

## Characteristics of Chemical Oscillators: Part III—Theory of Oscillatory Reactions

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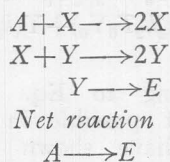
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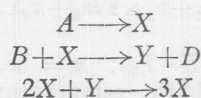
Normal mode analysis has been used to investigate the life time of oscillations for Lotka scheme. Solutions have been obtained for the case when three variables oscillate with time and in space for the reaction system. Analysis shows that oscillations in temperature are not possible in the system. If a side reaction step or a fresh reaction step is added to Lotka scheme, oscillatory solutions for differential equations are obtained under limited conditions. Both time and space oscillations have been examined.

OSCILLATORY phenomena in chemical systems have aroused considerable current interest and a number of laboratories are engaged in the study of such phenomena<sup>1,2</sup>. Amongst the chemical reactions Belousov-Zhabotinskii reaction has been intensively investigated<sup>3-5</sup>. Noyes *et al.*<sup>6</sup> have recently proposed a mechanism for time oscillation and space oscillation in Belousov-Zhabotinskii reaction. Although it has been shown by Clarke<sup>7</sup> that the mechanism does not lead to instability, the proposed mechanism is still the one which explains all the broad features of oscillating reaction. Quite recently, Rastogi and coworkers<sup>8,9</sup> have investigated the oscillatory characteristics of cerium ion and manganese ion catalysed reaction between potassium bromate and malonic acid in sulphuric acid medium. Reactions with malic acid and citric acid as the reactants in place of malonic acid have also been studied in detail by Rastogi *et al.*<sup>10</sup> Oscillations occur in these systems although a few reaction steps are added or subtracted in addition to those expected in the case of cerium ion catalysed reaction with malonic acid. It has also been found that the rate of temperature rise oscillates in the reaction medium rather than temperature<sup>11</sup>.

Lotka<sup>12</sup> suggested the following hypothetical set of chemical reactions:



The above scheme does lead to sustained oscillations in the concentration of intermediates  $X$  and  $Y$  and a close trajectory in the  $X, Y$  plane is obtained. However, this does not lead to limit cycle behaviour. A chemical scheme proposed by Prigogine and coworkers<sup>13</sup>



Net reaction



does show a limit cycle behaviour with only two intermediate species. A lot of activity on the theory of oscillating reaction has been stimulated by the work of Prigogine's group in Brussels. Some of the unanswered questions are the following. Whether it is necessary for the reaction intermediates to oscillate with the same frequency for the occurrence of oscillatory reaction? What would be the life time of the reactions? In what way the oscillatory characteristics of the reactions are expected to be modified if a side reaction is added to the Lotka scheme? The purpose of the present paper is to answer these related questions. The stability analysis when three intermediates are oscillating is known to be difficult<sup>14,15</sup>. A procedure for the same has been discussed in the present paper. In spite of the several techniques available<sup>16,17</sup>, we shall use normal mode analysis<sup>13</sup> on account of simplicity and elegance.

### Normal Mode Analysis

The Lotka scheme has been subjected to normal mode analysis in order to determine the life-time of the oscillations. The variation in the concentration of  $X$  and  $Y$  under conditions of very efficient stirring would be given by

$$\frac{dX}{dt} = k_1AX - k_2XY \quad \dots(1)$$

$$\frac{dY}{dt} = k_2XY - k_3Y \quad \dots(2)$$

Since at the steady state  $(dX/dt)$  and  $(dY/dt)$  would be zero, we have,

$$X_0 = \frac{k_3}{k_2}; Y_0 = \frac{k_1A}{k_2}$$

where the subscript 0 denotes the steady state.

Let us suppose that in the neighbourhood of the steady state,  $X$  and  $Y$  are given by

$$X = X_0 + xe^{wt} \quad \dots(3)$$

$$Y = Y_0 + ye^{w't} \quad \dots(4)$$

where  $t$  is the time and  $w' = nw$ ,  $n$  being any positive integer. In the conventional treatment  $w$  and  $w'$  are assumed to be identical and, therefore, we make a departure here. Accordingly we have,

$$\frac{dX}{dt} = wxe^{wt} \quad \dots(5)$$

$$\frac{dY}{dt} = nwy e^{nwt} \quad \dots(6)$$

Combining Eqs. (3), (4), (5) and (6) with Eqs. (1) and (2), we get

$$wx e^{wt} = k_1 A (X_0 + x e^{wt}) - k_2 (X_0 + x e^{wt})(Y_0 + y e^{nwt}) \quad \dots(7)$$

$$nwy e^{nwt} = k_2 (X_0 + x e^{wt})(Y_0 + y e^{nwt}) - k_3 (Y_0 + y e^{nwt}) \quad \dots(8)$$

which yield following secular equation on simplification.

$$\begin{vmatrix} w & k_3 e^{(n-1)wt} \\ -k_1 A & w e^{(n-1)wt} \end{vmatrix} = 0 \quad \dots(9)$$

From Eq. (9) we obtain

$$w = \pm i \sqrt{k_1 k_3 A / n} \text{ and } w' = \pm i \sqrt{k_1 k_3 A n} \quad \dots(10)$$

which shows that both  $X$  and  $Y$  would oscillate with time. The overall frequency of oscillation has to be a combination of  $w$  and  $w'$  in order that the system may conform to phase plane analysis.

For examining the conditions for the occurrence of space oscillations, we have also to consider the concentration change due to diffusion under condition of no stirring by using Fick's law of diffusion so that,

$$\frac{dX}{dt} = k_1 A X - k_2 X Y + D_x \frac{d^2 X}{dr^2} \quad \dots(11)$$

$$\frac{dY}{dt} = k_2 X Y - k_3 Y + D_y \frac{d^2 Y}{dr^2} \quad \dots(12)$$

where  $D_x$  and  $D_y$  are the diffusion coefficient of the species  $X$  and  $Y$ . We assume that  $X$  and  $Y$  in the neighbourhood of steady state are given by

$$X = X_0 + x e^{(wt+pr)} \quad \dots(13)$$

$$Y = Y_0 + y e^{(wt+pr)} \quad \dots(14)$$

where  $t$  is the time,  $p$  is any positive integer and  $r$  is the distance in space from a point of reference. We, thus, arrive at Eqs. (14a-14d).

$$\frac{dX}{dt} = wx e^{(wt+pr)} \quad \dots(14a)$$

$$\frac{dY}{dt} = wy e^{(wt+pr)} \quad \dots(14b)$$

$$\frac{d^2 X}{dr^2} = p^2 x e^{(wt+pr)} \quad \dots(14c)$$

$$\frac{d^2 Y}{dr^2} = p^2 y e^{(wt+pr)} \quad \dots(14d)$$

Therefore Eqs. (11) and (12) can be written as

$$wx e^{(wt+pr)} = k_1 A [X_0 + x e^{(wt+pr)}] - k_2 [X_0 + x e^{(wt+pr)}] \times [Y_0 + y e^{(wt+pr)}] + p^2 D_x x e^{(wt+pr)} \quad \dots(15)$$

$$wy e^{(wt+pr)} = k_2 [X_0 + x e^{(wt+pr)}] [Y_0 + y e^{(wt+pr)}] - k_3 [Y_0 + y e^{(wt+pr)}] + p^2 D_y y e^{(wt+pr)} \quad \dots(16)$$

Simplification of the Eqs. (15) and (16) yields the secular Eq. (17).

$$\begin{vmatrix} (w-a) & k_3 \\ -k_1 A & (w-b) \end{vmatrix} = 0 \quad \dots(17)$$

where  $a = p^2 D_x$ ;  $b = p^2 D_y$ . From Eq. (17), we obtain the following condition for oscillations,

$$4k_1 k_3 A > (a-b)^2 \quad \dots(18a)$$

If  $D_x = D_y$ , then

$$4k_1 k_3 A > 0 \quad \dots(18b)$$

### Temperature Oscillations

If  $m$  is the average mass of the system,  $C_v$  is the average specific heat and  $H_1$ ,  $H_2$  and  $H_3$  are the enthalpy changes of the reactions (1), (2) and (3) respectively, we have

$$m C_v \frac{dT}{dt} = k_1 A X H_1 + k_2 X Y H_2 + k_3 Y H_3 \quad \dots(19)$$

and

$$m C_v \frac{d^2 T}{dt^2} = k_1 A \dot{X} H_1 + k_1 A X \dot{H}_1 + k_2 \dot{X} Y H_2$$

$$+ k_2 X \dot{Y} H_2 + k_2 X Y \dot{H}_2 + k_3 \dot{Y} H_3 + k_3 Y \dot{H}_3 \quad \dots(20)$$

where dot denotes time derivative and  $(d^2 T / dt^2)$  is the rate of temperature rise. Our object is now to determine the conditions under which temperature or  $(dT/dt)$  would oscillate. Combining Eqs. (1), (2) and (19) and putting

$$T = T_0 + t_1 e^{wt}$$

$$X = X_0 + x e^{wt}$$

$$Y = Y_0 + y e^{wt}$$

where  $T_0$  is the mean value of temperature, we get the following relation which obviously does not lead to an imaginary value of  $w$ .

$$w m C_v t_1 e^{wt} = k_1 A h_1 (X_0 + x e^{wt})(T_0 + t_1 e^{wt}) + k_2 h_2 (T_0 + t_1 e^{wt})(X_0 + x e^{wt})(Y_0 + y e^{wt}) + k_3 h_3 (Y_0 + y e^{wt})(T_0 + t_1 e^{wt}) \quad \dots(21)$$

or

$$t_1 (k_1 A h_1 X_0 + k_2 h_2 X_0 Y_0 + k_3 h_3 Y_0 - w m C_v) + x (k_1 A h_1 T_0 + k_2 h_2 T_0 Y_0) + Y (k_2 h_2 X_0 T_0 + k_3 T_0 h_3) = 0 \quad \dots(22)$$

Therefore, according to Eq. (22) temperature oscillations are not possible in Lotka's scheme. Yang and Gray<sup>18</sup> have shown that during cool flame combustion of hydrocarbon, interplay of thermal conduction and enthalpy change during chemical reaction occurs. Accordingly taking into account the conductive heat loss  $L$ , Eq. (19) can be written as

$$m C_v \frac{dT}{dt} = k_1 A X H_1 + k_2 X Y H_2 + k_3 Y H_3 - L \quad \dots(23)$$

where  $L = \tau \lambda / d^2 (T - T_0)$ ;  $\tau$  = heat exchange of coefficient;  $T_0$  = bath temperature;  $T$  = average

temperature of the mixture in the vessel;  $\lambda =$  conductivity of the mixture; and  $d =$  diameter of the vessel.

On solving Eqs. (1), (2) and (23), we get

$$t_1 = \frac{\begin{vmatrix} -k_1 A(H_1 + H_2) & -k_3(H_2 + H_3) & Le^{-wt} \\ w & k_3 & 0 \\ -k_1 A & w & 0 \end{vmatrix}}{\begin{vmatrix} -k_1 A(H_1 + H_2) & -k_3(H_2 + H_3) & w \\ w & k_3 & 0 \\ -k_1 A & w & 0 \end{vmatrix}} \dots (24)$$

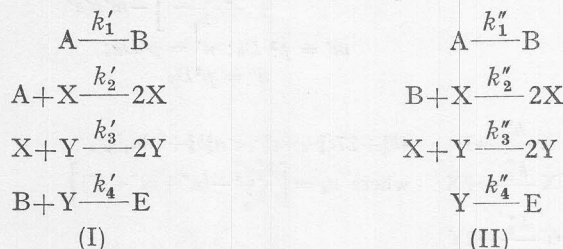
On simplification of Eq. (24), we get

$$t_1 = \frac{Le^{-wt}}{w} \quad (24a)$$

Since  $w$  is imaginary, the above solution is not admissible and the obvious conclusion is that the temperature does not oscillate with a frequency similar to that for the concentration of the other oscillating species for Lotka's reaction model. Same is true about the possibility of oscillation of  $(dT/dt)$ .

### Effects on Modification of Lotka Scheme on the Oscillatory Behaviour

We shall now modify the Lotka scheme by adding a side reaction and a reaction step as follows:



We shall first consider the oscillatory characteristics of scheme (I). At the steady state

$$X_0 = \frac{k_2' A}{k_3'}; B_0 = \frac{k_1' k_3'}{k_2' k_4'} \text{ and } X_0 = \frac{k_1'}{k_2'}$$

Using normal mode analysis and putting

$$\begin{aligned} X &= X_0 + x e^{wt} \\ Y &= Y_0 + y e^{wt} \\ B &= B_0 + b e^{wt} \end{aligned}$$

where  $t$  is the time and  $x, y$  and  $b$  are the real values. We obtain the following condition for the real values of  $x, y$  by following the procedure adopted in the previous sections:

$$\begin{vmatrix} \left[ w + \frac{k_1' k_4'}{k_3'} A \right] & \frac{k_1' k_3'}{k_2'} & 0 \\ \frac{k_2' k_4'}{k_3'} A & w & -k_4' A \\ 0 & \frac{k_3' k_1'}{k_2'} & w \end{vmatrix} = 0 \quad \dots (25)$$

On solving Eq. (25) we get

$$w^3 + \frac{k_2' k_4'}{k_3'} A w^2 + k_1' A (k_3' + k_4') w - k_1' k_2' k_4' A^2 = 0 \quad \dots (26)$$

This leads to the following condition for oscillation (see Appendix)

$$4b_1^3 + 27c_1^2 + 4a_1^3 c_1 < a_1^2 b_1^2 + 18a_1 b_1 c_1 \quad \dots (27)$$

where

$$a_1 = \frac{k_2' k_4'}{k_3'} A; b_1 = k_1' A (k_3' - k_4') \text{ and } c_1 = k_1' k_2' k_4' A^2$$

Similarly for the space oscillations, the normal mode analysis yields the following condition:

$$4b_2^3 + 27c_2^2 + 4a_2^3 c_2 < a_2^2 b_2^2 + 18a_2 b_2 c_2 \quad \dots (28)$$

where

$$a_2 = \left[ \frac{k_2' k_4'}{k_3'} A - (m' + n' + d') \right];$$

$$= \left[ n' d' + k_1 A (k_3' - k_4') - (n' + d') \left\{ \frac{k_2' k_4'}{k_3'} - m' \right\} \right]$$

$$c_2 = A \left[ k_1' k_4' n' - k_1' k_3' m' + k_1' k_2' k_4' A + \frac{k_2' k_4' n' d'}{k_3'} \right] - m' n' d'$$

where

$$m' = p^2 D_b; n' = p^2 D_x \text{ and } d' = p^2 D_y$$

Scheme (II) can also exhibit the time oscillations under certain conditions. The normal mode analysis yields the following condition (Eq. 29)

$$4b_3^3 + 27c_3^2 + 4a_3^3 c_3 < a_3^2 b_3^2 + 18a_3 b_3 c_3 \quad \dots (29)$$

where

$$a_3 = \frac{k_2'' k_4''}{k_3''}; b_3 = k_1'' A (k_2'' + k_3'') \text{ and } c_3 = k_1'' k_2'' k_4'' A$$

Similarly for space oscillations, the normal mode analysis yields the following condition (Eq. 30)

$$4b_4^3 + 27c_4^2 + 4a_4^3 c_4 < a_4^2 b_4^2 + 18a_4 b_4 c_4 \quad \dots (30)$$

where

$$a_4 = \left[ \frac{k_2'' k_4''}{k_3''} - (m'' + n'' + d'') \right]$$

$$b_4 = \left[ n'' d'' + k_1'' A (k_2'' + k_3'') - (n'' + d'') \left\{ \frac{k_2'' k_4''}{k_3''} + m'' \right\} \right]$$

$$c_4 = A \left[ \frac{k_2'' k_4''}{k_3''} - k_1'' (k_2'' d'' + m'' k_3'') \right] + n'' d'' \left[ \frac{k_2'' k_4''}{k_3''} - m'' \right]$$

where

$$m'' = p^2 D_b; n'' = p^2 D_x \text{ and } d'' = p^2 D_y$$

$p$  is any positive integer and  $D_b, D_x$  and  $D_y$  are the diffusion coefficients of the corresponding species B, X and Y.

### Discussion

The results obtained are summarized in Tables 1 and 2. Several conclusions follow from the above analysis.

According to Eq. (10), frequency of oscillation for Lotka's reaction model is proportional to the square root of the concentration of A. Since A will steadily be consumed in the reaction,  $w$  will decrease with time but oscillation would continue indefinitely till A disappears. Thus,

(a) If the temperature is kept constant and the concentration of A is maintained constant, sustained oscillations for indefinite time would be obtained.

TABLE 1—CONDITIONS FOR TIME OSCILLATION FOR DIFFERENT REACTION MODELS

Model	Condition
$A + X \xrightarrow{k_1'} 2X$	$w = \pm i\sqrt{k_1 k_3 A/n}$ ; $w' = \pm i\sqrt{k_1 k_3 A n}$
$X + Y \xrightarrow{k_2} 2Y$	where $n$ is any positive integer
$Y \xrightarrow{k_3} E$	
$A \xrightarrow{k_1} B$	$4b_1^3 + 27c_1^2 + 4a_1^3 c_1 < a_1^2 b_1^2 + 18a_1 b_1 c_1$
$A + X \xrightarrow{k_2'} 2X$	where $a_1 = k_2' k_4' / k_3'$ ; $b_1 = k_1' A (k_3' - k_4')$
$X + Y \xrightarrow{k_3'} 2Y$	$c_1 = k_1' k_2' k_4' A^2$
$B + Y \xrightarrow{k_4'} E$	
$A \xrightarrow{k_1''} B$	$4b_3^3 + 27c_3^2 + 4a_3^3 c_3 < a_3^2 b_3^2 + 18a_3 b_3 c_3$
$B + X \xrightarrow{k_2''} 2X$	where $a_3 = k_2'' k_4'' / k_3''$ ; $b_3 = k_1'' A (k_3'' + k_4'')$
$X + Y \xrightarrow{k_3''} 2Y$	$c_3 = k_1'' k_2'' k_4'' A^2$
$Y \xrightarrow{k_4''} E$	

(b) If A goes on being consumed, the time period would go on changing with time and would be inversely proportional to the square root of concentration of A. Similar behaviour is obtained in the case of Belousov-Zhabotinskii reaction<sup>9,10</sup>.

Since  $k_1$  and  $k_3$  would be temperature dependent  $\log w$  is expected to be proportional to the temperature.

When step  $A \rightarrow B$  is added to the Lotka reaction model, time oscillations would occur under certain conditions given in Table 1. Space oscillations can also occur under certain condition given in Table 2. Minor modifications in Lotka scheme do not rule out the possibility of time and space oscillations.

It is obvious from the above results that when  $a = b$  i.e.  $D_x = D_y$ , space oscillations would always occur so long as A is present.

Eq. (10) gives the solution when stirring is efficient so that the space derivatives of concentration gradient are zero. However, Eq. (18) corresponds to the situation when stirring is negligible.

Detailed data on oscillatory characteristics of (1) malonic acid +  $KBrO_3 + Ce^{3+} + H_2SO_4$  system; (2) malonic acid +  $KBrO_3 + Mn^{2+} + H_2SO_4$  system; (3) malic acid +  $KBrO_3 + Ce^{4+} + H_2SO_4$  system; and (4) citric acid +  $KBrO_3 + Ce^{4+} + H_2SO_4$  system are now available<sup>8-10</sup>. In system (4), a few more reaction steps as compared to that for (1) are added and yet oscillations are observed. This is not unexpected as shown by above analysis. Time period is found to be strongly temperature dependent and depends on concentration of the reacting species as we observe in the above cases.

TABLE 2—CONDITIONS FOR SPACE OSCILLATION FOR DIFFERENT REACTION MODELS

Model	Condition
$A + X \xrightarrow{k_1} 2X$	$4k_1 k_3 A > (a-b)^2$ where $a = p^2 D_x$ ; $b = p^2 D_y$
$X + Y \xrightarrow{k_2} 2Y$	if $D_x = D_y$
$Y \xrightarrow{k_3} E$	$4k_1 k_3 A > 0$
$A \xrightarrow{k_1'} B$	$4b_2^3 + 27c_2^2 + 4a_2^3 c_2 < a_2^2 b_2^2 + 18a_2 b_2 c_2$
$A + X \xrightarrow{k_2'} 2X$	where $a_2 = \left[ \frac{k_2' k_4'}{k_3'} A - (m' + n' + d') \right]$
$X + Y \xrightarrow{k_3'} 2Y$	
$B + Y \xrightarrow{k_4'} E$	
	$b_2 = \left[ n' d' + k_1' A (k_3' - k_4') - (n' + d') \left( \frac{k_2' k_4'}{k_3'} A - m' \right) \right]$
	$c_2 = A \left[ k_1' k_4' n' - k_1' k_3' m' + k_1' k_2' k_4' A + \frac{k_2' k_4' n' d'}{k_3'} \right] - m' n' d'$
	$m' = p^2 D_b$ ; $n' = p^2 D_x$ ; $d' = p^2 D_y$
$A \xrightarrow{k_1''} B$	$4b_4^3 + 27c_4^2 + 4a_4^3 c_4 < a_4^2 b_4^2 + 18a_4 b_4 c_4$
$B + X \xrightarrow{k_2''} 2X$	where $a_4 = \left[ \frac{k_2'' k_4''}{k_3''} - (n'' + m'' + d'') \right]$
$X + Y \xrightarrow{k_3''} 2Y$	
$Y \xrightarrow{k_4''} E$	
	$b_4 = \left[ n'' d'' + k_1'' A (k_3'' + k_4'') - (n'' + d'') \left( \frac{k_2'' k_4''}{k_3''} + m'' \right) \right]$
	$c_4 = A \left[ \frac{k_2'' k_4''}{k_3''} - k_1'' (k_2'' d'' + k_3'' m'') + n'' d'' \left[ \frac{k_2'' k_4''}{k_3''} - m'' \right] \right]$
	$m'' = p^2 D_b$ ; $n'' = p^2 D_x$ ; $d'' = p^2 D_y$

### Acknowledgement

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### APPENDIX

In order to determine the condition for obtaining imaginary roots<sup>19</sup> from Eq. (26), we write Eq. (26) as follows:

$$w^3 + a_1 w^2 + b_1 w + c_1 = 0 \quad \dots(26.1)$$

where

$$a_1 = \frac{k_2' k_4'}{k_3'} A$$

$$b_1 = k_1' A (k_3' + k_4')$$

$$c_1 = k_1' k_2' k_4' A^2$$

Let us assume

$$X = \left[ w + \frac{a_1}{3} \right]$$

$$w = \left[ X - \frac{a_1}{3} \right]$$

On putting the value of  $w$  in Eq. (26.1) we get

$$\left[ X - \frac{a_1}{3} \right]^3 + a_1 \left[ X - \frac{a_1}{3} \right]^2 + b_1 \left[ X - \frac{a_1}{3} \right] + c_1 = 0 \quad \dots(26.2)$$

On simplification we get

$$X^3 + p_1 X + q_1 = 0 \quad \dots(26.3)$$

where

$$p_1 = \left[ b_1 - \frac{a_1^2}{3} \right]; q_1 = - \left[ \frac{a_1 b_1}{3} - c_1 - \frac{2a_1^3}{27} \right]$$

Let us assume

$$X = r_1^{1/3} + s_1^{1/3}$$

putting the value of  $X$  in Eq. (26.3) we get

$$\left[ r_1^{1/3} + s_1^{1/3} \right]^3 + p_1 \left[ r_1^{1/3} + s_1^{1/3} \right] + q_1 = 0 \quad \dots(26.4)$$

On simplification we get

$$r_1 + s_1 = -q_1 \quad \dots(26.5)$$

$$r_1 s_1 = -\frac{p_1^3}{27} \quad \dots(26.6)$$

$$r_1 = -\frac{p_1^3}{27s_1}$$

putting the value of  $s_1$  in Eq. (26.5) we get

$$r_1 - \frac{p_1^3}{27r_1} = -q_1$$

$$r_1^2 + r_1 q_1 - \frac{p_1^3}{27} = 0 \quad \dots(26.7)$$

On simplifying Eq. (26.7) we get

$$r_1 = \frac{q_1}{2} \pm \sqrt{\frac{q_1^2}{4} + \frac{p_1^3}{27}}$$

The value of  $r_1$  will be imaginary only when

$$\frac{q_1^2}{4} + \frac{p_1^3}{27} < 0$$

On account of the above solutions  $s_1$  and  $X$  will also be imaginary. Hence the value of  $w$  will be imaginary. By putting the value of  $p_1$  and  $q_1$ , we get

$$4b_1^3 + 27c_1^2 + 4a_1^3 c_1 < a_1^2 b_1^2 + 18a_1 b_1 c_1$$

The above procedure can be used for normal mode analysis where three intermediates are present whose concentration is oscillating.

**Nomenclature**

- A = concentration of A.
- X = concentration of X
- Y = concentration of Y
- B = concentration of B
- X<sub>0</sub> = steady state concentration of X
- Y<sub>0</sub> = steady state concentration of Y
- B<sub>0</sub> = steady state concentration of B
- x = small perturbation in the concentration of X
- y = small perturbation in the concentration of Y

- b = small perturbation in the concentration of B
- t<sub>1</sub> = small perturbation in the temperature of the reaction system
- T = temperature of the reaction system
- T<sub>0</sub> = steady state temperature of the reaction system
- k<sub>1</sub> = Arbitrary constant
- k<sub>2</sub> = do
- k<sub>3</sub> = do
- k<sub>1</sub>' = do
- k<sub>2</sub>' = do
- k<sub>3</sub>' = do
- k<sub>4</sub>' = do
- k<sub>1</sub>'' = do
- k<sub>2</sub>'' = do
- k<sub>3</sub>'' = do
- k<sub>4</sub>'' = do
- w = frequency of the oscillating species
- t = time
- n = any positive integer
- p = do
- r = distance in space
- D<sub>x</sub> = diffusion coefficient of X
- D<sub>y</sub> = diffusion coefficient of Y
- D<sub>b</sub> = diffusion coefficient of B
- H<sub>1</sub> = heat of reaction
- H<sub>2</sub> = do
- H<sub>3</sub> = do
- τ = heat exchange coefficient
- T<sub>0</sub>' = bath temperature
- T = Average temperature of the mixture in the vessel
- λ = conductivity of the mixture
- d = diameter of the vessel
- n' = p<sup>2</sup>D<sub>x</sub>
- m' = p<sup>2</sup>D<sub>y</sub>
- d' = p<sup>2</sup>D<sub>b</sub>
- C<sub>v</sub> = specific heat at constant volume
- h<sub>1</sub> = arbitrary constant
- h<sub>2</sub> = do
- h<sub>3</sub> = do

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