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Oscillatory and isochronous rate equations possibly describing chemical reactions

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Abstract

We study a simple mathematical model that can be interpreted as a description of the kinetics of the following four reactions involving the two chemicals U and W: (i) $U + U \Longrightarrow U$ with rate α, (ii) $U + W \Longrightarrow U$ with rate β, (iii) $W + W \Longrightarrow U$ with rate γ and (iv) $W + W \Longrightarrow W + W + W$ with rate $\delta + 2\gamma$. The model can be generally solved by quadratures, and in the special case $\beta = 2\alpha$, explicitly in terms of elementary functions.We focus on the case characterized by the two inequalities $\gamma\beta^2 > \alpha\delta^2$ and $2\beta\gamma > \delta^2$, and we show that in this case the solutions vanish asymptotically at large times. But if a constant decay with rate θ of chemical U is added, then a *nonvanishing* equilibrium configuration arises. Moreover, for arbitrary strictly positive initial conditions, the solutions remain bounded. They either tend asymptotically (in the remote future) to this *nonvanishing* equilibrium configuration, or are periodic, or tend to a limit cycle. Indeed, we find that this system goes through a standard supercritical Hopf bifurcation at an appropriate value of the parameters. Another interesting case arises when, in addition to the original reaction, a negative constant term is added to the equation corresponding to chemical U, corresponding to siphoning out a constant amount of chemical U per unit time, independent of its concentration. A very remarkable feature of this (possibly not very realistic) model is the following: in the special case $\beta = 2\alpha$, we again find an explicit solution in terms of elementary functions, which oscillates at a *fixed* frequency, independent of the initial condition. In other words, it is an *isochronous* system. If $\beta \neq 2\alpha$, however, no periodic orbits exist, implying that the nature of the bifurcation at $\beta = 2\alpha$ is rather peculiar.

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1. Introduction and main results

Recently, we have investigated systems of evolutionary *nonlinear* ordinary differential equations (ODEs) amenable to neat mathematical treatment (including, in some cases, an explicit solution of the initial-value problem) and yielding time evolutions exhibiting *oscillatory* phenomena, possibly including *periodicity* and even *isochrony*; see [1] and other papers referred to there, and, for a review of previous work, the monograph [2]. In this paper, we begin to explore possible applications of these mathematical findings. The first context selected is that of chemical reactions, which lend themselves rather naturally to a mathematical representation in terms of (systems of) nonlinear first-order ODEs. The possibility that chemical reactions give rise to oscillatory behavior is of course well known, the classical example being the chemical reaction associated with the names of Belousov [3] and Zhabotinskii [4] (although the name of Bray should also be associated with this reaction [5]). Other oscillatory chemical reactions have also been investigated, for instance, the Briggs–Rauscher reaction [6], the 'Brussellator' [7], the 'Oregonator' [8]: indeed the literature on such reactions—both their chemistry and their mathematical modeling—is vast; for reviews and references see, for instance, the standard books [9–11]. In this paper, we report some findings the interest of which is, still, mainly mathematical, although we hope that they will also be appreciated by chemists and shall eventually lead to experimental verifications and possibly even to industrial applications.

Our main results are reported in this section; the corresponding proofs are provided in the following section. Some additional considerations are given in section 3, entitled 'Outlook'.

But before dealing with chemical reactions let us tersely recall—also to establish notation—the classical Lotka–Volterra model of chemical reactions and population dynamics [12, 13], as the archetype of a nonlinear evolutionary system of two ODEs amenable to neat mathematical treatment and displaying certain 'paradoxical' features somewhat analogous to those of the systems described herein. This model is characterized by the following simple system of two coupled ODEs:

$$\dot{x} = ax - bxy = (a - by)x, \qquad \dot{y} = -cy + dxy = (-c + dx)y. \tag{1a}$$

Notation: the superimposed dot indicates differentiation with respect to the independent variable (time t), the two dependent variables $x \equiv x(t)$ and $y \equiv y(t)$ indicate respectively (in the Volterra model of interacting populations) the numbers of preys and predators (and are therefore *positive* numbers), and the four constants a, b, c and d are as well *positive*. Indeed, hereafter all the quantities appearing in our equations are assumed to be *positive* numbers, and if any of the dependent variables become *negative* over time, or *diverge*, this occurrence shall be interpreted as a breakdown of the validity of the model under consideration. In this Volterra case, the very structure of these ODEs clearly shows that if the initial data $x(0)$ and $y(0)$ are *positive*, the dependent variables $x(t)$ and $y(t)$ remain *positive* for all time. Clearly this model admits—besides the uninteresting, unstable equilibrium solution $x(t) = y(t) = 0$—the equilibrium configuration

$$x(t) = \bar{x} = \frac{c}{d}, \qquad y(t) = \bar{y} = \frac{a}{b}, \tag{1b}$$

and it can moreover be easily shown that *all* the other solutions of this model rotate *periodically* around this center, (1b). This is due to the existence of a conserved quantity—obtained by integrating the relation $(d - c/x)\,\mathrm{d}x = -(b - a/y)\,\mathrm{d}y$ implied by (1a). It is evident from the equilibrium formula (1b) that the addition to this model of any intervention resulting in an *increase* of the constant c (the natural rate of *decrease* of the predators in the absence of preys), even if associated with a simultaneous *decrease* of the constant a (the natural rate of *increase* of the preys in the absence of predators)—for instance by any kind of indiscriminate fishing or hunting (if the populations under consideration are fishes or huntable games)—results in a *decrease* in the equilibrium number of predators but—somewhat paradoxically—in an *increase* in the equilibrium number of preys.

In the following, we describe equations which could, in principle, describe the kinetics of some very simple and idealized reactions. We do not claim that these can be realized, but the mathematical behavior of the resulting equations is of sufficient interest to warrant the study.

Consider the following four chemical reactions, which we assume to be taking place simultaneously in a reactor guaranteeing at all time that the two chemicals U and W are uniformly mixed:

$$U + U \Longrightarrow U \quad \text{with rate } \alpha,$$
$$U + W \Longrightarrow U \quad \text{with rate } \beta,$$
$$W + W \Longrightarrow U \quad \text{with rate } \gamma,$$
$$W + W \Longrightarrow W + W + W \quad \text{with rate } \delta + 2\gamma.$$

Here and hereafter α, β, γ and δ are four *positive* constants. Hereafter, we indicate by $u \equiv u(t)$ and $w \equiv w(t)$ the amounts (say, the numbers of molecules) of chemicals U and W respectively contained in the reactor at time t. Hence, we model the chemical kinetics regarding the two chemicals U and W via the following system of two nonlinear ODEs:

$$\dot{u} = -\alpha u^2 + \gamma w^2, \qquad \dot{w} = -\beta u w + \delta w^2 = (-\beta u + \delta w) w. \tag{2}$$

Note that this system guarantees that, if $u(0) > 0$ and $w(0) > 0$, then $u(t) > 0$ and $w(t) > 0$ for all (subsequent) time: indeed (2) entails that $\dot{u} > 0$ when $u = 0$ and $\dot{w} = 0$ when $w = 0$—and we show below that no blow-up can occur from the first quadrant of the $u - w$ (phase-space) Cartesian plane.

Clearly this model, (2), admits (aside from the equilibrium solution $u(t) = w(t) = 0$) no equilibrium configuration, unless the four reaction rates satisfy the equality $\alpha\delta^2 = \gamma\beta^2$. We mainly focus hereafter on the case characterized by the following three inequalities:

$$\gamma\beta^2 > \alpha\delta^2, \tag{3a}$$

$$2\beta\gamma > \delta^2, \tag{3b}$$

$$2\beta \leqslant \alpha, \tag{3c}$$

and we accordingly introduce the *positive* quantity η setting

$$\eta^2 = \frac{\gamma\beta^2 - \alpha\delta^2}{\alpha}. \tag{4}$$

Note that a large part of what follows holds without requiring the inequality (3c). However, as we shall see, the inequality (3c) is a necessary condition for oscillatory reactions to occur in the systems to be discussed later.

This model then has the remarkable feature that, in the special case $\beta = 2\alpha$, it can actually be solved *analytically* in terms of elementary functions, as shown in the following proposition.

Proposition 1. *If the equality*

$$\beta = 2\alpha, \tag{5a}$$

holds—in which case the two inequalities (3a) and (3b) coincide, both reading

$$\eta^2 = 4\alpha\gamma - \delta^2 > 0, \tag{5b}$$

—the solution of the initial-value problem of the model (2) can be exhibited explicitly:

$$u(t) = \frac{C}{\alpha}\left[\frac{\delta}{\eta} + C(t - t_0)\right][1 + C^2(t - t_0)^2]^{-1}, \qquad (6a)$$

$$w(t) = \frac{2C}{\eta}[1 + C^2(t - t_0)^2]^{-1}, \qquad (6b)$$

$$C = \frac{\eta w(0)}{2}\left\{1 + \frac{1}{\eta^2}\left[\delta - 2\alpha\frac{u(0)}{w(0)}\right]^2\right\}, \qquad (6c)$$

$$Ct_0 = \frac{1}{\eta}\left[\delta - 2\alpha\frac{u(0)}{w(0)}\right]. \qquad (6d)$$

The two constants C and t_0 in the first two of these four formulae are arbitrary, yielding thereby the *general solution* of the model (2); the last two formulae provide their values yielding the solution of the initial-value problem. The way to arrive at this result will be sketched in the following section, but it can, of course, be verified through a straightforward computation. Note that *all* these solutions are *nonsingular* and *vanish asymptotically* (as $t \to +\infty$); they moreover imply that $u(t)$ and $w(t)$ remain *positive* for all (positive) time (assuming of course that the initial data $u(0)$ and $w(0)$ are *positive*). These qualitative features are in fact more general, as shown by the following result.

Proposition 2. *For arbitrary positive initial data, $u(0) > 0, w(0) > 0$, the dependent variables $u(t)$ and $w(t)$ of model (2) with (3) remain positive and finite for all (positive) time (i.e., no blow-up) and both vanish asymptotically,*

$$u(\infty) = 0, \qquad w(\infty) = 0. \qquad (6e)$$

The proof is given in the following section; it is a straightforward consequence of the solution by quadratures of system (2) which will be shown in the following section. The chemical reactions described above thus lead to the eventual (asymptotic) *disappearance* of both chemicals, U and W. Let us now discuss two variants of this model.

First, we suppose that there occurs additionally a constant decay of chemical U—say, caused by a fifth chemical reaction, $U \Longrightarrow Z$ with rate θ, with the inert chemical Z giving no further reaction—or, equivalently, caused by an outflow of chemical U from the reactor, proportional to the quantity of this chemical contained in it. The modeling of the process is now provided by the system

$$\dot{u} = -\theta u - \alpha u^2 + \gamma w^2, \qquad \dot{w} = -\beta u w + \delta w^2 = (-\beta u + \delta w)w, \qquad (7)$$

which differs from (2) due to the appearance—on the right-hand side of the first of these two ODEs—of the additional term $-\theta u$, representing the decay of chemical U. Here of course θ is a *positive* constant, $\theta > 0$.

In this case, we have no analytic solutions, but again a qualitative description of the behavior of the system. This is provided by the following proposition.

Proposition 3. *The system of two nonlinear ODEs (7) features (in addition to the trivial equilibrium configuration $u = w = 0$) a second equilibrium configuration,*

$$u(t) = \bar{u} = \frac{\theta\delta^2}{\alpha\eta^2}, \qquad w(t) = \bar{w} = \frac{\theta\beta\delta}{\alpha\eta^2}, \qquad (8)$$

which is clearly inside the first quadrant of the $u - w$ (phase-space) Cartesian plane provided the inequalities (3) (the first of which justifies the definition (4) of η) continue to hold. And—from any initial configuration (of course with $u(0) > 0$, $w(0) > 0$)—the solution of this system, *(7), always remains inside the first quadrant of the Cartesian $u - w$ plane. The equilibrium defined by (8) is stable if and only if the quantity*

$$\rho = \gamma\beta^2 + (\alpha - \beta)\delta^2 = \alpha\eta^2 + (2\alpha - \beta)\delta^2 \tag{9}$$

is positive, $\rho > 0$. If instead ρ is negative, $\rho < 0$, the equilibrium configuration (8) is unstable. Then the system rotates (clockwise) around this equilibrium point. The motion remains bounded for all times, so that the orbit is either periodic, approaches a limit cycle or approaches the equilibrium point. The latter is, of course, only possible if the equilibrium point is stable, that is, if $\rho > 0$. We moreover show that the bifurcation at $\rho = 0$ is a supercritical Hopf bifurcation, so that in a neighborhood of $\rho = 0$ there is a stable limit cycle in a neighborhood of the equilibrium point when $\rho < 0$, corresponding to an unstable equilibrium point. This limit cycle does not exist when $\rho > 0$.

Again, this is proved by linearizing (7) around its non-trivial equilibrium and combining this with the result of standard phase-space analysis. The result concerning the supercritical Hopf bifurcation is obtained by showing that the system at $\rho = 0$ has a weakly attracting focus. Note at this stage that inequality (3*c*) is necessary in order for the condition $\rho \leqslant 0$, hence oscillatory behavior, to be possible.

Another interesting variant of the original model (2) obtains if a *negative* constant $-f$ is added to the equation describing the behavior of U; see (2). This describes a situation in which a *constant* flow of chemical U is siphoned out of the reactor tank, independently of the concentration of U present. This can presumably be realized in a suitable range of parameters via an appropriate control mechanism, letting the chemical U out at a controllable rate $r(t)$ inversely proportional to its concentration. Since the resulting equations do not, as we shall see, guarantee that positive initial conditions remain positive, a chemical implementation will clearly not always be possible. Again, a non-trivial equilibrium is created, so that the chemicals do not disappear asymptotically.

We thus now consider the system

$$\dot{u} = -f - \alpha u^2 + \gamma w^2, \qquad \dot{w} = -\beta u w + \delta w^2 = (-\beta u + \delta w)w, \tag{10}$$

which differs from (2) due to the additional term $-f$ on the right-hand side of the first of these two ODEs. Here f is a *positive* constant, $f > 0$. Note that, while the second of these two ODEs guarantees that if $w(0) > 0$, then $w(t) > 0$ for all later times, now the first ODE does *not* guarantee automatically that if $u(0) > 0$, then $u(t) > 0$ for all later times. We discuss below under which circumstances $u(t)$ changes sign during the evolution, signaling a breakdown of the interpretation of the system (10) in terms of chemical reactions. Again, a remarkable, exactly solvable, special case exists, as described in the following proposition.

Proposition 4. *If $\beta = 2\alpha$ (see (5a)), the solution of the initial-value problem of this model (10) can be exhibited explicitly:*

$$u(t) = \sqrt{\frac{f}{\alpha}}\frac{(1 - A^2)\delta - 2A\eta\sin(\omega t + \varphi)}{\eta\left[1 + A^2 + 2A\cos(\omega t + \varphi)\right]}, \tag{11a}$$

$$w(t) = \sqrt{\frac{f}{\alpha}}\frac{2\alpha(1 - A^2)}{\eta\left[1 + A^2 + 2A\cos(\omega t + \varphi)\right]}, \tag{11b}$$

where the different constants are defined as follows:

$$\omega = 2\sqrt{f\alpha}, \tag{11c}$$

$$A = \sqrt{\frac{v^2 + v_-^2}{v^2 + v_+^2}}, \tag{11d}$$

$$\varphi = -\arcsin\left\{\frac{2\omega v}{\sqrt{v^4 + 2v^2 V_+ + V_-^2}}\right\}, \tag{11e}$$

$$v = 2\alpha u(0) - \delta w(0) = 2\alpha \frac{\bar{w}u(0) - \bar{u}w(0)}{\bar{w}}, \tag{11f}$$

$$v_\pm = \eta w(0) \pm \omega = \eta\,[w(0) \pm \bar{w}]\,, \tag{11g}$$

$$V_\pm = \eta^2 [w(0)]^2 \pm \omega^2 = \eta^2\{[w(0)]^2 \pm \bar{w}^2\}. \tag{11h}$$

Here $\eta > 0$ is of course defined by (5b) and the equilibrium values $\bar{u}$, $\bar{w}$ by (14) with (5b): note that this implies $\bar{w} = \omega/\eta$. Clearly, for arbitrary initial data $u(0) > 0$, $w(0) > 0$, this solution is nonsingular and isochronous, traveling clockwise around the equilibrium configuration (14) with period $T = \pi/\sqrt{f\alpha}$ (independent of the initial data, and remarkably also of the two rates γ and δ). The trajectory of the system in the $u - w$ (phase-space) Cartesian plane is the ellipse defined by the equation

$$4\alpha^2(\bar{w}u - \bar{u}w)^2 + \omega^2[w - \bar{w} - A^2(w + \bar{w})]^2 = \left(\frac{\omega^2 A}{\eta}\right)^2, \tag{12}$$

which shrinks to the equilibrium point if the initial data coincide with the equilibrium configuration, see (14) with (5a), since then A vanishes (see (11e) and (11g)). This trajectory remains inside the first quadrant of the $u - w$ (phase-space) Cartesian plane provided the initial data $u(0) > 0, w(0) > 0$ are inside the ellipse (enclosing of course the equilibrium point (14)) defined by the equation

$$4\alpha u(\alpha u - \delta w) + (2\sqrt{\alpha\gamma}\,w - \omega)^2 = 0. \tag{13}$$

Once more, we can also describe in qualitative terms the more general system in which the condition $\beta = 2\alpha$ does not hold.

Proposition 5. *The system of two nonlinear ODEs (10) features, in the first quadrant of the $u - w$ (phase-space) Cartesian plane, the single equilibrium configuration*

$$u(t) = \bar{u} = \frac{\delta}{\eta}\sqrt{\frac{f}{\alpha}}, \qquad w(t) = \bar{w} = \frac{\beta}{\eta}\sqrt{\frac{f}{\alpha}}, \tag{14}$$

with $\eta > 0$ defined of course by (4) (recall that we always assume validity of the inequality (3a)). This configuration is stable if $\beta < 2\alpha$, and is unstable if $\beta > 2\alpha$. Again, one can show that the motion remains bounded, at least as long as it remains within the positive quadrant. If $\beta < 2\alpha$, provided that the initial data are sufficiently close to the (stable) equilibrium configuration (14), the trajectory of the dependent variables $u(t)$, $w(t)$ approaches it asymptotically—exponentially in time, and spiraling or not depending on whether $8\beta^3\gamma$ is larger or smaller than $(2\alpha + \beta)^2\delta^2$. Moreover, if $\beta \neq 2\alpha$ there is no periodic orbit inside the positive quadrant. Thus, if $\beta < 2\alpha$, any initial conditions that do not approach equilibrium must eventually leave the positive quadrant and thus lose their chemical significance. If instead $\beta > 2\alpha$, the trajectories tend to move away from the (unstable) equilibrium configuration (14). In this case, the absence of periodic orbits entails that $u(t)$ becomes negative at some finite time, so that the system again loses its chemical significance.

Again, the results of proposition 5 are obtained through a straightforward phase-space analysis combined with linearization around the non-trivial equilibrium point. At this point, it should be pointed out that our results do not favor an interpretation of (10) as a chemical oscillator: indeed, we find that the solutions of (10) for $\beta \neq 2\alpha$, that is, in the generic case, either tend to an equilibrium or eventually leave the positive quadrant. However, we believe the possibility of obtaining isochronous solutions for these equations is nevertheless of interest in itself.

The last two propositions provide a description of the system's behaviour as a function of its parameters, which can be summarized as follows. The model (7) undergoes a supercritical Hopf bifurcation as the equilibrium becomes *unstable*, thereby giving rise to a *stable* limit cycle in the vicinity of the *unstable* equilibrium point. On the other hand, the model (10) loses its chemical interpretation by yielding anomalous behavior immediately above the appearance of oscillations, namely as soon as β exceeds 2α. This behavior consists of the appearance of negative values of $u(t)$ at finite times. Qualitatively, this can be understood as follows: as implied by proposition 4, at the very point at which the equilibrium becomes marginally stable, the system displays a highly nongeneric and quite remarkable behavior: it has a center at the equilibrium, instead of a weakly attracting focus, and moreover the oscillation has a period which is independent of its amplitude. This suggests that any perturbation of this system gets amplified indefinitely through resonance, entailing instability and leading to the behavior described in the last part of proposition 5. In this sense, the system behaves almost as if it were a linear system.

2. Proofs

To prove proposition 1, we first show how the system (2) can be solved by quadratures. First define $\phi = u/w$. One then has

$$\frac{1}{w}\frac{\mathrm{d}}{\mathrm{d}t}\phi = (\beta - \alpha)\phi^2 - \delta\phi + \gamma. \tag{15}$$

If we now introduce

$$\mathrm{d}\tau = w(t)\,\mathrm{d}t, \tag{16}$$

then it clearly follows that $\phi(\tau)$ can be evaluated by a quadrature. The system (2) is now rewritten as

$$\frac{\mathrm{d}u}{\mathrm{d}\tau} = (-\alpha\phi^2 + \gamma)w = (-\alpha\phi + \gamma\phi^{-1})u, \tag{17a}$$

$$\frac{\mathrm{d}w}{\mathrm{d}\tau} = (-\beta\phi + \delta)w, \tag{17b}$$

entailing that both $u(\tau)$ and $w(\tau)$ can be evaluated by quadratures. Finally, the relation between t and τ can also be obtained via the quadrature

$$t = \int_{\tau_0}^{\tau} \frac{\mathrm{d}\tau'}{w(\tau')}. \tag{18}$$

In the general case, these formulae cannot be made more explicit. In the special case $\beta = 2\alpha$, however, one finds

$$w\frac{\mathrm{d}\phi}{\mathrm{d}w} = \frac{\alpha\phi^2 - \delta\phi + \gamma}{-2\alpha\phi + \delta}, \tag{19}$$

which is readily solved to yield

$$\alpha u^2 - \delta u w + \gamma w^2 = C w, \tag{20}$$

where C is an integration constant. From this via (2) one gets

$$\alpha \left(\frac{\dot{w}}{2\alpha w}\right)^2 = C w - \left(\gamma - \frac{\delta^2}{4\alpha}\right) w^2. \tag{21}$$

And finally, the substitution $z = 1/w$ leads to the following readily solved equation:

$$\dot{z} = [4C\alpha z - (4\alpha\gamma - \delta^2)]^{1/2} \tag{22}$$

from which the results stated in proposition 1 follow through routine computations.

To prove proposition 2, we make use of (15): using inequalities (3*a*), (3*b*) and (3*c*), we see that the right-hand side of (15) has no real zeros. This entails that $\phi(\tau)$ and hence also $\phi(t)$ is a monotonically increasing function. It therefore tends to a limit, either finite or infinite, as $t \to \infty$. In either case, the limiting value of $\tau(t)$ as $t \to \infty$ is finite. Let us then consider the two possible limiting behaviors of $\phi(t)$ as $t \to \infty$: if it remains finite, then, as follows from (17*b*), the limiting value of $w(t)$ is nonzero, which contradicts the finiteness of the limiting value of $\tau(t)$. Hence the limit of $\phi(\tau)$ must be infinite. But this immediately leads to the conclusion, via (17*a*) and (17*b*), that $u(t)$ and $w(t)$ tend to zero as $t \to \infty$. The entire motion is hence bounded, which is what was to be shown.

To prove proposition 3, one notes first that the system (7) possesses two equilibrium configurations, the trivial one at $u = w = 0$, and a second one *inside* the first quadrant of the $u - w$ Cartesian plane; see (8). By linearizing the equations of motion (7) in the neighborhood of this second equilibrium point—via the assumption $u(t) = \bar{u} + \varepsilon u_1(t)$, $w(t) = \bar{w} + \varepsilon w_1(t)$ with ε infinitesimal—one gets

$$\dot{u}_1 = -\theta u_1 - 2\alpha\bar{u}u_1 + 2\gamma\bar{w}w_1, \qquad \dot{w}_1 = -\beta(\bar{u}w_1 + \bar{w}u_1) + 2\delta\bar{w}w_1, \tag{23a}$$

the general solution of which is, for each of the two dependent variables $\tilde{u}(t)$ and $\tilde{w}(t)$, a linear combination of two exponentials, $\exp(-\lambda_\pm t)$, with

$$\lambda_\pm = \frac{\theta\rho}{2\alpha\eta^2}\left(1 \pm \sqrt{1 - 4\frac{\alpha\beta\delta^2\eta^2}{\rho^2}}\right), \tag{23b}$$

with η and ρ defined of course by (4) and (9). Clearly the *real* parts of both λ_+ and λ_- have the same sign as ρ, and this confirms the statements of proposition 3 concerning the relation of the sign of ρ to the character (*stable* or *unstable*) of the equilibrium point (8). The behavior of the system near the equilibrium point (8) in the special case characterized by the *vanishing* of ρ, yielding for $\lambda_\pm$ the *imaginary* values $\lambda_\pm = \pm \mathrm{i}(\delta\theta/\eta)\sqrt{\beta/\alpha}$, requires a more detailed treatment. Let us now show that the Hopf bifurcation which this system undergoes as ρ goes through zero is in fact a supercritical Hopf bifurcation, that is, that a *stable* limit cycle arises in the neighborhood of the equilibrium point when it becomes *unstable*. This follows, as is well known, from the fact that the equilibrium is weakly stable when $\rho = 0$. The proof of this fact involves rather tedious calculations which are relegated to appendix A.

To complete the proof of the main part of proposition 3, it is then enough to show that the trivial equilibrium point $u = w = 0$ cannot be reached from inside the first quadrant of the $u - w$ plane, as well as the fact that the orbits always remain bounded. To prove the first point, note that the asymptotic approach of the trajectories of the system (7) to the trivial equilibrium point $u = w = 0$ can only happen from the sector defined by

$$u > \frac{\beta w}{\delta}, \tag{24}$$

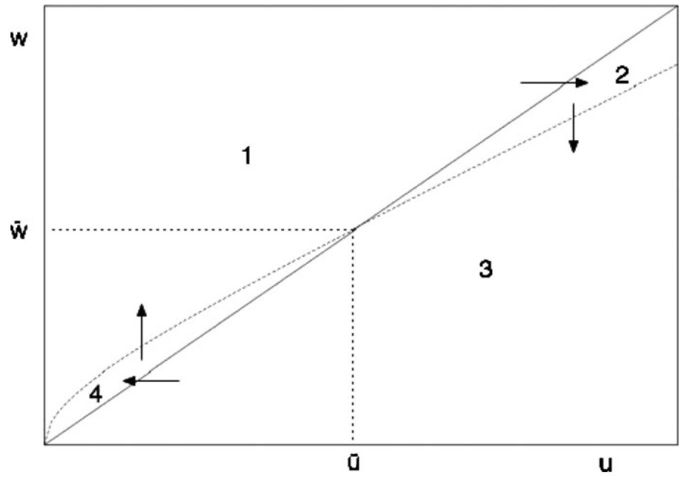

Figure 1. Phase-space portrait of equation (7). In sector 1, both $\dot{u} > 0$ and $\dot{w} > 0$, in sector 2, $\dot{u} > 0$ and $\dot{w} < 0$, in sector 3, $\dot{u} < 0$ and $\dot{w} < 0$ and in sector 4, $\dot{u} > 0$ and $\dot{w} < 0$. The continuous line is the locus of points for which $\dot{w} = 0$ and the dotted line is the locus of points for which $\dot{u} = 0$. The arrows indicate the way in which these lines must be traversed by the solutions of (7).

since only there are both derivatives $\dot{u}$ and $\dot{w}$ negative. However, the first of the two equations (7) can obviously be rewritten in the following integral form:

$$u(t) = \int_0^t \mathrm{d}t'\, \mathrm{e}^{-\theta(t-t')}[-\alpha u(t')^2 + \beta w(t')^2]$$
$$\leqslant \beta \int_0^t \mathrm{d}t' w(t')^2 \exp[\theta(t'-t)], \tag{25}$$

which is clearly incompatible with (24) as u and w go to zero.

Note however that the trivial equilibrium point $u = w = 0$ can be reached if the trajectory starts, rather than *inside* the first quadrant of the $u - w$ Cartesian plane, on its lower border, as entailed by the following solution of (7):

$$w(t) = w(0) = 0, \tag{26a}$$

$$u(t) = \frac{u(0)}{1 + u(0)(\alpha/\theta)[\exp(\theta t) - 1]}. \tag{26b}$$

The proof of proposition 3 is thereby essentially completed except for the last qualitative statement and the boundedness of the orbits. To ascertain the former, one performs a phase-space analysis. One partitions the first quadrant of the $u - w$ Cartesian plane into four sectors separated by the straight line $w = (\beta/\delta)u$ (at which $\dot{w}$ vanishes, and by the hyperbola $w = \sqrt{(\alpha u^2 + \theta u)/\gamma}$ (at which $\dot{u}$ vanishes) which starts at the origin of the $u - w$ Cartesian plane (with an infinite derivative) and becomes eventually asymptotic (from above) to the straight line $w = \sqrt{\alpha/\gamma}\,[u + \theta/(2\alpha)]$; these two curves cross of course at the equilibrium point (8). These four sectors are characterized by the four possible pairs of signs of the two quantities $\dot{u}$ and $\dot{w}$; see figure 1 for details. It is thereby easily seen that from sector 1 the trajectory can either escape to infinity (but this will be shown to be impossible) or go to sector 2. From sector 2, it can only proceed to sector 3, from sector 3 it can either go to the equilibrium point (8) (but this is of course not possible in the unstable case, when $\rho < 0$)

or go to the trivial equilibrium point $u = w = 0$ (also excluded, see above) or proceed to sector 4. From sector 4, once more, it can only go to sector 1. The qualitative description of the behavior of all the solutions of the system (7) starting inside the first quadrant of the Cartesian $u - w$ plane—as formulated in proposition 3—is thereby completed.

We are now only lacking two points: we must show that the solution cannot blow up to infinity when it finds itself in sector 1, and we must show the entire motion to be bounded. The former follows from the similar result for (2), since both systems are very close in this part of phase space. The second result is shown, once more, by introducing the variable $\phi = u/w$, which satisfies the equation

$$\frac{1}{w}\frac{\mathrm{d}}{\mathrm{d}t}\phi = (\beta - \alpha)\phi^2 - (\delta + \theta w^{-2})\phi + \gamma. \tag{27}$$

Let us now consider an arbitrary initial condition. From the above analysis, we see that the orbit must eventually reach sector 4, from which it will come back to sector 1. Since the values of w in sector 4 are bounded by $\bar{w}$ (see (8)), if w is to reach large values, it must necessarily pass through the value $2w_c$, where w_c is the value of w for which the right-hand side of (27) has no real zeros for $w > w_c$. Let this happen at time t_0. From then on, the following estimate holds, where we now once more introduce the variable τ defined by (16)

$$\tau - \tau_0 = \int_{t_0}^{t} w(t')\,\mathrm{d}t' = \int_{\phi(t_0)}^{\phi(t)} \mathrm{d}\phi \frac{1}{(\beta - \alpha)\phi^2 - [\delta + \theta w(t')^{-2}]\phi + \gamma}. \tag{28}$$

But, as long as $w(t')$ is larger than, say, $2w_c$, the right-hand side of (28) is uniformly bounded by a constant, independently of the values of $\phi(t_0)$ or ϕ. Since in this case one has, see (17*b*),

$$\frac{\mathrm{d}w}{\mathrm{d}\tau} = w(\delta - \beta\phi), \tag{29}$$

and since ϕ varies from $\phi(0)$ to δ/β and from δ/β to infinity in a uniformly bounded range of the variable τ, it is clear that $w(t)$ remains bounded throughout this part of the orbit. From this the entire proposition 3 follows.

Next, let us prove proposition 4. Its first part is shown as follows: note first that the conservation law of (2) stated in (20) also follows from the fact that (2) can be written as follows when $\beta = 2\alpha$:

$$w^{-2}\dot{u} = \frac{\partial}{\partial w}\left(\frac{\alpha u^2 - \delta u w + \gamma w^2}{w}\right), \tag{30a}$$

$$w^{-2}\dot{w} = -\frac{\partial}{\partial u}\left(\frac{\alpha u^2 - \delta u w + \gamma w^2}{w}\right). \tag{30b}$$

This is, of course, a Hamiltonian system, up to a rescaling of the time variable. Similarly, when $\beta = 2\alpha$, (10) can be written as

$$w^{-2}\dot{u} = \frac{\partial}{\partial w}\left(\frac{\alpha u^2 - \delta u w + \gamma w^2 + f}{w}\right), \tag{31a}$$

$$w^{-2}\dot{w} = -\frac{\partial}{\partial u}\left(\frac{\alpha u^2 - \delta u w + \gamma w^2 + f}{w}\right). \tag{31b}$$

From this, the following conservation law follows:

$$\frac{\alpha u^2 - \delta u w + \gamma w^2 + f}{w} = C, \tag{32}$$

where C is an integration constant. We proceed as we did for (2) and obtain

$$\alpha\left(\frac{\dot{w}}{2\alpha w}\right)^2 = Cw - f - \left(\gamma - \frac{\delta^2}{4\alpha}\right)w^2. \tag{33}$$

Once more, we define $z = 1/w$ and obtain

$$\dot{z} = [4\alpha Cz - 4\alpha f z^2 - (4\alpha\gamma - \delta^2)]^{1/2}, \tag{34}$$

which is once more readily solved and yields the result stated in proposition 4. Let us also note, for completeness, that in the (excluded) case $w(0) = 0$ one gets rather trivially the (unchemical) solution

$$w(t) = 0, \tag{35a}$$

$$u(t) = -\sqrt{\frac{f}{\alpha}}\tan\left[\frac{\omega(t - t_0)}{2}\right], \tag{35b}$$

$$t_0 = \frac{2}{\omega}\arctan\left[\sqrt{\frac{f}{\alpha}}u(0)\right], \tag{35c}$$

which becomes negative at time t_0 and then blows up (or rather down) at time $t_0 + \pi/\omega$.

To complete the proof of proposition 4, one must justify the last statements, concerning the ellipses (12) and (13). The first one, describing the trajectory, obtains by computing $\sin(\omega t + \varphi)$ from the ratio of (11*a*) and (11*b*) and $\cos(\omega t + \varphi)$ from (11*b*) and then using the identity $\sin^2 z + \cos^2 z = 1$. As for the second, it is a consequence of the following three inequalities (whose equivalence is easily seen to be implied by (11*e*), (11*g*) and (11*h*)):

$$4A^2\eta^2 < (1 - A^2)^2\delta^2, \tag{36a}$$

$$v^4 + 4\eta^2\bar{w}w(0)v^2 + \eta^4 V_-^2 < [2\omega\delta w(0)]^2, \tag{36b}$$

$$4\alpha u(0)[\alpha u(0) - \delta w(0)] + [2\sqrt{\alpha\gamma}w(0) - \omega]^2 < 0. \tag{36c}$$

Indeed the first, (36*a*), is clearly necessary and sufficient—see (11*a*)—for the positivity of $u(t)$; while the last, (36*c*), clearly entails the last statement of proposition 4, which is thereby proven. Also note that the second of these inequalities, (36*b*), is clearly satisfied by the equilibrium configuration (and by initial data sufficiently close to it), since both v and V_- vanish if the initial data coincide with the equilibrium data (see (11*g*) and (11*h*)). The diligent reader may wish to complete the diagram in the $u - w$ (phase-space) Cartesian plane described above, by drawing in it the ellipse defined by (13).

To prove proposition 5, one performs first—as in the proof of proposition 3, see above—a standard analysis of the behavior of the system (10) in the immediate neighborhood of its equilibrium configuration (14) by setting $u(t) = \bar{u} + \varepsilon u_1(t)$, $w(t) = \bar{w} + \varepsilon w_1(t)$ with ε infinitesimal, thereby linearizing the equations of motion satisfied by $u_1(t)$ and $w_1(t)$. Solving these linear ODEs one concludes again that $\tilde{u}(t)$ and $\tilde{w}(t)$ are a linear combination of two exponentials, $\exp(-\mu_\pm t)$, now with

$$\mu_\pm = \tfrac{1}{2}\left[\bar{u}(2\alpha - \beta) \pm \sqrt{\bar{u}^2(2\alpha - \beta)^2 - 8f\beta}\right], \tag{37}$$

where $\bar{u}$ is of course defined by (14). These formulae show that the *real* parts of both μ_+ and μ_- have the same sign as $2\alpha - \beta$, confirming the statement about the character— *stable* or *unstable*—of the equilibrium configuration (14). Also note that, via (14) and (4), the inequality

$8f\beta > \bar{u}^2(2\alpha - \beta)^2$, guaranteeing that $\mu_\pm$ have a *nonvanishing* imaginary part, corresponds to the inequality $8\beta^3\gamma > (2\alpha + \beta)^2\delta^2$.

We proceed to perform a phase-space analysis similar to that provided above in the proof of proposition 3: now the first quadrant of phase-space should be divided into four sectors separated by the straight line $w = (\beta/\delta)u$ (corresponding to $\dot{w} = 0$, see (10)) and by the hyperbola $w = \sqrt{(f + \alpha u^2)/\gamma}$ (corresponding to $\dot{u} = 0$, see (10)). We may now refer back to figure 1, which also qualitatively describes the present situation. It is then easy to see that the orbits also in this case turn clockwise around the equilibrium point $(\overline{u}, \overline{w})$, see (14), as long as they stay within that quadrant. On the other hand, as we show below, for $\beta \neq 2\alpha$ there are no periodic orbits lying in that quadrant, whereas for $\beta = 2\alpha$ the solution is fully characterized in proposition 4. From the absence of periodic orbits and the Poincaré–Bendixson theorem, it follows that any orbit must either leave the first quadrant or tend to that equilibrium point. The latter possibility, however, only arises if that equilibrium configuration is linearly *stable*, which, as shown above, only happens if $\beta < 2\alpha$. Finally, we may use the above phase-space analysis together with an argument entirely similar to that used in the proof of proposition 3 to show that the solutions of (10) remain bounded for all times and cannot blow up to infinity. We have thus proved all of proposition 5.

Let us finally show that, if $\beta \neq 2\alpha$, there can be no (nontrivial) periodic orbit lying entirely inside the positive quadrant. For this purpose, it is convenient to introduce the function $s = w^{-1}$, in terms of which the system (10) reads as follows:

$$\dot{u} = -f - \alpha u^2 + \gamma s^{-2}, \qquad \dot{s} = \beta u s - \delta. \tag{38}$$

Next, we introduce the Lyapunov function

$$L = \frac{(\ddot{s})^2}{2} + \beta f (\dot{s})^2. \tag{39}$$

It can then be shown that the equations of motion (38) entail that, if $\beta \neq 2\alpha$ and $u > 0$, this quantity is a *strictly monotonic* function of time. This is implied by the equation

$$\dot{L} = (\beta - 2\alpha)(\ddot{s})^2 u, \tag{40}$$

which is a consequence of the system (38), as shown in appendix B. (Note in passing that the *conservation* of L for $\beta = 2\alpha$ offers yet another way to show proposition 4). Clearly (40) immediately implies that, if $\beta \neq 2\alpha$, there cannot be any periodic solution of our system in the first quadrant of the $u - w$ (phase-space) plane where of course $u > 0$.

Finally, if the system is considered in the abstract, independently of its possible interpretation as a chemical process, we may ask how it behaves after becoming negative. Let us just note that the statements made above concerning the boundedness of the solution of course fail, since the proof of boundedness rested essentially on positivity.

3. Outlook

In this short paper, we refrained from displaying any numerical solution of the three mathematical models, (2), (7) and (10), discussed above, focusing rather on their exact mathematical treatment. If the chemical interpretations we outlined turn out to be a realistic possibility and chemical engineers wish to implement them, such numerical simulations will of course become useful—and quite easy to perform.

Let us complete this paper by outlining, in this same spirit (i.e., without recourse to numerics), a more general variant of the models discussed above and by tersely mentioning how to manufacture other models of chemical reactions also featuring explicit solutions displaying *isochrony*.

The more general model reads

$$\dot{u} = -f - \theta u - \alpha u^2 + \gamma w^2, \tag{41a}$$

$$\dot{w} = -\kappa w - \beta u w + \delta w^2 = (-\kappa - \beta u + \delta w) w. \tag{41b}$$

This model encompasses all those discussed above, inasmuch as it reduces to (2) for $f = \theta = \kappa = 0$, to (7) for $f = \kappa = 0$ and to (10) for $\theta = \kappa = 0$; but we now assume, as we always did in this paper, that all these quantities are *positive*. Note that, as in the case of (10), this model allows $u(t)$ to possibly become *negative*, signifying a possible breakdown of its chemical significance. A chemical narrative appropriate to it envisages, in addition to that described above in connection with the system (10), a decay of both chemicals U and W with rates θ and κ, either via chemical reactions $U \Longrightarrow Z$ and $W \Longrightarrow Y$ with Z and Y two inert chemicals (or possibly the same one) not interacting with U and W, or via the addition to the original model, see (2), of an outflow of each chemical, appropriately modulated according to the quantity of it present in the reactor (note that, for simplicity, we omitted to include a term independent of w on the right-hand side of the second ODE (41*b*)). A standard analysis shows that in this case there is still a *single* equilibrium configuration in the first quadrant of the $u - w$ (phase-space) Cartesian plane,

$$\bar{u} = \frac{\delta \bar{w} - \kappa}{\beta}, \tag{42a}$$

$$\bar{w} = \frac{\delta(2\alpha\kappa - \beta\theta)}{2\alpha\eta^2} \left[\sqrt{1 + \frac{4\alpha\eta^2[(\alpha\kappa - \beta\theta)\kappa + \beta^2 f]}{\delta^2(2\alpha\kappa - \beta\theta)^2}} - 1 \right], \tag{42b}$$

provided that the reaction rates are restricted by the three inequalities

$$\gamma\beta^2 - \alpha\delta^2 > 0, \qquad (\alpha\kappa - \beta\theta)\kappa + \beta^2 f > 0, \qquad \delta^2 f > \gamma\kappa^2, \tag{42c}$$

the first of which coincides with (3*a*) and justifies the definition (4) of the quantity η, the second of which is necessary and sufficient to guarantee that $\bar{w}$ is *positive*, $\bar{w} > 0$, and the third of which is necessary and sufficient to guarantee that $\bar{w} > \kappa/\delta$ hence that $\bar{u}$ is as well *positive*, $\bar{u} > 0$. It is moreover easily seen that this equilibrium configuration is *unstable* if *either one* of the following two (additional) inequalities holds

$$(\beta - 2\alpha)\delta\bar{w} + 2\alpha\kappa - \beta\theta > 0 \quad \text{or} \quad 2(\alpha\delta + \beta^2)\bar{w} - 2\alpha\kappa + \beta\theta > 0. \tag{42d}$$

Note that the first one of these two inequalities holds automatically if $\beta > 2\alpha$ and $\alpha\kappa > \beta\theta$ (also entailing validity of the second inequality (42*c*)). The qualitative behavior of this system is then easily seen to be analogous to that of the model (10) (see proposition 4), by taking advantage, as in the previous cases, of the phase-space picture yielded by the separation of the first quadrant of the $u - w$ Cartesian plane into four sectors, now via the straight line $w = (\beta u + \kappa)/\delta$ (corresponding to $\dot{w} = 0$) and the hyperbola $w = \sqrt{\alpha u^2 + \theta u + f/\gamma}$ (corresponding to $\dot{u} = 0$), crossing of course at the equilibrium point (42*b*).

Other models of chemical reactions amenable to exact treatment and yielding interesting phenomenologies—such as *isochronous* evolutions—may be evinced from results reported in [1]: their treatment will be reported in a subsequent paper.

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Appendix A. Weak stability at criticality

We consider the system (7) at criticality, that is, when $\rho = 0$. To simplify the formulae, we normalize the system as follows:

$$\dot{u} = -\alpha u^2 + \gamma w^2 - u, \tag{A.1a}$$

$$\dot{w} = w(w - u), \tag{A.1b}$$

which can be attained by scaling appropriately u, w and t. The case $\rho = 0$ then corresponds to $\gamma = 1 - \alpha$, and the inequalities (3) then reduce to $\alpha < 1/2$. Shifting (A.1) to $u_1 = u - \bar{u}$ and $w_1 = w - \bar{w}$, where $\bar{u} = \bar{w} = 1/(1 - 2\alpha)$, one obtains

$$\dot{u_1} = -\alpha u_1^2 + (1 - \alpha) w_1^2 - \frac{1}{1 - 2\alpha} u_1 + \frac{2 - 2\alpha}{1 - 2\alpha} w_1, \tag{A.2a}$$

$$\dot{w}_1 = w_1(w_1 - u_1) + \frac{1}{1 - 2\alpha} w_1. \tag{A.2b}$$

One now defines

$$L(u_1, w_1) = \frac{u_1^2}{2} - u_1 w_1 + (1 - \alpha) w_1^2 - \left(c_1 u_1^3 + c_2 u_1^2 w_1 + c_3 u_1 w_1^2 + c_4 w_1^3\right) - \left(d_1 u_1^4 + d_2 u_1^3 w_1 + d_3 u_1^2 w_1^2 + d_4 u_1 w_1^3 + d_5 w_1^4\right) \tag{A.3}$$

with

$$c_1 = \frac{1}{3}(1 - 2\alpha) \tag{A.4a}$$

$$c_2 = -2\alpha^2 + 3\alpha - 1 \tag{A.4b}$$

$$c_3 = 4\alpha^2 - 4\alpha + 1 \tag{A.4c}$$

$$c_4 = \frac{1}{3}(8\alpha^3 - 14\alpha^2 + 7\alpha - 1) \tag{A.4d}$$

$$d_1 = 0 \tag{A.4e}$$

$$d_2 = -\frac{32\alpha^5 - 112\alpha^4 + 160\alpha^3 - 88\alpha^2 + 14\alpha + 1}{12\alpha^2 - 28\alpha + 23} \tag{A.4f}$$

$$d_3 = -\frac{96\alpha^6 - 432\alpha^5 + 768\alpha^4 - 616\alpha^3 + 126\alpha^2 + 69\alpha - 25}{2(12\alpha^2 - 28\alpha + 23)} \tag{A.4g}$$

$$d_4 = -\frac{-96\alpha^6 + 336\alpha^5 - 464\alpha^4 + 216\alpha^3 + 66\alpha^2 - 83\alpha + 18}{12\alpha^2 - 28\alpha + 23} \tag{A.4h}$$

$$d_5 = -\frac{1}{4}(-192\alpha^7 + 768\alpha^6 - 1168\alpha^5 + 560\alpha^4 + 428\alpha^3 - 616\alpha^2 + 257\alpha - 37) \cdot (12\alpha^2 - 28\alpha + 23)^{-1}. \tag{A.4i}$$

It is then straightforward—using computer algebra—to show that

$$\frac{\mathrm{d}}{\mathrm{d}t} L\,[u_1(t), w_1(t)] = -\frac{(1-\alpha)(1-2\alpha)^3(u_1(t)^2 + w_1(t)^2)^2}{12\alpha^2 - 28\alpha + 23} + g_5(u_1, w_1) < 0, \tag{A.5}$$

since $12\alpha^2 - 28\alpha + 23 > 0$ for all (*real*) α. Here $g_5(u_1, w_1)$ stands for a function bounded by a homogeneous polynomial of fifth order in u_1 and w_1. Since $L(u_1, w_1)$ is positive definite for small enough u_1 and w_1, it follows from (A.5) that the origin of (A.2) is stable.

Appendix B. Lyapunov function for (10)

In this appendix we prove the formula (40).

Differentiation of the second ODE of the system (38) yields

$$\ddot{s} = \beta(\dot{u}s + u\dot{s}), \tag{B.1}$$

and via the first ODE of the system (38) this yields

$$\ddot{s} = \beta(-fs - \alpha u^2 s + \gamma s^{-1} + u\dot{s}), \tag{B.2}$$

and using again the second ODE of the system (38) to eliminate u and multiplying by s one gets

$$s\ddot{s} = \beta(-fs^2 + \gamma) - \frac{\alpha}{\beta}(\dot{s} + \delta)^2 + \dot{s}(\dot{s} + \delta). \tag{B.3}$$

By differentiating this ODE (and then dividing by s) we then get

$$\dddot{s} = -2\beta f\dot{s} + \frac{\beta - 2\alpha}{\beta}\frac{(\dot{s} + \delta)}{s}\ddot{s}. \tag{B.4}$$

On the other hand, on time-differentiating L, see (39), we get

$$\dot{L} = (\dddot{s} + 2\beta f\dot{s})\ddot{s}, \tag{B.5}$$

and via (B.4) this becomes

$$\dot{L} = (\beta - 2\alpha)\frac{(\dot{s} + \delta)}{\beta s}(\ddot{s})^2, \tag{B.6}$$

hence, via the second ODE of the system (38), precisely (40), which is thereby proven.

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