Some Differences between Thermokinetic and Chemical Oscillating Reactions

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Abstract: This experimental work points out the main qualitative and quantitative differences between two kinds of oscillating reactions. It is shown that some oscillations cannot be disturbed by heat transport, whereas some others are only observed when the heat flux takes adequate values. Two oxidation reactions in aqueous medium, one of each type, have been studied to illustrate this fact. Moreover their thermal properties have been measured in both oscillating and stationary states. Whatever the thermal property concerned, the thermokinetic reaction leads to values higher by at least 1 order of magnitude. Therefore qualitative as well as quantitative criteria allow us to discriminate between thermokinetic and chemical oscillations.

Introduction

Over the recent past years many papers[1] have been devoted to the study of several oscillating reactions such as, for instance, the well-known Belousov–Zhabotinsky (BZ) reaction. As far as sustained oscillations can only occur in open systems, quantitative experimental study of this kind of reaction[2] must be performed in continuous-flow well-stirred tank reactors (CSTR). Now chemical engineering science provides a lot of examples[3] where competition between heat exchange with the surrounding and heat production by the reaction itself results in so-called "thermokinetic oscillations". On the other hand kinetic analysis of reaction schemes[4,5] shows that periodicity may appear in an isothermal medium, provided a suitable feedback mechanism is involved,[6] leading to genuine "chemical oscillations". The question which rises immediately is whether sustained BZ-like oscillations are of the chemical type, as usually assumed, and, if so, how they differ from thermokinetic ones. However, among the lot of papers dealing with BZ-like oscillations, very few[7–10] are those where temperature oscillations are taken into account, although the calorimetric measurements of Kôrös et al.[11] have shown that the heat of reaction is larger than 600 KJ/mol of bromate in the oscillatory phase of the BZ reaction. The aim of the present work is an attempt to bring some light on this problem, investigating the qualitative and quantitative influence of heat exchange upon two reactions: the first is the oxidation of malonic acid by bromate ions (i.e., the BZ reaction itself) and the second the oxidation of ethyl alcohol by hydrogen peroxide (which we shall call the Hafke–Gilles reaction,[12] HG), both occurring in an aqueous medium.

Even though the stability of open reactors is a problem studied for a while,[13] a theoretical approach fitted to our experimental purpose is to be set up. Accordingly we develop in a first step the linear stability analysis of an open homogeneous nonisothermal system, like a CSTR. Then the results obtained during the experimental study of the HG and BZ reactions are described, both in oscillatory as well as stationary phases.

Linear Stability Analysis

The mass and heat balance equations of a CSTR (see eq 1),

$$\nu_i X_i \xrightarrow{k_r} \nu_j' X_j' \quad r = 1, \ldots, \rho \tag{1}$$

where a chemical reaction involving ρ elementary steps takes place, are derived in the appendix. With the assumption that the heat exchange is to be governed by the Fourier law of heat conduction, expression 2 is obtained (eq A5 and A9 of the apprendix). Among

$$\dot{X}_l = \frac{1}{\tau}(X_l^0 - X_l) + \sum_r (\nu_{lr}' - \nu_{lr}) k_r \prod_i X_i^{\nu_{ir}} \tag{2}$$

$$\beta \dot{T} = \sum_n \gamma_n (T_n - T) - V \sum_r \Delta h_r k_r \prod_i X_i^{\nu_{ir}}$$

$$i, l = 1, \ldots, N \quad r = 1, \ldots, \rho$$

the various solutions of this set of $N + 1$ differential equations, some of them may correspond to stationary states, where the composition and temperature of the reacting medium are time independent. In that case the temperature T_s and concentrations $X_{1s}, X_{2s}, \ldots, X_{Ns}$ are given by a set of $N + 1$ algebraic equations. To write them down explicitly, one should not forget that the rate constants k_r are temperature dependent according to the Arrhenius law given in eq 3.

$$k_r(T) = k_{0r} \exp(-E_r/RT) \tag{3}$$

On the other hand the enthalpies Δh_r depend much less on temperature and may be assumed constant over a reasonable range, as we shall do here. Thus the $N + 1$ algebraic equations are shown in eq 4.

$$\frac{1}{\tau}(X_l^0 - X_{ls}) + \sum_r (\nu_{lr}' - \nu_{lr}) k_{0r} \exp(-E_r/RT_s) \prod_i X_{is}^{\nu_{ir}} = 0 \tag{4}$$

$$\sum_n \gamma_n (T_n - T_s) - V \sum_r \Delta h_r k_{0r} \exp(-E_r/RT_s) \prod_i X_{is}^{\nu_{ir}} = 0$$

$$i, l = 1, \ldots, N \quad r = 1, \ldots, \rho$$

Obviously the detailed chemical mechanism must be known before this system can be solved. Let us suppose however that such a stationary state does exist. Then we can try to see if it is stable or not, according to the well-known linear stability analysis techniques.[14] To this end one looks at the eigenvalues of the so-called stability matrix **A**, the components of which are derived

(1) For a general review, see for example: Nicolis, G.; Portnow, J. *Chem. Rev.* **1973**, *73*, 365; Field, R. J. In "Theoretical Chemistry"; Eyring, H., Henderson, D., Eds; Academic Press: New York, 1978; Volume 4, p 53.
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(12) Hafke, C.; Gilles, E. D. *Mess., Steuern, Regeln.* **1968**, *11*, 204.
(13) Aris, R.; Amundson, N. R. *Chem. Eng. Sci.* **1958**, *7*, 121. Bush, S. F. *Proc. R. Soc. London, Sect. A* **1969**, *309*, 1. Aris, R. *Chem. Eng. Sci.* **1969**, *24*, 149. Uppal, A.; Ray, W. H.; Poore, A. B. *Chem. Eng. Sci.* **1974**, *29*, 967.

(14) Sattinger, D. "Topics in Stability and Bifurcation Theory"; Springer-Verlag: Berlin, 1973.

from (2) taking (4) into account (Scheme I).

Scheme I

$$a_{lj} = \left(\frac{\partial \dot{X}_l}{\partial X_j}\right)_s = \frac{1}{X_{js}}\sum_r \nu_{jr}(\nu_{lr}' - \nu_{lr})W_{rs}$$

$$a_{ll} = \left(\frac{\partial \dot{X}_l}{\partial X_l}\right)_s = \frac{1}{X_{ls}}\sum_r \nu_{lr}(\nu_{lr}' - \nu_{lr})W_{rs} - \frac{1}{\tau}$$

$$a_{N+1,l} = \left(\frac{\partial \dot{T}}{\partial X_l}\right)_s = -\frac{V}{\beta X_{ls}}\sum_r \nu_{lr}\Delta h_r W_{rs}$$

$$a_{l,N+1} = \left(\frac{\partial \dot{X}_l}{\partial T}\right)_s = \frac{1}{RT_s^2}\sum_r (\nu_{lr}' - \nu_{lr})E_r W_{rs}$$

$$a_{N+1,N+1} = \left(\frac{\partial \dot{T}}{\partial T}\right)_s = -\frac{V}{\beta RT_s^2}\sum_r E_r \Delta h_r W_{rs} - \frac{1}{\beta}\sum_n \gamma_n$$

$$j, l = 1, ..., N \quad r = 1, ..., \rho$$

When all the eigenvalues of the matrix **A** have a negative real part, the stationary state is linearly stable. If one of them has a postive real part, then the stationary state is unstable.

Some years ago Tyson[15] proposed a classification of instabilities occurring in isothermal chemical systems. It will be simply remembered, without any further details, that this classification relies on the sign of diagonal elements a_{ii} and of different products ($a_{ij}a_{ji}$ for $i \neq j$; $a_{ij}a_{jk}...a_{pq}a_{qi}$ for any sequence of three or more indices $i \neq j \neq k \neq ... \neq p \neq$ q), whatever their amplitude. Thanks to these mathematical criteria one can also discriminate between three different types of instability in nonisothermal reacting systems. We discuss (a) chemical instability when the matrix elements involved (by one of several destabilizing conditions) belong only to the first N lines and N columns of the matrix **A**, (b) thermal instability when no other element than $a_{N+1,N+1}$ is concerned, i.e., eq 5, or eq 6, which implies necessarily at least

$$a_{N+1,N+1} = -\frac{V}{\beta RT_s^2}\sum_r E_r \Delta h_r W_{rs} - \frac{1}{\beta}\sum_n \gamma_n > 0 \quad (5)$$

$$\sum_r E_r \Delta h_r W_{rs} < -\frac{RT_s^2}{V}\sum_n \gamma_n \quad (6)$$

one exothermic step, and (c) mixed instability in all other cases; hence one element $a_{l,N+1}$ or $a_{N+1,l}$—and perhaps several—is certainly involved.

We must emphasize that the above classification is a little bit different from the one already introduced in previous papers.[16] Our first proposal has been slightly improved here, in order to get a better separation between purely chemical and purely thermal effects. Now one would perhaps be tempted in the third case to speak about thermokinetic instability rather than the mixed one, because kinetic (W_{rs}) and thermal (Δh_r and/or E_r) parameters appear simultaneously in $a_{l,N+1}$ and/or $a_{N+1,l}$. To date, however, thermokinetic instability is not usually understood in the very accurate meaning linked with the foregoing analysis. This is the reason why we feel better talking about mixed instability, in order to prevent any kind of misunderstanding.

The set of differential equations (2) may also have solutions which are not stationary but, for instance, periodic so that sustained oscillations (limit cycle) may be observed. From a mathematical point of view, several theorems are available when the problem has only two independent variables: e.g., any periodic solution surrounds at least one unstable stationary state (Poincaré index rule). Very little is known, unfortunately, if the number of state variable exceeds two, which is certainly the case for most of the

Table I. Main Characteristics of CSTR and the Spiral

	reactor	spiral
material	Pyrex	gold
width of wall, cm	0.26	0.06
exchange area, cm^2	65.5	60.0
heat conductivity, J·cm^{-1}·deg^{-1}·min^{-1}	0.677	188

Table II. Calibrated Values of γ_0, γ_1, and β for Two Sets of Experimental Conditions

reactn	τ, min	$\langle T \rangle$, °C	γ_0, J· deg^{-1}· min^{-1}	γ_1, J· deg^{-1}· min^{-1}	β, J· deg^{-1}
BZ	3.8	38	169	982	223
HG	13.8	68	149	990	218

realistic physicochemical systems. Nevertheless let us take the previous statement as a working hypothesis, whatever its lack of mathematical proof. In other words we assume that any periodic solution of (2) arises through the bifurcation of a stationary one. The stability matrix of the stationary state which may be surrounded by a periodic orbit becomes of the greatest interest because some of its elements can be changed experimentaly much more than the others. For instance, a modification in the mass flux through the reactor, i.e., a change in the mean residence time τ, will give rise to the same shift in the value of all the diagonal elements, while the off-diagonal elements remain constant (at least to the first order). Even more attractive, one sees the way to vary $a_{N+1,N+1}$ alone, via the quantity $\sum_n \gamma_n$. Indeed it is not very difficult to change either the number of isothermal baths or else any of the heat-exchange coefficients γ_n. In the framework of our working hypothesis one can guess that two different behaviors will be observed, depending upon the link between $a_{N+1,N+1}$ and the stability: (a) either the stationary state is unstable whatever the value of $a_{N+1,N+1}$, so that a periodic solution always prevails (The stationary state instability lies clearly elsewhere and can only have a chemical or a mixed origin. As far as oscillations stand for any heat-exchange condition, temperature variations can be reduced at will. Therefore one would readily name chemical such oscillations.) (b) or the stationary state losses its stability beyond some critical value of the heat flux, giving rise to a periodic solution. In other words, the reaction oscillates or not, depending upon heat exchange conditions. When such oscillations occur, they are in general called thermokinetic.[22]

The straightforward conclusion of the foregoing analysis leads to build up of an experimental device allowing large amplitude variations of $\sum_n \gamma_n$. Then one can perform an experimentation designed to bring out the main differences between thermokinetic and chemical oscillating reactions.

Experimental Section

Our apparatus is made of the CSTR itself, a gold spiral immersed in it, and a chromel–alumel thermocouple connected to a Wheastone bridge and a null detector. The reacting volume is equal to 44 mL. The main characteristics of the CSTR are summarized in Table I, detailed description being given elsewhere.[16,17] A synchronous engine, driving a glass stirrer, mixed the feed solutions supplied by a peristaltic pump. The CSTR is placed into an isothermal bath at temperature T_0, which is also the temperature of the inlet reagents. Through the gold spiral a regulatory fluid at temperature T_1 can be forced with adjustable flow up to 32 L·h^{-1}. The typical parameters of this spiral appear in Table I too. Gold has obviously been chosen thanks to its adequate chemical and thermal properties. Because the BZ reaction yields always rather low-temperature variations, the signal given by the thermocouple needs to be amplified. This explains why a set bridge + null detector is used, so that temperature differences of, say, 10^{-3} °C are easily detectable. At the same time we could also monitor the course of the reaction by recording the redox potential of the reacting medium measured with a platinum electrode.

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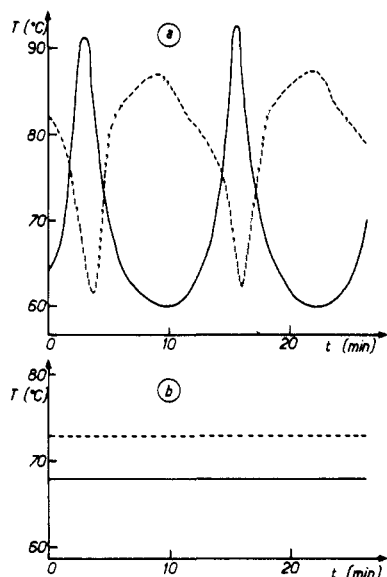
Figure 1. HG reaction: temperature (full line) and redox potential (dotted line, arbitrary scale) records at (a) low and (b) high heat fluxes.
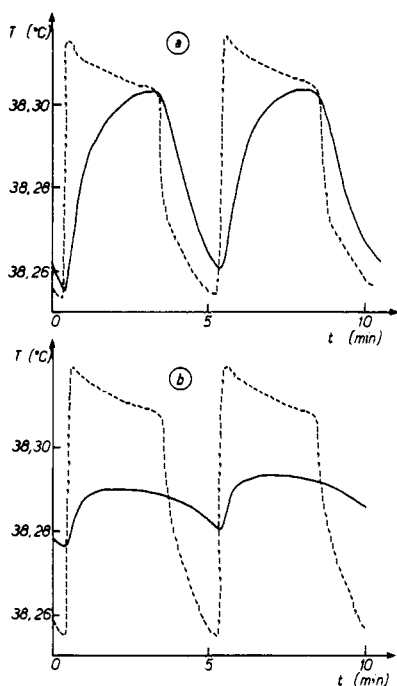

Figure 2. BZ reaction: temperature (full line) and redox potential (dotted line, arbitrary scale) records at (a) low and (b) high heat fluxes.

Let γ_0 and γ_1 quote respectively the heat-exchange coefficient of the CSTR (including the contribution of mass flux) and of the gold spiral. The heat balance equation writes down either eq 7a when the gold spiral

$$\beta \dot{T} = \sigma(Q) + \gamma_0(T_0 - T) \tag{7a}$$

is inactive or eq 7b when the regulatory fluid runs through the spiral. In

$$\beta \dot{T} = \sigma(Q) + \gamma_0(T_0 - T) + \gamma_1(T_1 - T) \tag{7b}$$

both equations β has the same value because the spiral always remains immersed into the reacting medium. Therefore the term $\sum_n \gamma_n$ may take two different values (see eq 8) as necessary to carry out the planned

$$\sum_n \gamma_n = \gamma_0 \qquad \sum_n \gamma_n = \gamma_0 + \gamma_1 \tag{8}$$

experimentation. The three parameters β, γ_0, and γ_1 (this last for the maximum value of the regulatory fluid flow) have been calibrated in a preliminary experiment. The reactor was filled with water instead of the reagents in order to cancel out any unknown heat source. Furthermore a wire of negligible mass, heated by Joule effect, supplied an easily measured heat release. Measuring the electric power dissipated by the
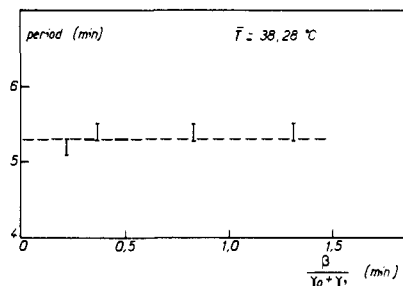

Figure 3. Period of BZ oscillations vs. the thermal relaxation time of the CSTR.

wire and recording the temperature until a stationary state is reached, one can deduce directly from eq (7a) and (7b) the values of γ_0, γ_1, and then β. The results are displayed in Table II for the two sets of running conditions corresponding to the mean residence time and temperature chosen later to study the HG and BZ reactions. All chemical products, standard analytical reagent grade, were used without any further purification.

Results

A. Oscillatory Regime. To determine the influence of heat exchanges on the HG and BZ reactions, we carried out two different experiments with each of them. In the first experiment no regulatory fluid is forced through the spiral so that the heat exchange keeps its minimum value. During the second one, the flow of the regulatory fluid is maximum and the heat exchange is too. Figures 1 and 2 show what happens when the other experimental conditions are as in Scheme II.

Scheme II

HG reaction

$$[H_2O_2]^\circ = 3 \text{ mol·L}^{-1}; \ [C_2H_5OH]^\circ = 1.4 \text{ mol·L}^{-1}$$

$$[Fe(NO_3)_3]^\circ = 0.015 \text{ mol·L}^{-1}; \ \tau = 13.8 \text{ min}$$

1st experiment (Figure 1a): $T_0 = 49.6 \ ^\circ C$; $\sum_n \gamma_n = \gamma_0 =$
$$149 \text{ J·deg}^{-1}\text{·min}^{-1}$$

2nd experiment (Figure 1b): $T_0 = 49.6 \ ^\circ C$, $T_1 = 68.1 \ ^\circ C$;
$$\sum_n \gamma_n = \gamma_0 + \gamma_1 = 1139 \text{ J·deg}^{-1}\text{·min}^{-1}$$

BZ reaction

$$[KBrO_3]^\circ = 5.10^{-3} \text{ mol·L}^{-1}; \ [CH_2(COOH)_2]^\circ =$$
$$2.10^{-2} \text{ mol·L}^{-1}$$

$$[Ce_2(SO_4)_3]^\circ = 1.10^{-3} \text{ mol·L}^{-1}; \ [H_2SO_4]^\circ = 1.5 \text{ mol·L}^{-1}; \ \tau = 3.8 \text{ min}$$

1st experiment (Figure 2a): $T_0 = 38.3 \ ^\circ C$; $\sum_n \gamma_n = \gamma_0 =$
$$169 \text{ J·deg}^{-1}\text{·min}^{-1}$$

2nd experiment (Figure 2b): $T_0 = 38.3 \ ^\circ C$, $T_1 = 38.3 \ ^\circ C$;
$$\sum_n \gamma_n = \gamma_0 + \gamma_1 = 1151 \text{ J·deg}^{-1}\text{·min}^{-1}$$

The HG reaction gives rise to large amplitude temperature oscillations in the first case, whereas these oscillations disappear completely in the second, indicating a stationary state where both temperature and redox potential are time independent (Figure 1). The analysis developed in Linear Stability Analysis leads to the conclusion that (i) HG oscillations are of thermokinetic type and (ii) the instability of the stationary state originates most likely in the matrix element $a_{N+1,N+1}$.

On the contrary the BZ oscillations are insensitive to heat exchange as can be seen in Figure 2. Of course the temperature oscillations are flattened when the heat exchange becomes higher, but they still stand. Moreover it is noteworthy that the two experiments provide the same record for the redox potential: the BZ reaction does oscillate quite similarly, although the heat flux varies by a factor of 7. Then one interesting question is certainly: does the oscillatory period depend upon heat exchanges? To clarify
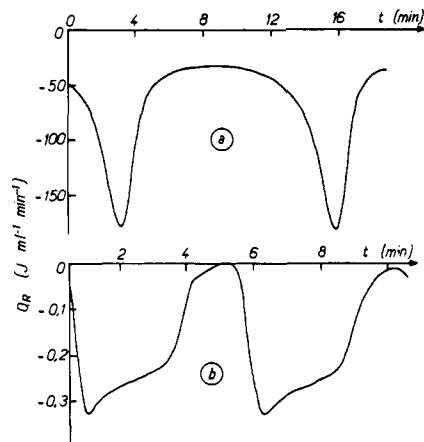
Figure 4. Thermicity of (a) the HG and (b) the BZ reactions in their oscillatory regime.

Table III. Thermicity of the HG and BZ Reactions in the Oscillatory Phase

Q_R	HG	BZ
max value, $J \cdot mL^{-1} \cdot min^{-1}$	-180	-0.33
mean value, $J \cdot mL^{-1} \cdot min^{-1}$	-63	-0.17
sum over one period, $J \cdot mL^{-1}$	-794	-0.92

this point, we did four experiments involving different regulatory fluid flows through the spiral. For each, the measured period is plotted in Figure 3 vs. the thermal relaxation time of the CSTR, that is to say the ratio $\beta / \sum_n \gamma_n$. Within the range of experimental errors, no shift can be noticed. Thus the BZ reaction leads to oscillations which are very likely of the chemical type, even though the existence of an unstable stationary state cannot be proved.

Apart from this different behavior, a quantitative difference between the HG and BZ reactions is also worth noting. One might say that the foregoing result cannot surprise anybody because the temperature variations are much bigger in the first reaction than in the second. This is true, but simply because the heat-exchange coefficients have close values. As a matter of fact the amplitude of temperature oscillations is not meaningful by itself since, for thermokinetic ones, it can be reduced at will, increasing $\sum_n \gamma_n$. The relevant property is the heat released by the reaction itself (see eq 9). According to eq A9 the thermicity Q_R of the reaction

$$\sum_r \Delta h_r W_r = Q_R = -\sigma(Q)/V \qquad (9)$$

is deduced in a straightforward manner from the temperature records. Using standard numerical techniques[18] to compute the first time derivative of the curves $T = f(t)$, one gets the plot of Figure 4, displaying the thermicity Q_R vs. time in the oscillatory phase. As expected the scales are very different for the two reactions, roughly speaking in a ratio of 500 (see Table III). In the case of the BZ reaction one should be careful due to a secondary effect,[19] namely, the heat of dilution of malonic acid inside the CSTR, which must be measured and substracted before reaching $\sum_r \Delta h_r W_r$. Although both reactions are exothermic, one is able, once again, to discriminate their oscillations thanks to thermal properties differing by more than 2 orders of magnitude.

B. Stationary State. As far as an unstable stationary state is assumed to exist, one would like to point out some of its characteristics. From an experimental viewpoint, the two reactions under study cannot be treated in the same way, simply because instability does not have the same origin in both cases.

HG Reaction. For that reaction we have previously seen that a stationary state may be reached, the temperature T_* of which satisfies eq 10, according to eq 7b. Now the temperature T_1 is

$$-V\sum_r \Delta h_r W_{r*} + \gamma_0(T_0 - T_*) + \gamma_1(T_1 - T_*) = 0 \qquad (10)$$
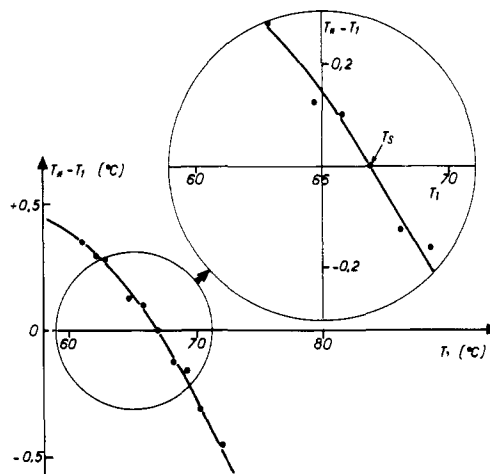
(18) Savitsky, A.; Golay, M. J. E. *Anal. Chem.* **1964**, *36*, 1627.
(19) We are indebted to Dr. Orbán, who called our attention to this point.

Figure 5. Determination of the unstable stationary state temperature T_s of the HG reaction.

an experimental parameter which can be changed at will. If it is adjusted in such a way that T_1, the temperature of the regulatory fluid, equals T_*, the measured temperature of the reacting medium, then eq 11 applies.

$$-V\sum_r \Delta h_r W_{r*} + \gamma_0(T_0 - T_*) = 0 \qquad (11)$$

On the other hand, when no regulatory fluid runs through the spiral, the oscillatory regime prevails around an unstable stationary state, the temperature T_s of which is given by eq 7a:

$$-V\sum_r \Delta h_r W_{rs} + \gamma_0(T_0 - T_s) = 0 \qquad (12)$$

In other words the temperature T_s of the unstable stationary state when oscillations occur is numerically equal to the temperature T_* of the stable stationary state when, and only when, the condition $T_1 = T_*$ is fulfilled. Therefore one has simply to perform an experimentation where T_1 is the relevant variable and to record the stationary temperature of the reacting medium T_*. Plotting the difference $T_* - T_1$ vs. T_1, one gets the curve of Figure 5. The intersection between this curve and the T_1 axis shows that there is a unique unstable stationary state at temperature

$$T_s = T_1 = T_* = 66.9 \pm 0.1 \ °C \qquad (13)$$

Moreover the thermicity Q_{Rs} of the reaction in this unstable stationary state is given by eq 14 and 15. Thus we have been able to determine the temperature and the thermicity of the HG reaction in its unstable steady state, even though this last one cannot be studied directly.

$$Q_{Rs} = \sum_r \Delta h_r W_{rs} = -\frac{\gamma_0}{V}(T_0 - T_s) \qquad (14)$$

$$Q_{Rs} = -58 \pm 4 \ J \cdot mL^{-1} \cdot min^{-1} \qquad (15)$$

Although no definite proof can be given, as discussed above, the instability originates most likely in the matrix element $a_{N+1,N+1}$. Thus, if this diagonal element is truly the leading term, marginal stability is reached when $a_{N+1,N+1}$ itself either changes sign or, at least, has a very low absolute value. At the bifurcation stationary state $\leftrightarrow$ oscillatory regime one sees that $a_{N+1,N+1}$ is more or less equal to zero. If the critical value of $\sum_n \gamma_n$ for which the oscillatory regime rises (or vanishes) was known, an estimation of the quantity $\sum_r E_r \Delta h_r W_{rs}$ would become possible. The desired variation of $\sum_n \gamma_n$ may be obtained, for instance, by changing the value of γ_1. Let γ_{1c} be the critical value of this parameter for which oscillations appear (or disappear since no hystersis occurs) and then

$$\sum_r E_r \Delta h_r W_{rs} \simeq -\frac{RT_s^2}{V}(\gamma_0 + \gamma_{1c}) \qquad (16)$$

We carried out this experiment, keeping the temperature T_1 and

T_* equal to 66.9 °C. This necessary condition must obviously be satisfied to get the value of $\sum_r E_r \Delta h_r W_{rs}$ for the unstable stationary state we are interested in. We found

$$\gamma_{1c} = 335 \ \text{J·mL}^{-1}\text{·min}^{-1} \tag{17}$$

that is to say

$$\sum_r E_r \Delta h_r W_{rs} \simeq -1.10^7 \ \text{J}^2\text{·mol}^{-1}\text{·mL}^{-1}\text{·min}^{-1} \tag{18}$$

Turning back now to the value of $a_{N+1,N+1}$ in the first experiment, i.e., when the gold spiral remains inactive, one finds

$$a_{N+1,N+1} = -\frac{V}{\beta R T_s^2} \sum_r E_r \Delta h_r W_{rs} - \frac{\gamma_0}{\beta} \simeq +1.5 \ \text{min}^{-1} \tag{19}$$

This positive value of the diagonal element $a_{N+1,N+1}$ may give rise to instability, in agreement with one of the available mathematical criteria.[15]

BZ Reaction. Since for this reaction the stability is not governed by heat exchanges, it is impossible to reach a stationary state in the same manner as above. If the instability of the assumed stationary state leading to oscillations would result from another diagonal element a_{ll} belonging to the first N lines of the matrix **A**, one could try to modify the mass flux of the chemical species l in a way very similar to the one used for the heat flux in the HG reaction. Unfortunately neither the origin of instability nor the species involved, if any, are known and, furthermore, the existence itself of an unstable stationary state still remains an hypothesis. Nevertheless stable stationary states given by the BZ reaction in a CSTR have been observed for several years. Also the emergence of oscillations arises through the bifurcation of a stationary solution as the concentration of some input reagents (e.g., malonic acid, bromate) varies.[20] Thus the BZ reaction leads certainly to unstable stationary states, the thermal properties of which are likely not very different from the stable stationary state ones. Thanks to our present purpose, only an order of magnitude is needed and we can try to get it by studying a stable stationary state. Now the question is: what kind of experimentation can be performed to measure these thermal properties? One thinks immediately to look how the system behaves in the temperature neighborhood of the stationary state. Around the stationary value T_s, the temporal evolution of the temperature may be expanded:

$$\dot{T} = 0 + \left(\frac{\partial \dot{T}}{\partial T}\right)_s (T - T_s) + \frac{1}{2}\left(\frac{\partial^2 \dot{T}}{\partial T^2}\right)_s (T - T_s)^2 + \dots \tag{20}$$

For little enough deviations from T_s, the terms of higher degree than one are negligible so that

$$\dot{T} = (T - T_s) = \left(\frac{\partial \dot{T}}{\partial T}\right)_s (T - T_s) \tag{21}$$

Starting with an initial condition $(T - T_s)_i$ and remembering that $(\partial \dot{T}/\partial T)_s = a_{N+1,N+1}$, it comes after integration

$$T - T_s = (T - T_s)_i \exp\left[-\frac{1}{\beta}\left(\frac{V}{RT_s^2}\sum_r E_r \Delta h_r W_{rs} + \sum_n \gamma_n\right)t\right] \tag{22}$$

Therefore the temperature relaxes exponentially to its stationary value and the quantity $\sum_r E_r \Delta h_r W_{rs}$ can be deduced from the relaxation time θ (see eq 23) provided it is not negligible with respect to $\sum_n \gamma_n$. According to this analysis one must certainly increase the ratio $V\sum_r E_r \Delta h_r W_{rs}/RT_s^2 \sum_n \gamma_n$ as much as possible. So we were led to use another CSTR, well isolated in order to lower the heat loss through the walls; of course the gold spiral

$$\theta = \frac{\beta}{\dfrac{V}{RT_s^2}\sum_r E_r \Delta h_r W_{rs} + \sum_n \gamma_n} \tag{23}$$

(20) De Kepper, P.; Rossi, A.; Pacault, A. *C. R. Acad. Sci. Paris, Ser. C* **1976**, *283*, 371. De Kepper, P. Ph.D. Thesis, University of Bordeaux I, 1979.

Table IV. Thermal Properties of the HG Reaction (Unstable) and the BZ Reaction (Stable) in a Stationary State

property	HG	BZ
$\sum\limits_r \Delta h_r W_{rs}$, J·mL^{-1}·min^{-1}	58 ± 4	5.4 ± 0.4
$\sum\limits_r E_r \Delta h_r W_{rs}$, J^2·mol^{-1}·mL^{-1}·min^{-1}	-1×10^7	-3×10^4, -11×10^4
$a_{N+1,N-1}$, min^{-1}	$+1.5$	-0.03

was removed during this experiment. This second CSTR, calibrated in the same way as before, has the following characteristics: $V = 47$ mL; $\gamma_0 = 19.8 \pm 0.6$ J·deg^{-1}·min^{-1} (at $\tau = 14.55$ min); $\beta = 514 \pm 29$ J·deg^{-1}. On the other hand W_{rs} was increased by taking high inlet concentrations of bromate and malonic acid: $[\text{KBrO}_3]^\circ = 0.1$ mol·L^{-1}; $[\text{CH}_2(\text{COOH})_2]^\circ = 1$ mol·L^{-1}; $[\text{Ce}_2(\text{SO}_4)_3]^\circ = 1.10^{-3}$ mol·L^{-1}; $[\text{H}_2\text{SO}_4]^\circ = 3$ mol·L^{-1}; $\tau = 14.55$ min. The stationary temperature T_s of the reacting medium reaches 50.5 °C for an isothermal bath temperature T_0 equal to 37 °C. That means a thermicity in the stationary state:

$$\sum_r \Delta h_r W_{rs} = -5.4 \pm 0.4 \ \text{J·mL}^{-1}\text{·mn}^{-1} \tag{24}$$

This value is, of course, much larger than the mean thermicity observed in the oscillatory regime (0.17 J·mL^{-1}·min^{-1}). But one should not be surprised by this result since we took voluntarily high concentrations in order to increase W_{rs}.

A wire heated by the Joule effect provided the necessary shift from the stationary temperature T_s. Several relaxation experiments were made, involving various values of the initial difference $(T - T_s)_i$. They yield a relaxation time θ distributed over the range 30.7 to 32.5 min. In any case the diagonal element $a_{N+1,N+1}$ is negative:

$$a_{N+1,N+1} = -\frac{1}{\theta} = -0.03 \ \text{min}^{-1} \tag{25}$$

this sign being in agreement with the observed stability of the stationary state. If one computes the value of $\sum_r E_r \Delta h_r W_{rs}$ (eq 23), taking into account all the uncertainties, one gets

$$-3.\ 10^4 \geq \sum_r E_r \Delta h_r W_{rs} \geq -11.\ 10^4 \ \text{J}^2\text{·mol}^{-1}\text{·mL}^{-1}\text{·min}^{-1} \tag{26}$$

Certainly the accuracy is a poor one, but it does not matter so much because we simply want to compare this value to the one given by the HG reaction. Table IV, which gathers the thermal properties of the two reactions, helps to make this comparison. A difference of at least 1 order of magnitude is always noticed, once again. If the peculiar conditions chosen to carry out the BZ reaction in order to get rather high values of its thermal properties are not forgotten, this gap takes its full implication.

Conclusion

Thermokinetic oscillations result from a competition between physical transport and chemical release of heat. They appear only when the amplitude—and, therefore, the rate—of both the physical and the chemical processes is adequate. In other words not only the chemical reaction but also the vessel into which it develops play a major role in the emergence of a periodic behavior. On the contrary the oscillatory regime of some other reactions such as the BZ one for instance is quite insensitive to heat flux conditions, so that these oscillations appear to be an intrinsic and essential feature of the reaction itself. Hence it is well-founded to call them chemical oscillations. Another striking difference between thermokinetic and chemical oscillating reactions lies in the absolute value of their thermal properties, whether they oscillate or are in a stationary state. Taking as an example the HG and BZ reactions, we found a ratio going from 1 up to 3 orders of magnitude, depending upon the property concerned. At the very end, the assumption usually made on the BZ reaction, i.e., that temperature variations can be neglected, is widely supported by our present investigation. According to the significant exothermicity measured by Kőrös et al.,[11] this can only result from the fact that the reaction proceeds at a rather slow rate. In any case, thanks to its insensitiveness with respect to heat flux, the

BZ reaction may serve as a good experimental model to simulate several patterns of biological interest.

Appendix

Let a chemical reaction involving N chemical species take place in ρ elementary steps quoted:

$$\nu_{ir} X_i \xrightarrow{k_r} \nu_{jr}' X_j' \quad r = 1, ..., \rho \tag{A1}$$
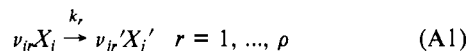
X_i and X_j' being the reagents and products of step r. In a closed system of constant volume, the concentration changes of species l are given by eq A2. The above summation over r assumes ν_{lr}

$$\sum_r (\nu_{lr}' - \nu_{lr}) W_r \quad r = 1, ..., \rho \tag{A2}$$

$= 0$ or $\nu_{lr}' = 0$ when the species l is not a reagent or a product of step r. With the same convention, the specific rate W_r of step r takes the form of eq A3. Now if such a reaction is carried out

$$W_r = k_r \prod_i X_i^{\nu_{ir}} \quad i = 1, ..., N \tag{A3}$$

in a CSTR, one has to write down, for each species l, a mass balance equation according to *total variation inside the reactor = exchange with the surrounding (flux term) + variation due to the chemical reaction (source term)*. Because the CSTR works at constant volume, the related equation applies to concentration as well as to mass itself. X_l^0 being the concentration of species l in the input flow, one has eq A4. The set of N differential

$$\frac{dX_l}{dt} = \dot{X}_l = \frac{1}{\tau}(X_l^0 - X_l) + \sum_r (\nu_{lr}' - \nu_{lr}) W_r \tag{A4}$$

equations can be summarized in matrix notation in eq A5.

$$\dot{\mathbf{X}} = \frac{1}{\tau}(\mathbf{X}^0 - \mathbf{X}) + \mathbf{C} \cdot \mathbf{W} \tag{A5}$$

$$\mathbf{X}, (X_1, X_2, ..., X_N)$$

$$\mathbf{X}^0, (X_1^0, X_2^0, ..., X_N^0)$$

$$\dot{\mathbf{X}}, (\dot{X}_1, \dot{X}_2, ..., \dot{X}_N)$$

$$\mathbf{C}, C_{lr} = \nu_{lr}' - \nu_{lr} \quad l = 1, ..., N \quad r = 1, ..., \rho$$

$$\mathbf{W}, (W_1, W_2, ..., W_\rho)$$

If the temperature variations are to be taken into account, the heat balance equation must also be derived. As above it is the sum of a flux term and a source term. Therefore if the heat capacity β of the immersed masses and the reacting medium is time independent

$$\beta \dot{T} = J(Q) + \sigma(Q) \tag{A6}$$

If the Fourier law of heat transport is valid, the first term takes the form of eq A7, when the CSTR exchanges heat with several

$$J(Q) = \sum_n \gamma_n (T_n - T) \tag{A7}$$

isothermal baths, T_n and γ_n being the temperature and the heat-exchange coefficient of bath n. Furthermore the heat exchange associated with the mass flux is also accounted for by the previous relation, provided the summation is extended to it. The heat sink or release by the chemical reaction is equal to eq A8

$$\sigma(Q) = -V \sum_r \Delta h_r W_r \tag{A8}$$

so that the heat balance equation writes down eq A9. One can

$$\beta \dot{T} = \sum_n \gamma_n (T_n - T) - V \sum_r \Delta h_r W_r \tag{A9}$$

try to go into more detail and to link β and γ_n to the physical properties of the experimental device. This has been done, for instance, by Chang and Schmitz.[21] However several assumptions are needed which are irrelevant in our case.[17] Moreover such a calculation is unecessary for the present purpose, β and γ_n being parameters easily calibrated in some preliminary experiment.

Notation

$\mathbf{A}$	stability matrix
a_{ij}	element of matrix $\mathbf{A}$
$\mathbf{C}$	matrix of N lines and ρ columns
i, j, l, n, r	indices
$J(Q)$	heat flux
k_{0r}, k_r	(absolute) rate constant of step r
N	number of chemical species
Q_R	thermicity of the chemical reaction
R	ideal gas constant
s	subscript for stationary state
t	time
T	temperature of the reading medium
T_n	temperature of bath n
T_s, T_*	stationary temperature of the reacting medium
V	reacting volume
W_r	rate of step r
X_l^0, X_l	(inlet) concentration of species l
β	heat capacity of the CSTR and the reacting medium
γ_n	heat exchange coefficient of bath n
Δh_r	enthalpy of step r
ν_{lr}, ν_{lr}'	molecular coefficient of species l in step r
θ	thermal relaxation time
$\sigma(Q)$	heat source
ρ	number of elementary steps
τ	mean residence time

(21) Chang, M.; Schmitz, R. A. *Chem. Eng. Sci.* **1975**, *30*, 21.
(22) It follows that a thermal instability may well give rise to such thermokinetic oscillations. Hence, one should take care to make a clear cut between the instability of the stationary state and the kind of stable regime involved.