

Jug handle bifurcation and complex oscillations in reactive systems

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Bifurcation features and deformation of limit cycles for $\text{NaH}_2\text{PO}_2 + \text{cyclohexanone}/\text{acetone} + \text{Mn}^{2+} + \text{BrO}_3^- + \text{H}_2\text{SO}_4$ oscillatory reaction systems have been reported. Acetone system yields unperturbed limit cycles whereas in the case of cyclohexanone system, the limit cycles are deformed and knot is obtained. It is found that quasi periodicity and appearance of loop are not necessarily related. Computer analysis shows that deformation of limit cycle can occur when there is a phase difference or new harmonics appear in the time series.

Non-linear chemical dynamics is an area of current interest¹. The nature of limit cycle and the bifurcation behaviour seems to be intimately related to chemical mechanism². However, studies on this aspect are very few and a further probe is imperative. In particular, it is desirable to understand how tinkering the hard core of oscillatory mechanism by (i) induction of some additional reaction steps or by (ii) acceleration and deacceleration of some steps, can change the oscillatory features and bifurcation mechanism. The subject has physiological and medical application as has been pointed by Milton *et al.*³.

Hopf bifurcation and jug handle (JH) type bifurcation are most commonly observed in chemical systems⁴⁻⁶. In the former case, at the bifurcation point, time period remains finite but amplitude tends to zero. However in the latter case, both the time period and amplitude have finite values. Hence, these can be detected⁷ from the time series, although other tests are necessary⁸.

Belousov-Zhabotinskii (B-Z) oscillators with mixed organic substrates⁹ provide examples of rich dynamic behaviour. If nitrogen is flushed through the system¹⁰⁻¹², it can act as a bromine scavenger. Thus, Noszticzius *et al.*¹⁰ reported oscillations in oxalic acid + $\text{BrO}_3^- + \text{Ce}^{4+} + \text{H}_2\text{SO}_4$ system when nitrogen was flushed through the system. In this case indications of saddle node infinite period bifurcation (SNIPER) are observed¹⁰ although Bar-Eli and Noyes¹³ hold the view that this may not be true. Noszticzius *et al.*¹⁴ have studied similar systems having glucose + acetone, arabinose + acetone and $\text{H}_2\text{PO}_2^- + \text{acetone}$ as mixed substrates and compared the rate of production of CO_2 in these systems. Quite recently bifurcation behaviour in a number of systems⁴⁻⁶,

having mixed organic substrates, has been studied, in which occurrence of both JH as well as Hopf bifurcations have been reported. It was thought to investigate bifurcation characteristic, deformation of limit cycle and formation of knots¹⁵ in B-Z systems having inorganic reductant and ketone as mixed substrates which also show complex oscillations in certain concentration region. Results of studies on $\text{NaH}_2\text{PO}_2 + \text{cyclohexanone}/\text{acetone} + \text{Mn}^{2+} + \text{BrO}_3^- + \text{H}_2\text{SO}_4$ systems are reported in this paper from this viewpoint.

Materials and Methods

Chemical used and experimental procedure were similar to those reported in earlier paper⁴. NaH_2PO_2 (AR, Thomas Baker), acetone (GR, E. Merck) and manganese(II) sulphate monohydrate (E. Merck) were used as received.

Results and Discussion

A few typical traces of change in potential against time are recorded in Figs 1 and 2. The systems also display an upper limit and lower limit of [ketone] between which oscillatory behaviour is observed and beyond which the systems are stable and move toward a focus. The corresponding phase-plane plots are given in Figs 3 and 4. The behaviour of (i) $\text{NaH}_2\text{PO}_2 + \text{acetone}$ and (ii) $\text{NaH}_2\text{PO}_2 + \text{cyclohexanone}$ systems is different in following respects:

- (a) On increasing [cyclohexanone], increase in amplitude of redox potential oscillations along with decrease in Br^- potential oscillations is observed whereas in the case of acetone reverse is the case.

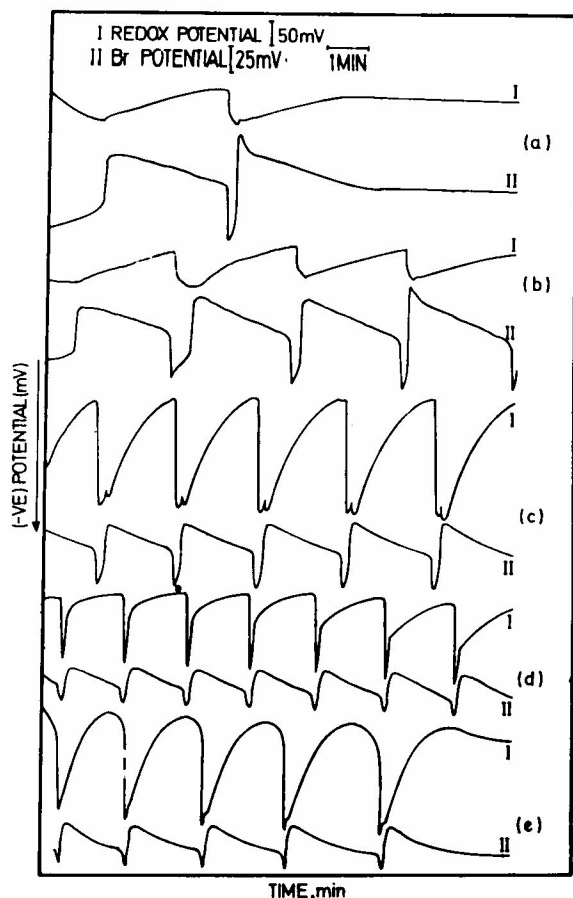


Fig. 1 - Oscillations in redox potential (I) and bromide ion potential (II) [System: NaH_2PO_2 ($11.36 \times 10^{-2} M$) + Mn^{2+} ($1.57 \times 10^{-3} M$) + KBrO_3 ($2.5 \times 10^{-2} M$) + H_2SO_4 ($1.5 M$) + cyclohexanone = (a) $1.12 \times 10^{-2} M$; (b) $1.60 \times 10^{-2} M$; (c) $11.2 \times 10^{-2} M$; (d) $16.0 \times 10^{-2} M$; and (e) $22.35 \times 10^{-2} M$; temp = $32 \pm 0.5^\circ\text{C}$.]

- (b) Near the upper limit, redox potential oscillations are complex in the case of cyclohexanone.
- (c) At the upper limit, Hopf bifurcation is obtained in the case of acetone while JH bifurcation is obtained in the case of cyclohexanone.
- (d) Cyclohexanone system shows that (i) biperiodic time series does not necessarily yield a deformed limit cycle and (ii) a periodic time series need not always generate an unperturbed limit cycle.

The present reaction systems belong to the class of mixed substrate systems discovered earlier by Rastogi and coworkers⁹. However, these have the novel feature in that the carboxylic acid is replaced by NaH_2PO_2 which is a strong reductant.

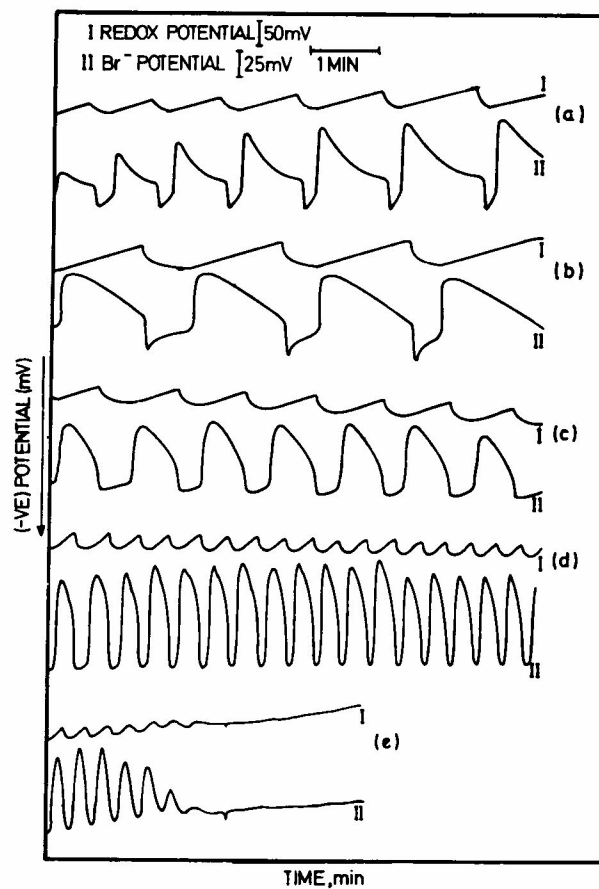


Fig. 2 - Oscillations in redox potential (I) and bromide ion potential (II) [System: NaH_2PO_2 ($11.36 \times 10^{-2} M$) + Mn^{2+} ($1.57 \times 10^{-3} M$) + KBrO_3 ($2.5 \times 10^{-2} M$) + H_2SO_4 ($1.5 M$) + acetone = (a) $9.0 \times 10^{-2} M$; (b) $2.25 \times 10^{-1} M$; (c) $2.25 M$; (d) $7.2 M$; and (e) $10.36 M$ Temp. = $32 \pm 0.5^\circ\text{C}$]

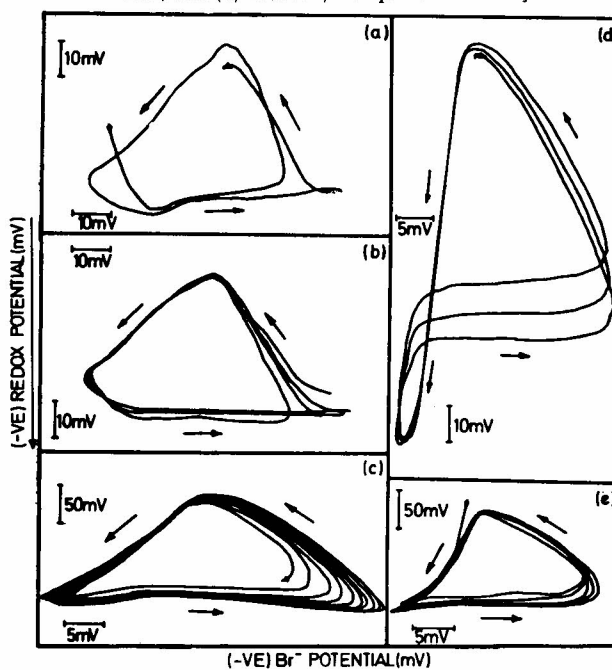


Fig. 3 - Phase-plane plots for the batch reactor [System and concentrations are the same as given in Fig. 1]

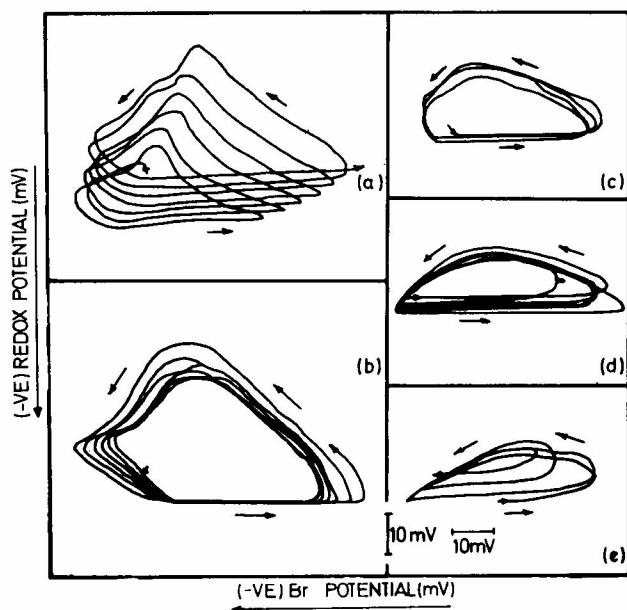


Fig. 4 – Phase-plane plots for the batch reactor [System and concentrations are the same as given in Fig. 2]

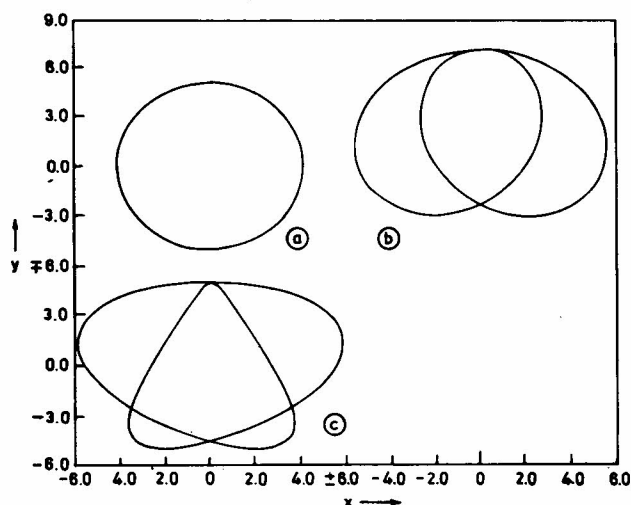
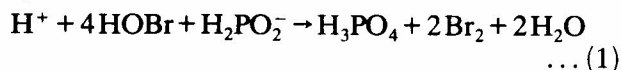


Fig. 5 – Plot of computed values of Y against X showing the appearance of loop [(a) $X = 4 \sin(60t)$; $Y = 5 \cos(60t)$; (b) $X = 4 \sin(60t) + 2 \sin(30t)$; $Y = 5 \cos(60t)$; and (c) $X = 4 \sin(60t) + 2 \sin(90t)$; $Y = 5 \cos(60t)$]

Hypophosphite can react with HOBr producing Br_2 (see Eq. 1) which is scavenged by acetone/cyclohexanone¹.



while Mn(III) can be reduced to Mn(II) in steps (2) and (3) by following two steps

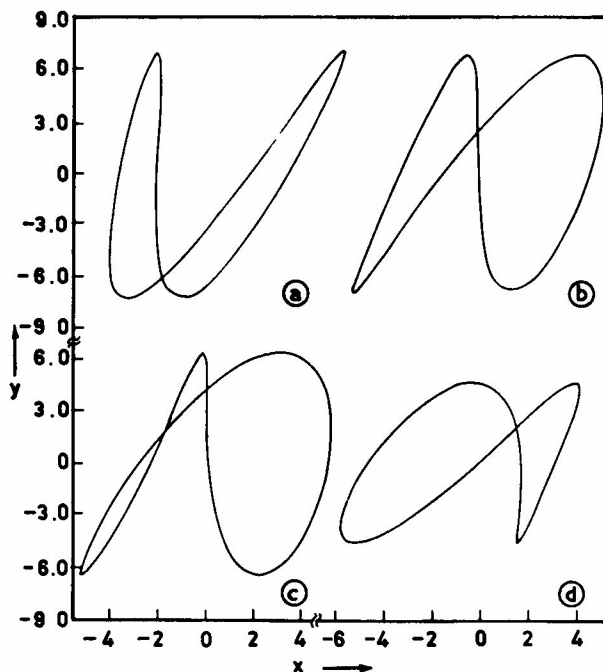
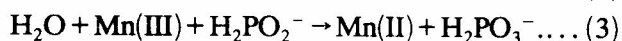
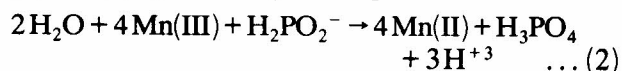
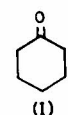
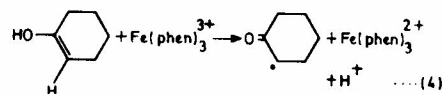
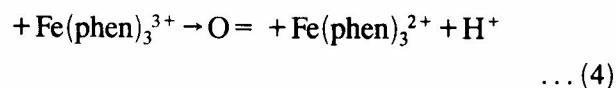


Fig. 6 – Plot of computed values of Y against X, based on Eqs (5) and (6) showing the distortion of phase-plane when phase difference is taken into account. [(a) $X = 4 \sin(30t + 90)$; $Y = 5 \sin(60t) + 2 \sin(120t)$; (b) $X = 4 \sin(30t) + 2 \sin(60t)$; $Y = 5 \sin(60t + 90) + 2 \sin(120t)$; (c) $X = 4 \sin(30t) + 2 \sin(60t)$; $Y = 5 \sin(60t + 180) + 2 \sin(120t)$; and (d) $X = 4 \sin(30t + 360) + 2 \sin(60t)$; $Y = 5 \sin(60t) + 2 \sin(120t + 360)$]

The behaviour of cyclohexanone is different in certain respects with acetone system. Whether this is due to the fact that cyclohexanone can yield a radical of the type(I),



on oxidation with $\text{Mn(III)} + \text{BrO}_3^-$ has to be examined further. It may be noted that evidence for the cyclohexanone free radical has been obtained in the following systems. (a) Outer sphere oxidation of cyclohexanone by tris(polypyridine) complexes of iron(III) and ruthenium(III) which occurs by the reaction¹⁶ (4).



(b) Ring opening in the case of 2-hydroxycyclohexanone¹⁷.

Complexity in oscillations is reflected both in time series and experimentally observed limit cycles. Power spectrum¹⁸ based on Fourier analysis of the time series enables one to identify the harmonics and the corresponding amplitudes in the time series. At the moment, let us try to understand how the limit cycle is perturbed. Figure 3 shows how the limit cycle is perturbed when [ketone] is changed leading to the appearance of bi-periodic attractor. Let us consider how the phase difference and appearance of higher harmonics can deform the limit cycle and form knot(s)¹⁵. For this purpose, we consider the two times series (Eqs 5 and 6) for the variables X and Y

$$X = a_1 \sin(\omega_1 t + \phi_1) + a_2 \sin(\omega_2 t + \phi_2) + a_3 \sin(\omega_3 t + \phi_3) + \dots + b_1 \cos(\omega_1 t + \phi_1) + b_2 \cos(\omega_2 t + \phi_2) + \dots \quad \dots (5)$$

$$Y = a'_1 \sin(\omega'_1 t + \phi'_1) + a'_2 \sin(\omega'_2 t + \phi'_2) + a'_3 \sin(\omega'_3 t + \phi'_3) + \dots + b'_1 \cos(\omega'_1 t + \phi'_1) + b'_2 \cos(\omega'_2 t + \phi'_2) + \dots \quad \dots (6)$$

where $\omega_1, \omega_2, \dots$ are the frequencies and ϕ 's are the phase difference; $a_1, a'_1, \dots$ and $b_1, b'_1, \dots$ are constants.

Figure 5(a) shows a limit cycle when $X = 4 \sin(60t)$; $Y = 5 \cos(60t)$. When $X = 4 \sin(60t) + 2 \sin(30t)$ or $X = 4 \sin(60t) + 2 \sin(90t)$, loop appears as shown in Fig. 5. It is found that the nature of perturbations depend on the magnitude of phase difference and number and magnitude of additional frequencies. Computer plots for a few more typical cases are given in Fig. 6 which show the manner in which limit cycle can be distorted when phase difference appears. One may imagine that small changes in the chemistry of the reaction system can bring about changes in the phase angle

or frequencies. It would be interesting to identify such chemical effects in the present system.

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References

- 1 *Oscillations and travelling waves in chemical systems*, edited by R J Field and M Burger (John Wiley, New York) 1985.
- 2 Noszticzius Zoltan, McCormik William D & Swinney Harry L, *J phys Chem*, 93 (1989) 2796.
- 3 Milton John G, Longtin Andre, Beuter Anne, Mackey Michael C & Glass Leon, *J theor Biol*, 138 (1989) 129.
- 4 Rastogi R P & Misra G P, *J phys Chem*, 91 (1987) 3007.
- 5 Rastogi R P & Misra G P, *J chem Soc Faraday Transactions I*, under publication (1989).
- 6 Rastogi R P & Srivastava Sangita, *Chem phys Letters*, 164 (1989) 173.
- 7 Noszticzius Z, Stirling P & Witmann Maria, *J phys Chem*, 89 (1985) 4914.
- 8 Noszticzius Zoltan, Witmann Maria & Stirling Peter, *J chem Phys*, 86 (1987) 1922.
- 9 Rastogi R P, Yadav K D S & Rastogi P, *Indian J Chem*, 15A (1977) 338.
- 10 Noszticzius Z & Bodiss J, *J Am chem Soc*, 101 (1979) 3177.
- 11 Adamcikova L & Sevcik P, *Int J chem Kinet*, 14 (1982) 735.
- 12 Sevcik P & Adamcikova L, *J phys Chem*, 89 (1985) 5178.
- 13 Bar-Eli K & Noyes R M, *J chem Phys*, 86 (1987) 1927.
- 14 Ouyang Qi, Tam W Y, De Kepper P, McCormik W D, Noszticzius Z & Swinney Harry L, *J phys Chem*, 91 (1987) 2181.
- 15 *Fractals, quasicrystals, chaos, knots and algebraic quantum mechanics*, edited by A Amann, L Cederbaum & W Gans. NATO ASI Series (Kluwer Academic, Dordrecht), 1988.
- 16 Ng F T T & Henry P M, *J Am chem Soc*, 98 (1976) 3606.
- 17 Druliner J D & Wasserman E, *J Am chem Soc*, 110 (1988) 5270.
- 18 Heinz George Schuster, *Deterministic chaos: An introduction* (Weinheim; Basel, Cambridge) 1988, p. 9.