\delta Y}{Y} - \frac{\delta X}{X} \right) + (k_{1A} \delta Y - k_{-1P} \delta X) \left(\frac{\delta Y^*}{Y^*} - \frac{\delta X^*}{X^*} \right) + k_2 \left\{ (X^* \delta Y^* + Y^* \delta X^*) \right. \\ & \times \left(\frac{\delta X}{X} + \frac{\delta Y}{Y} \right) + (X \delta Y + Y \delta X) \left(\frac{\delta X^*}{X^*} + \frac{\delta Y^*}{Y^*} \right) \left. \right\} - \left\{ (k_3 B \delta X^* - 2k_{-3} X^* Z^* \delta X^* - k_{-3} X^{*2} \delta Z^*) \left(\frac{\delta X}{X} + \frac{\delta Z}{Z} \right) \right. \\ & + (k_3 B \delta X - 2k_{-3} X Z \delta X - k_{-3} X^2 \delta Z) \left(\frac{\delta X^*}{X^*} + \frac{\delta Z^*}{Z^*} \right) \left. \right\} + \left\{ \frac{8k_4 X^* \delta X^* \delta X}{X} + \frac{8k_4 X \delta X \delta X^*}{X^*} \right\} \\ & + \left\{ (k_5 \delta Z^* - k_{-5} \delta Y^*) \left(\frac{\delta Z}{Z} - \frac{\delta Y}{Y} \right) + (k_5 \delta Z - k_{-5} \delta Y) \left(\frac{\delta Z^*}{Z^*} - \frac{\delta Y^*}{Y^*} \right) \right\} \left. \right]. \end{aligned}$$

In the neighborhood of the steady state and expressing δX , δY , and δZ as $\delta X_r + i\delta X_i$, $\delta Y_r + i\delta Y_i$, and $\delta Z_r + i\delta Z_i$, respectively, one gets

$$\begin{aligned} \delta_m P = & \frac{RT}{2} \int dV \left[(\delta Y_r^2 + \delta Y_i^2) \left(\frac{2k_{1A}}{Y_0} + \frac{2k_2 X_0}{Y_0} + \frac{2k_{-5}}{Y_0} \right) + (\delta Z_r^2 + \delta Z_i^2) \left(\frac{2k_{-3} X_0^2}{Z_0} + \frac{2k_5}{Z_0} \right) \right. \\ & + (\delta X_r^2 + \delta X_i^2) \left(\frac{2k_{-1} P}{X_0} + \frac{2k_2 Y_0}{X_0} - \frac{2k_3 B}{X_0} + 4k_{-3} Z_0 + 16k_4 \right) - (\delta Y_r \delta Z_r + \delta Y_i \delta Z_i) \left(\frac{2k_{-5}}{Z_0} + \frac{2k_5}{Y_0} \right) \\ & \left. - (\delta Z_r \delta X_r + \delta Z_i \delta X_i) \left(\frac{2k_3 B}{Z_0} - 6k_{-3} X_0 \right) + (\delta X_r \delta Y_r + \delta X_i \delta Y_i) \left(-\frac{2k_{1A}}{X_0} - \frac{2k_{-1} P}{Y_0} + 4k_2 \right) \right] \end{aligned}$$

or

$$\begin{aligned} \delta_m P = & \frac{RT}{2} \int dV [(\delta Y_r^2 + \delta Y_i^2) \phi(k_1, k_2, k_{-5}) + (\delta Z_r^2 + \delta Z_i^2) \phi(k_{-3}, k_5) + (\delta X_r^2 + \delta X_i^2) \phi(k_{-1}, k_2, k_3, k_{-3}, k_4) \\ & - (\delta Y_r \delta Z_r + \delta Y_i \delta Z_i) \phi(k_{-5}, k_5) - (\delta Z_r \delta X_r + \delta Z_i \delta X_i) \phi(k_3, k_{-3}) + (\delta X_r \delta Y_r + \delta X_i \delta Y_i) \phi(k_1, k_{-1}, k_2)] \end{aligned} \quad (9)$$

(ϕ terms are the functions of the rate constants indicated in the parentheses).

$\delta_m \pi$ as presented earlier in Eq. (4) can be calculated in an almost identical way (see the Appendix) and found to be a real quantity as given by

$$\delta_m \pi = RT \int dV [(\delta X_r \delta Y_i - \delta X_i \delta Y_r) \phi(k_{-1}, k_1) + (\delta Y_r \delta Z_i - \delta Y_i \delta Z_r) \phi(k_{-5}, k_5) + (\delta Z_r \delta X_i - \delta Z_i \delta X_r) \phi(k_{-3}, k_3), \quad (10)$$

where

$$\phi(k_{-1}, k_1) = [(k_{-1} P / Y_0) - (k_{1A} / X_0)], \quad \phi(k_{-5}, k_5) = [(k_{-5} / Z_0) - (k_5 / Y_0)],$$

and

$$\phi(k_{-3}, k_3) = (k_{-3} X_0 - k_3 B / Z_0).$$

DISCUSSION

Expressions (9) and (10) yield two thermodynamic transition points satisfying Eqs. (11) and (12):

$$\begin{aligned} \int dV [(\delta Y_r^2 + \delta Y_i^2) \phi(k_1, k_2, k_{-5}) + (\delta Z_r^2 + \delta Z_i^2) \phi(k_{-3}, k_5) + (\delta X_r^2 + \delta X_i^2) \phi(k_{-1}, k_2, k_3, k_{-3}, k_4) \\ - (\delta Y_r \delta Z_r + \delta Y_i \delta Z_i) \phi(k_{-5}, k_5) - (\delta Z_r \delta X_r + \delta Z_i \delta X_i) \phi(k_3, k_{-3}) + (\delta X_r \delta Y_r + \delta X_i \delta Y_i) \phi(k_1, k_{-1}, k_2)] = 0 \end{aligned} \quad (11)$$

and

$$\int dV [(\delta X_r \delta Y_i - \delta X_i \delta Y_r) \phi(k_{-1}, k_1) + (\delta Y_r \delta Z_i - \delta Y_i \delta Z_r) \phi(k_{-5}, k_5) + (\delta Z_r \delta X_i - \delta Z_i \delta X_r) \phi(k_{-3}, k_3)] = 0. \quad (12)$$

It is well known that the irreversibility of the Oregonator model⁴ maintains it far from equilibrium and beyond the range of validity of Onsager relations. Thus the model has no possibility to attain the transition states described by expressions (11) and (12). Due to the introduction of reversibility into the model, however, the

system in some favorable circumstances [defined by the concentrations of A , B , P , the steady state concentrations of the intermediates and the rate constants of the steps (M1)–(M5)] may be maintained near equilibrium and passes through the states expressed by the Eqs. (11) and (12), which are the points of transitions from the stable

to unstable steady states or vice versa. Instability of the steady states is ensured when either $\delta_m\pi \neq 0$ or $\delta_m P < 0$.

An interesting feature of the stability analysis of the reversible Oregonator is that the negative contributions to the excess entropy production are provided not only by the autocatalytic^{10,11} and cross catalytic steps like reactions (M3) and (M5), but by steps like reaction (M1) also; the steps (M3) and (M5) are also found to contribute positive values to the $\delta_m P$ term. It is therefore the integrated contribution which has to be taken into consideration and the negative values will favor steady state instability leading the model system to oscillatory states.

We mention that the explicit positive contributions to the excess entropy production arising from diffusion of intermediate species are ignored here since it is assumed that the Belousov-Zhabotinskii system is stirred uniformly throughout the experiment. This assumption has been made to avoid mathematical complexity.

CONCLUSION

The Belousov-Zhabotinskii reaction⁵ is the most widely studied oscillatory chemical reaction discovered so

far. The "Reversible Oregonator" model was devised by Field⁷ to model the real chemistry involved in the mechanistic aspects of this fascinating reaction. Some workers¹² have established phase diagrams for this reaction in the constraint space which separate oscillatory and nonoscillatory zones. It is therefore a general curiosity of everyone to understand which steps favor and which steps oppose the oscillatory phases to be established. This work at least gives a qualitative understanding to this question from thermodynamic point of view.

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APPENDIX: CALCULATION OF $\delta_m\pi$

$$\begin{aligned} \delta_m\pi &= \frac{i}{2} \int dV \sum_{\rho=1}^5 (\delta\omega_\rho^* \delta A_\rho - \delta\omega_\rho \delta A_\rho^*) \\ &= \frac{i}{2} \int dV [(\delta\omega_1^* \delta A_1 - \delta\omega_1 \delta A_1^*) + (\delta\omega_2^* \delta A_2 - \delta\omega_2 \delta A_2^*) \\ &\quad + (\delta\omega_3^* \delta A_3 - \delta\omega_3 \delta A_3^*) + (\delta\omega_4^* \delta A_4 - \delta\omega_4 \delta A_4^*) + (\delta\omega_5^* \delta A_5 - \delta\omega_5 \delta A_5^*)] \\ &= \frac{i}{2} \int dV \left[\delta(k_1 A Y^* - k_{-1} X^* P) \delta \left(RT \log \frac{K_1 A Y}{X P} \right) \right. \\ &\quad - \delta(k_1 A Y - k_{-1} X P) \delta \left(RT \log \frac{K_1 A Y^*}{X^* P} \right) + \delta(k_2 X^* Y^* - k_{-2} P^2) \delta \left(RT \log \frac{K_2 X Y}{P^2} \right) \\ &\quad - \delta(k_2 X Y - k_{-2} P^2) \delta \left(RT \log \frac{K_2 X^* Y^*}{P^2} \right) + \delta(k_3 B X^* - k_{-3} X^{*2} Z^*) \delta \left(RT \log \frac{K_3 B}{X Z} \right) \\ &\quad - \delta(k_3 B X - k_{-3} X^2 Z) \delta \left(RT \log \frac{K_3 B}{X^* Z^*} \right) + \delta(2k_4 X^{*2} - 2k_{-4} B P) \delta \left(RT \log \frac{K_4 X^2}{B P} \right) - \delta(2k_4 X^2 - 2k_{-4} B P) \delta \\ &\quad \times \left(RT \log \frac{K_4 X^{*2}}{B P} \right) + \delta(k_5 Z^* - k_{-5} Y^*) \delta \left(RT \log \frac{K_5 Z}{Y} \right) - \delta(k_5 Z - k_{-5} Y) \delta \left(RT \log \frac{K_5 Z^*}{Y^*} \right) \left. \right]. \end{aligned}$$

Considering A , B , P , and K constant throughout one gets

$$\begin{aligned} \delta_m\pi &= \frac{iRT}{2} \int dV \left[(k_1 A \delta Y^* - k_{-1} P \delta X^*) \left(\frac{\delta Y}{Y} - \frac{\delta X}{X} \right) - (k_1 A \delta Y - k_{-1} P \delta X) \left(\frac{\delta Y^*}{Y^*} - \frac{\delta X^*}{X^*} \right) \right. \\ &\quad + k_2 \left\{ (X^* \delta Y^* + Y^* \delta X^*) \left(\frac{\delta X}{X} + \frac{\delta Y}{Y} \right) - (X \delta Y + Y \delta X) \times \left(\frac{\delta X^*}{X^*} + \frac{\delta Y^*}{Y^*} \right) \right\} - \left\{ (k_3 B \delta X^* - 2k_{-3} X^* Z^* \delta X^* \right. \\ &\quad - k_{-3} X^{*2} \delta Z^*) \left(\frac{\delta X}{X} + \frac{\delta Z}{Z} \right) - (k_3 B \delta X - 2k_{-3} X Z \delta X - k_{-3} X^2 \delta Z) \left(\frac{\delta X^*}{X^*} + \frac{\delta Z^*}{Z^*} \right) \\ &\quad \left. + \left\{ \frac{8k_4 X^* \delta X^* \delta X}{X} - \frac{8k_4 X \delta X \delta X^*}{X^*} \right\} + \left\{ (k_5 \delta Z^* - k_{-5} \delta Y^*) \left(\frac{\delta Z}{Z} - \frac{\delta Y}{Y} \right) - (k_5 \delta Z - k_{-5} \delta Y) \left(\frac{\delta Z^*}{Z^*} - \frac{\delta Y^*}{Y^*} \right) \right\} \right]. \end{aligned}$$

In the neighborhood of the steady state and expressing δX , δY , and δZ as $\delta X_r + i\delta X_i$, $\delta Y_r + i\delta Y_i$, and $\delta Z_r + i\delta Z_i$, respectively, one gets

$$\delta_m \pi = RT \int dV \left[(\delta X_r \delta Y_i - \delta X_i \delta Y_r) \left(\frac{k_{-1}P}{Y_0} - \frac{k_1A}{X_0} \right) + (\delta Y_r \delta Z_i - \delta Y_i \delta Z_r) \left(\frac{k_{-5}}{Z_0} - \frac{k_5}{Y_0} \right) + (\delta Z_r \delta X_i - \delta Z_i \delta X_r) \left(k_{-3}X_0 - \frac{k_3B}{Z_0} \right) \right].$$

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