

The Belousov–Zhabotinskii Reaction: Improving the Oregonator Model with the Arrhenius Equation

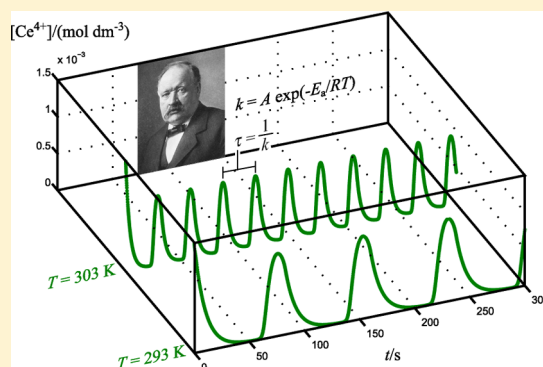
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S Supporting Information

ABSTRACT: Oscillating chemical reactions (OCRs) have been known since 1828, with the Belousov–Zhabotinskii (BZ) reaction the most studied example. Initially, OCRs were considered to be special cases due to the small number detected and because the oscillatory behavior did not seem to agree with the second law of thermodynamics. However, OCRs have become increasingly important not only in chemistry, but also in biology as they are the foundation of several significant phenomena: glycolysis, nerve signal transmission, heartbeats, and so forth. The BZ reaction has been examined both experimentally and theoretically. Temporal oscillations appear in both cases, but discrepancies are found between experimental results and theoretical calculations. This article addresses the discrepancies by describing (i) a simple, clear, and inexpensive experimental procedure for carrying out the reaction and determining the oscillation period and (ii) an innovative methodology that includes the effect of temperature on the original model using the Arrhenius equation. The equations resulting from this approach can easily be solved with the help of MATLAB. In addition, a user-friendly graphical interface has been developed that highlights the effects on the oscillating system caused by changes in different parameters. The effect of the temperature generated during the reaction is also analyzed. This analysis discloses temperature variations: a relevant issue that the theoretical model does not envisage. The exercise is appropriate for upper-level physical chemistry students.

KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Computer-Based Learning, Hands-On Learning/Manipulatives, Catalysis, Kinetics, Mathematics/Symbolic Mathematics, Oxidation/Reduction, Reactions, Thermal Analysis



In an article published in this *Journal*, Degn¹ reviewed the history of the oscillating chemical reactions (OCRs). Winfree² published, in 1984, a fairly detailed chronicle of the Belousov–Zhabotinskii (BZ) reaction, after meeting with A. Zhabotinskii. The articles of Nicolis and Portnow³ and Noyes and Field⁴ present an in-depth analysis of both general oscillating processes and the BZ reaction.

OCRs have always been considered a controversial issue. The origin of the controversy is due, mainly, to a misreading of the adjective “oscillating”, a term borrowed from physics, generally linked to the simple models commonly used in classical mechanics (a simple pendulum, a mass on a spring, etc.). In such models a mass oscillates around the end position (equilibrium). The chemical reactions also end at equilibrium. But the second law of thermodynamics prohibits oscillations around the equilibrium position.⁵ Once equilibrium is reached, any change entails a decrease (an impossibility) of the entropy. Therefore, the chemical oscillations can not be periodic changes in the concentrations of reactants and products around equilibrium. What does “oscillating” mean in chemistry?

Chemical equations may represent either a true microscopic process or the overall result of a set of microscopic processes. In the first case, it is stated that the chemical equation represents an elementary chemical reaction. In the second case,

we have a complex chemical reaction. The decomposition of a complex reaction to a set of elementary steps is called the reaction mechanism. An OCR is a complex chemical reaction moving toward equilibrium as the concentrations of the reactants decrease and those of the products increase, but some of the intermediates can undergo oscillations in their concentrations. The latter phenomenon allows one to characterize a chemical reaction as “oscillating”. The existence of such phenomenon requires that the mechanism fulfills a set of conditions. The status of OCRs changed dramatically when these conditions were rigorously established⁶ and explained the observed experimental facts. However, OCRs have not gained prominence in most physical chemistry courses, despite their appearance in some of the classic textbooks of the discipline.^{7,8} This article aims to promote these reactions and the content lies between the concise explanations given in the textbooks and the complex developments, both experimental and theoretical, that are found in research articles. The exercise is structured following the premises of the scientific method. First, a particular experiment is proposed: the BZ reaction. Several options are set to carry out the reaction (initial concentrations of reagents and temperatures). Several methods to quantita-

Table 1. Initial Concentrations of Reagents and Catalyst

Set ^a	[BrO ₃]/(mol dm ⁻³)	[CH ₂ (COOH) ₂]/(mol dm ⁻³)	[Br ₂]/(mol dm ⁻³)	[Ce ⁴⁺]/(mol dm ⁻³)	[H ⁺]/(mol dm ⁻³)
A	0.0600	0.1000	0.0015	0.0015	0.8000
B	0.1200	0.1000	0.0015	0.0015	0.8000

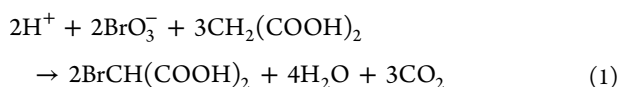
^aSet A is obtained when using stock solutions 1A, 2, and 3, and set B is obtained when using stock solutions 1B, 2, and 3.

tively record the oscillations are presented. The students actively participate in the design of the experiment, deciding the number of experiments to be executed (depending on time available), the specific conditions of the experiments, and the technique used to record the oscillations. Second, a theoretical model must be formulated to explain the observations recorded. The initial proposal will be the Oregonator. The discrepancies between the Oregonator and the experimental results can be minimized in a third step, the core of this exercise, improving the model with an equation as simple as the Arrhenius law. This exercise is for physical chemistry students in the final year of their studies after they have acquired the basic concepts of chemical kinetics and the mathematical skills associated with them during the first years of their studies.

EXPERIMENTAL SECTION

Procedure

The BZ reaction is the catalytic oxidation, in the presence of a strong acid, of an organic species by bromate anion, BrO₃⁻. Malonic acid, CH₂(COOH)₂, is the organic species chosen. The catalyst is the Ce⁴⁺–Ce³⁺ couple. Sulfuric acid, H₂SO₄, is used to obtain strongly acidic conditions.



Different choices of the organic species, the catalyst, or the strong acid lead to multiple variants of the BZ reaction.⁹ The presence of bromide anion (Br⁻) in the reaction medium is essential to reduce the bromate anion and generate bromine (Br₂), the actual oxidizing agent of malonic acid. Bromide anion was often present as an impurity associated with bromate, so in such cases its inclusion was not necessary. The quality of the reagents commonly used today makes the addition of a small amount of bromide necessary.

It is necessary to prepare 500 mL of four stock solutions (1A, lower concentration of bromate anion; 1B, higher concentration of bromate anion; 2, bromide anion and malonic acid; 3, cerium ion and acid; see the Supporting Information for details). Two solutions with different concentrations of KBrO₃ allow students to conduct two studies of temperature influence with different initial concentrations of reagents. Identical volumes of the three stock solutions (1A or 1B, 2, and 3) are used. The possible initial concentrations of reagents and catalyst are listed in Table 1.

The set of initial concentrations may be extended easily, not only varying the initial concentration of the KBrO₃ stock solution, but also changing the initial concentrations of the stock solutions of CH₂(COOH)₂ and H₂SO₄ (another possibility would be to mix different initial volumes). Before starting the reaction, it is imperative that the three solutions are at the same temperature because temperature strongly influences the kinetics of the processes (the kinetic constants depend strongly on the temperature; its pressure dependence can be neglected in most cases). The three solutions (and a

reaction beaker) are immersed in a water bath, which acts as a finite-size heat reservoir.¹⁰ A thermostat has been used to maintain the temperature of water adjusted to a preset value, the one to which the reaction will be carried out. If a thermostatic bath is not available, the experiment is still feasible. Because thermal equilibrium with environment is slow, the three solutions should be prepared in advance. After the three solutions have reached thermal equilibrium with the water bath (or the atmosphere), the reaction is initiated by mixing equal volumes (30 mL) of the three solutions in the beaker. The reaction mixture is stirred at a constant rate to prevent the appearance of spatial organization processes, which makes the periodicity of the temporal oscillations more stable. Oscillations begin after an initial period in which nothing is detected by the naked eye (the reaction medium seems unchanged), which is known as induction period. Although the oscillations are detected with the unaided eye (one of the phenomena associated with the oscillations are color changes, from yellow Ce⁴⁺ to colorless Ce³⁺), instrumental monitoring is required to obtain an accurate value of the period. Note that Ce⁴⁺ (a substance whose concentration oscillates) is not a reactant or a product; rather, it is the catalyst.

As the reaction involves colored substances, it is possible to use a spectrophotometer to track the oscillations. The requirement of constant stirring complicates the experimental setup, although recently, relatively simple spectrophotometers are available that allow stirring inside the sample holder.¹¹ Traditionally, the reaction has been studied potentiometrically using a bromide-selective electrode as the concentration of this anion undergoes periodic variations identical to Ce⁴⁺ (bromide, another oscillating species, is an intermediate). Potentiometric monitoring of the reaction has a big advantage (apart from reducing the cost) over the spectrophotometric method: it does not preclude visual monitoring of the reaction.

Another possibility is measuring the redox potential (*E*) of the solution, to which all redox couples contribute. The largest contribution is due to the Ce⁴⁺–Ce³⁺ pair. Therefore, to a first approximation, the redox potential of the solution can be related (using the Nernst equation) to the log([Ce⁴⁺]/[Ce³⁺]). This technique is simpler and less expensive than the previous two techniques. Consequently, a redox electrode is used to detect the oscillations of cerium. During the experiment, the redox potential versus time was recorded every second.

Owing to the importance of temperature in this work, the temperatures of the mixture contained in the reaction beaker and the water bath (or the atmosphere) were recorded using high-precision platinum resistance thermometers. The temperatures were recorded every second. This additional information is not essential in the development of this exercise, but it is useful to discuss the agreement between experimental and calculated data.

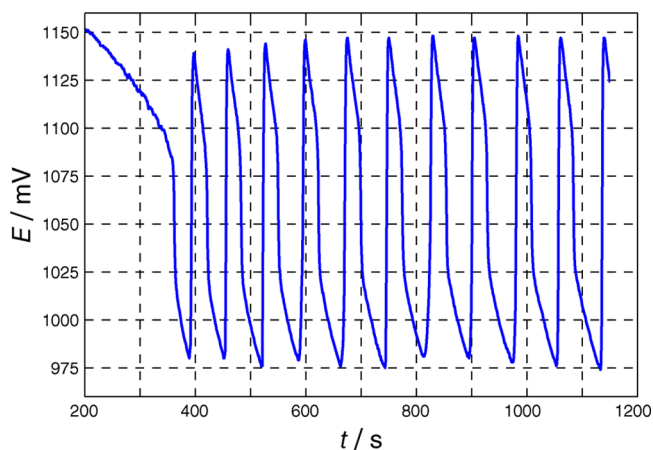
RESULTS

The results of six experiments are shown in Table 2. The oscillations (potential versus time) for experiment 4 are shown in Figure 1. During the induction time (not shown completely

Table 2. Experimental Oscillation Periods

Experiment	Set	Environment	$T_{\text{exp}}/\text{K}^{a,b}$	$\tau_{\text{exp}}/\text{s}$
1	A	Water bath	293.15(3)	111(3)
2	A	Atmosphere	295.44(3)	98(1)
3	A	Water bath	303.19(3)	42(3)
4	B	Water bath	293.15(3)	77(1)
5	B	Atmosphere	294.91(3)	73(1)
6	B	Water bath	303.19(3)	31(1)

^aTemperature values are expressed as the average value of the temperature of the environment during the experiments. ^bNumbers enclosed in parentheses are the numerical values of the combined standard uncertainty (see Supporting Information) referred to the corresponding last digits of the quoted results.

Figure 1. Results from experiment 4 for the set B, $T_{\text{exp}} = 293.15(3)$ K.

in Figure 1), the potential, E , attains a maximum value (just at the beginning of the reaction) and then decreases smoothly until the oscillations start. The oscillations persist beyond the time indicated in Figure 1 (oscillations are detected after 18 000 s). The presence of oscillations after that time does not mean that the period of oscillation remains invariant. The change in oscillation period over time is attributed, among other reasons, to a closed experimental system with regard to liquids and dissolved reactants and products but open to carbon dioxide,

which is free to escape from the beaker. For this reason, it is sufficient to record only the first oscillations. A peak search analysis is performed to accurately detect the positions of the peaks of the redox potential.¹² The average distance between the selected peaks, $\tau_{\text{exp}}/\text{s}$, is chosen as the period of the reaction.

It follows from the data in Table 2 that at constant temperature (experiments 1 and 4 or experiments 3 and 6), an increase in $[\text{BrO}_3^-]_0$ leads to a decrease in the oscillation period. Keeping the same initial concentrations of reagents (experiments 1, 2, and 3 or experiments 4, 5, and 6), an increase in the temperature leads to a decrease in the oscillation period. No chemist should be surprised by this relationship (although its theoretical explanation is far from obvious). What is truly striking is the linear relationship between $\ln(\tau_{\text{exp}}^{-1})$ and T_{exp}^{-1} (see Figure 2). In other words, an Arrhenius-type relationship exists between τ_{exp}^{-1} and T_{exp} . Arrhenius law^{15,16} is the simplest expression which connects the kinetic constants and the temperature:

$$k = A \exp(-E_a/RT) \quad (2)$$

where A is the pre-exponential factor and E_a is the activation energy. Lefelhocz¹⁷ was the first author who pointed out, in this *Journal*, this Arrhenius-type relationship. He further stated that an overall activation energy could be calculated from the slope obtained by a least-squares linear fit. Körös¹⁸ was able to rationalize this behavior by reducing the oscillatory process to a “monomolecular” reaction and considering the reciprocal oscillation period as a first-order rate constant. Substituting τ_{exp}^{-1} for k in eq 2 and taking natural logarithms, eq 3 is obtained:

$$\ln(\tau_{\text{exp}}^{-1}) = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (3)$$

Körös,¹⁸ Blandamer and Morris,¹⁹ Blandamer and Roberts,²⁰ Ruoff,²¹ and Nagy et al.²² calculated these global activation energies for different initial concentrations of reagents (even for different catalysts). The results of this exercise (Figure 2) are consistent with those reported by cited authors.

It is necessary to discuss in some detail the results of the regressions. The high values of the combined standard uncertainties are due to the small number of points (only

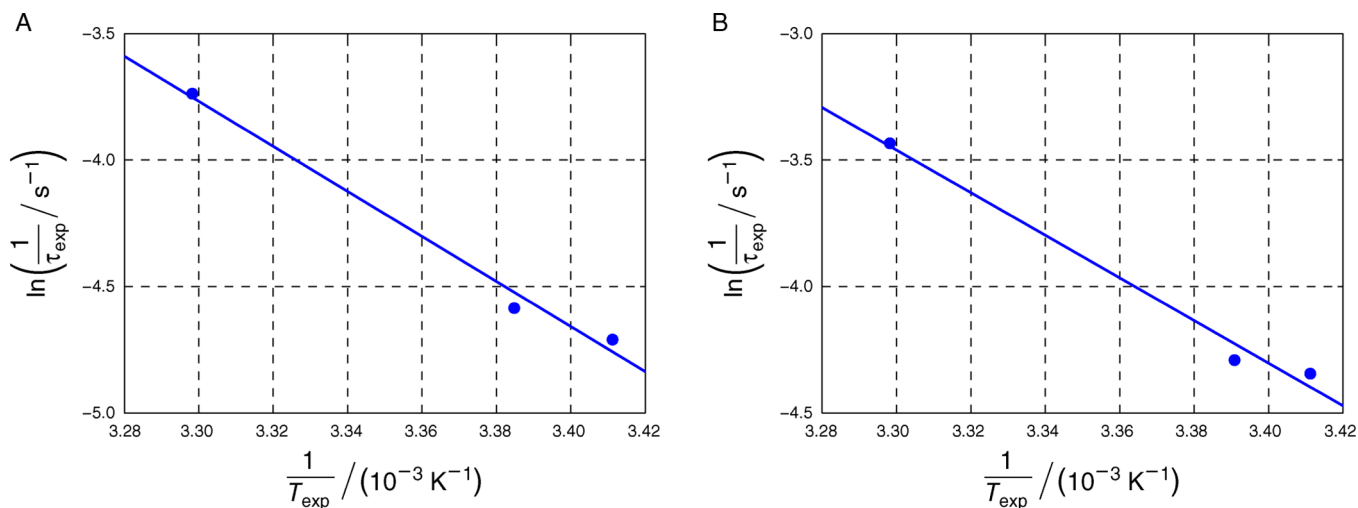


Figure 2. Arrhenius-type relationship between $\ln(\tau_{\text{exp}}^{-1})$ and T_{exp}^{-1} . Blue line is the result of a least-squares linear fit: (A) set A, slope = $-9(1) \cdot 10^3$ K, thus $E_a = 7(1) \cdot 10^4$ J/mol ($r = -0.99$) and (B) set B, slope = $-8(1) \cdot 10^3$ K, thus $E_a = 7(1) \cdot 10^4$ J/mol ($r = -0.99$).

three) that are being used in the fits. Further experiments are needed to know the activation energy values more precisely: however, it is not necessary to spend more time in the laboratory at this level as the obtained value is adequate (the values shown in the research literature contain only one additional significant figure). Another issue that must be noted is the use of weights in the least-squares fits, which is necessary as the original equation used to adjust the data is not linear.^{23,24} Although there is fully automated software to run weighted least-squares, at this time, this is an unnecessary subtlety.

THEORETICAL ANALYSIS

Oscillations in a chemical reaction must occur “far from equilibrium” and, of course, the reaction can not be elemental. The mechanism must also meet the following requirements: (i) one of its steps, at least, should be autocatalytic; and (ii) the autocatalytic reaction must be coupled to the other reactions (“feedback”). These two conditions are necessary but not sufficient: there are combinations of initial concentrations of reagents and temperature (which determines the values of the kinetic constants) that do not cause oscillations. Autocatalysis and feedback, which leads to nonlinearity in the ordinary differential equations describing the mechanism, deserve special consideration. The most common way to achieve these effects is through a chemical species that is, simultaneously, the reactant and product in an elemental chemical reaction. That species should also be involved in other elementary steps of the mechanism. This way is known as “chemical feedback”, but there is another possibility: “thermal feedback”. Suppose that one of the steps of the process is exothermic. If the heat released is not removed quickly, the temperature rise increases the kinetic constant, which in turn, increases the reaction rate (“autocatalysis”). The temperature rise also influences (“feedback”) the remaining kinetic constants of the other steps. The two types of feedback may occur simultaneously. Initially, it is assumed that the reactions proceed in strict isothermal conditions; that is, isothermal autocatalytic mechanisms are used. The thermal feedback will be discussed later. Lotka²⁵ proposed, in 1920, the first mechanism (containing two autocatalytic reactions) capable of generating oscillations. Prigogine’s research group proposed, in 1971, other oscillating mechanism: the Brusselator,²⁶ which also contains two autocatalytic steps.

The Mechanism of Field-Körös-Noyes

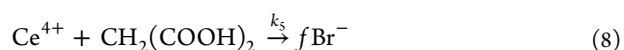
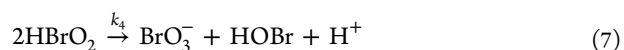
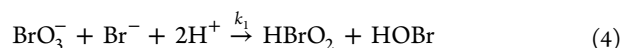
In 1972, Noyes and co-workers^{27,28} presented the first mechanism (known as Field-Körös-Noyes; FKN) to explain the temporal oscillations of the BZ, which consists of 10 elementary reactions (only one is autocatalytic). A detailed description of the FKN mechanism is shown in the Supporting Information (special emphasis has been paid to unravel the reasons that cause the oscillations). As time passed, the model was improved with up to 80 elementary reactions and 26 different chemical species.²⁹ Other sophisticated models have been proposed to account for the BZ reaction. The MBM model,³⁰ for example, uses 48 different chemical reactions. Once the mechanism has been established, it is possible to write the corresponding kinetic equations. Even in the simplest case (FKN), the ordinary differential equations obtained are too complex for an undergraduate course of physical chemistry.

It is possible to “simplify” a mechanism without losing its essential characteristics (the oscillations of the intermediates, in our case). The term “model” is often used to refer to the

simplified mechanism. Its goal is not to represent the whole chemistry of the process, but create a system of differential equations (easy to solve) to keep the essence of the original process. Fortunately, in 1974 the authors of the FKN mechanism suggested a reduced version of the mechanism (5 reactions and 3 independent chemical species) that also generates periodic oscillations: the Oregonator.³¹ This drastic reduction greatly simplifies the mathematical treatment required to obtain solutions. In their original work, the authors claim that the model produces results “comparable” to experimental values. The adjective “comparable” refers to oscillation periods, because the Oregonator can not, under any circumstances, give an account of induction time. There are other models³² that, although not as complex as a mechanism, are more sophisticated than the Oregonator. This exercise focuses only on the Oregonator.

The Oregonator Model

The original Oregonator uses 5 basic reactions that lead to a system of 3 nonlinear differential equations. Afterward, slightly different versions appeared. In this exercise, the following version will be used:



where f is a stoichiometric factor; its value has to be in a certain range (to ensure the existence of oscillations) and is dependent on the concentration of bromate, among other factors. A comparative study between this model and the FKN mechanism can be found in the Supporting Information. The BZ reaction (eq 1) is not the sum of these five equations, because this is a model, not a true mechanism. At 293.15 K, the values of the rate constants are:^{32,33}

$$\begin{aligned} k_1 &= 2 \text{ mol}^{-3} \text{ dm}^9 \text{ s}^{-1} \\ k_2 &= 10^6 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1} \\ k_3 &= 10 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1} \\ k_4 &= 2000 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \\ k_5 &= 1 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \end{aligned} \quad (9)$$

During the progress of the reaction, changes in the concentrations of H^+ , BrO_3^- , $\text{CH}_2(\text{COOH})_2$, and HOBr are small because the amount of catalyst used is minimal (note that $[\text{Ce}^{4+}]_0$ is 2 orders of magnitude lower than $[\text{BrO}_3^-]_0$ and $[\text{CH}_2(\text{COOH})_2]_0$). Assuming that $[\text{H}^+]$, $[\text{BrO}_3^-]$, $[\text{CH}_2(\text{COOH})_2]$, and $[\text{HOBr}]$ remain unchanged during the reaction, it is possible to write, using the eqs 4–8, the following system of three nonlinear (in the dependent variables) differential equations:

$$\frac{d[\text{HBrO}_2]}{dt} = k_1[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2 - k_2[\text{HBrO}_2][\text{Br}^-][\text{H}^+] + k_3[\text{BrO}_3^-][\text{HBrO}_2][\text{H}^+] - 2k_4[\text{HBrO}_2]^2 \quad (10)$$

$$\frac{d[\text{Br}^-]}{dt} = k_1[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2 - k_2[\text{HBrO}_2][\text{Br}^-][\text{H}^+] + f k_5[\text{Ce}^{4+}][\text{CH}_2(\text{COOH})_2] \quad (11)$$

$$\frac{d[\text{Ce}^{4+}]}{dt} = k_3[\text{BrO}_3^-][\text{HBrO}_2][\text{H}^+] - k_5[\text{Ce}^{4+}][\text{CH}_2(\text{COOH})_2] \quad (12)$$

The nonlinear terms are $2k_4[\text{HBrO}_2]^2$ (eq 10) and $k_2[\text{HBrO}_2][\text{Br}^-][\text{H}^+]$ (eqs 10 and 11). This system of equations is often described as “stiff” due to the wide range of values presented by the rate constants (eq 9). With appropriate software, it is not difficult to solve the system of eqs 10–12 and find out how $[\text{HBrO}_2]$, $[\text{Br}^-]$, and $[\text{Ce}^{4+}]$ vary over time. MATLAB R2012a is used to carry out all numerical calculations. A script that uses the initial concentrations of reagents and catalyst (set A or set B, see Table 1) as input parameters has been written. The stoichiometric factor f is set to 0.6, an arbitrarily chosen value which guarantees the existence of oscillations. Oscillation periods are obtained, again, using a simple peak search algorithm. Unlike the experimental case, it is not necessary to average various intervals as they are all identical. Table 3 shows

Table 3. Experimental and Calculated Oscillation Periods

Experiment	Set	Environment	T_{exp}/K	$\tau_{\text{exp}}/\text{s}$	$\tau_{\text{cal}}/\text{s}$	$\delta/\%$
1	A	Water bath	293.15(3)	111(3)	102	8
4	B	Water bath	293.15(3)	77(1)	77	0

the results ($\tau_{\text{cal}}/\text{s}$) of two calculations carried out for the indicated conditions. Calculated periods are in good agreement with the corresponding experimental periods at the same temperature. The result of a numerical calculations carried out for the indicated conditions is shown in Figure 3.

There is a remarkable difference between the calculated amplitudes of the experiments 1 and 4. This can be explained using eq 6: if $[\text{BrO}_3^-]$ decreases, the reaction rate diminishes and therefore the production of Ce^{4+} will be slower. Equation 8 gains significance in the mechanism and the amount of Ce^{4+} produced in each oscillation is reduced. No substantial differences were observed, however, in the observed amplitudes because they represent a different quantity: the logarithm of a quotient of concentrations.

It makes no sense to compare the calculated periods with experimental ones obtained at other temperatures because the Oregonator solutions depend strongly on the kinetic constants, and these, in turn, depend on temperature. Thus, a clear link is established between the temperature and the behavior of the Oregonator, which in many cases has been forgotten. The discrepancies between experimental results and theoretical calculations have always been attributed to the simplicity of the model. Although this is undeniable, the inclusion of temperature in the model significantly reduces these differences.

The Oregonator and the Arrhenius Law

Although the Arrhenius-type relationship between τ_{exp}^{-1} and T_{exp} was known¹⁷ from 1972, the successful application of the

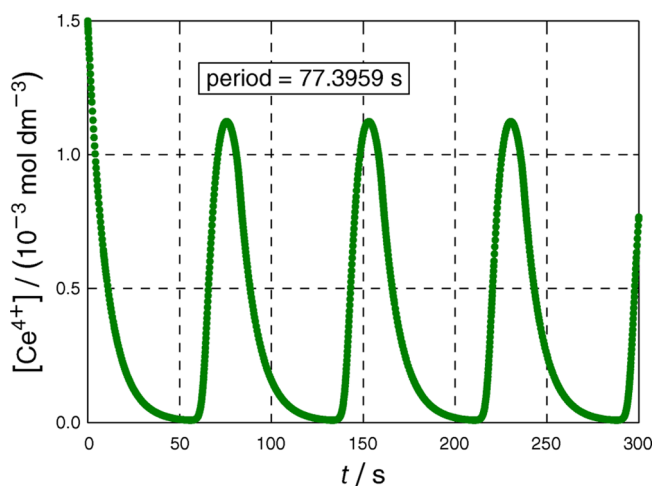


Figure 3. Theoretical result for the following conditions (initial concentrations of reagents and temperature): set B, $T_{\text{exp}} = 293.15$ K (experiment 4). The available kinetic constants have been used (values are listed in eq 9) as they are referred to 293.15 K. More details can be found in Supporting Information.

Arrhenius equation in the Oregonator was carried out only much later by Ruoff²¹ and Pullela et al.³⁴ Pullela's strategy was to introduce the Arrhenius equation in the system of differential equations that is derived from the Oregonator, while executing a change of variable (suggested in 1982 by Tyson³⁵) that turned the unknowns into dimensionless quantities. It is easier to calculate in advance, at the working temperature, the kinetic constants using the Arrhenius equation and solve the original system of equations using these new values (omitting, of course, the change of variable). Applying the Arrhenius equation requires knowing the activation energies at a reference temperature. The activation energies, reported by Pullela et al.³⁴ at 293.15 K, for the five stages of the Oregonator are

$$\begin{aligned} E_{a,\text{eq4}} &= 54 \text{ kJ mol}^{-1} \\ E_{a,\text{eq5}} &= 25 \text{ kJ mol}^{-1} \\ E_{a,\text{eq6}} &= 60 \text{ kJ mol}^{-1} \\ E_{a,\text{eq7}} &= 64 \text{ kJ mol}^{-1} \\ E_{a,\text{eq8}} &= 70 \text{ kJ mol}^{-1} \end{aligned} \quad (13)$$

Provided that the range of temperature that will be explored is small, and always close to room temperature, the dependence of the activation energy with temperature is ignored. The original script has been modified accordingly (temperature has been added as a new input parameter) to use the Arrhenius equation. The new script (*oregonator.m*)³⁶ is part of the Supporting Information. The results ($\tau_{\text{cal}}/\text{s}$) of four calculations are shown in Table 4. Calculated periods are, again, in good agreement with the corresponding experimental periods at the same temperature.

The script *oregonator.m* has also been applied to the two experiments in which the reaction beaker was in direct contact with the atmosphere. It is interesting to note that in these two cases the errors are much more pronounced than in the other four experiments. This is not surprising, because in the experiments 2 and 5 the surroundings were not kept at

Table 4. Experimental and Calculated Oscillation Periods

Experiment	Set	Environment	T_{exp}/K	$\tau_{\text{exp}}/\text{s}$	$\tau_{\text{cal}}/\text{s}$	$\delta/\%$
2	A	Atmosphere	295.44(3)	98(1)	83	15
3	A	Water bath	303.19(3)	42(3)	41	2
5	B	Atmosphere	294.91(3)	73(1)	65	11
6	B	Water bath	303.19(3)	31(1)	30	3

constant temperature and the theoretical model used (Oregonator) assumes the invariability of temperature.

These six examples clearly indicate that the inclusion of temperature as a variable significantly improves the results. Figure 4 shows a simultaneous plot of $\ln(1/\tau_{\text{exp}})$ and $\ln(1/\tau_{\text{cal}})$ against reciprocal temperature, which confirms the significant improvement undergone by the Oregonator when including in it the Arrhenius equation. Without the Arrhenius equation, Oregonator can only predict a single value (represented in Figure 4 by the horizontal red line).

Although predictions of Oregonator with the Arrhenius equation are much better than the direct application without the Arrhenius equation, the errors still exist (higher for set A) between the improved model (green lines) and the experimental values (blue lines). The origin of these errors is usually attributed to two factors:

- Oregonator is just a simplified version of the true mechanism.
- The Arrhenius equation was used in its most elementary form, assuming that the activation energy does not change with temperature.

But there is a third factor often omitted that should not be forgotten. It has been maintained throughout this work that the temperature in the reaction beaker should remain constant to avoid changes in the kinetic constants. In short, the chemical feedback has been accepted and the thermal feedback has been rejected. However, there are some nonzero enthalpy changes associated with three processes: the initial mixture of reactants ($\Delta_{\text{mix}}H$), the dilution (sulfuric acid, predominantly) of the reactants ($\Delta_{\text{dil}}H$), and the exothermicity of the reaction itself ($\Delta_{\text{rxn}}H$). If the heat generated in these processes is not

immediately removed from the system, the assumption of constant temperature vanishes and the mechanism (or the model) must incorporate an additional differential equation which controls the heat transfer between the system and the surroundings. The reaction beaker has been submerged in a water bath (in four experiments), which attempts to minimize these effects, but can not cancel them completely, as will now be displayed.

Figure 5A shows a thermogram (T vs t) of the finite-size heat reservoir and the reaction beaker for the indicated conditions. The temperature of the reservoir remains essentially constant (the temperature that is introduced into Oregonator corresponds to the finite-size heat reservoir, T_{exp}), but in the beaker are significant variations. The most remarkable (≈ 0.4 °C) occurs at the beginning of the reaction and is due to $\Delta_{\text{mix}}H$ and $\Delta_{\text{dil}}H$ of reagents. During the induction time, there is also a heat release: small at first, but more pronounced at the end. And finally, with each oscillation occurs a heat release ($\Delta_{\text{rxn}}H$). There is obviously a clear synchronization between temperature oscillations and redox potential oscillations (Figure 5B).

The substitution of the heat reservoir by the atmosphere further increases the temperature differences, as the temperature of the atmosphere is not constant. Figure 6A shows the thermogram of the atmosphere and the reaction beaker for the indicated conditions. Under these circumstances, the results of Oregonator necessarily have to be worse, as indeed it happens (see Table 4).

The thermograms show that it is necessary to include the thermal feedback in the model to get an accurate description of the experimental reality. This possibility would lead to a marked improvement in the model results at the expense of increasing the mathematical complexity. Although this possibility is beyond the undergraduate level, its influence (within the set of limitations of the Oregonator) must not be forgotten, because it is as important as the others.

CONCLUSIONS

The BZ reaction is a complex process that can not be fully described with a simple mathematical model, such as the

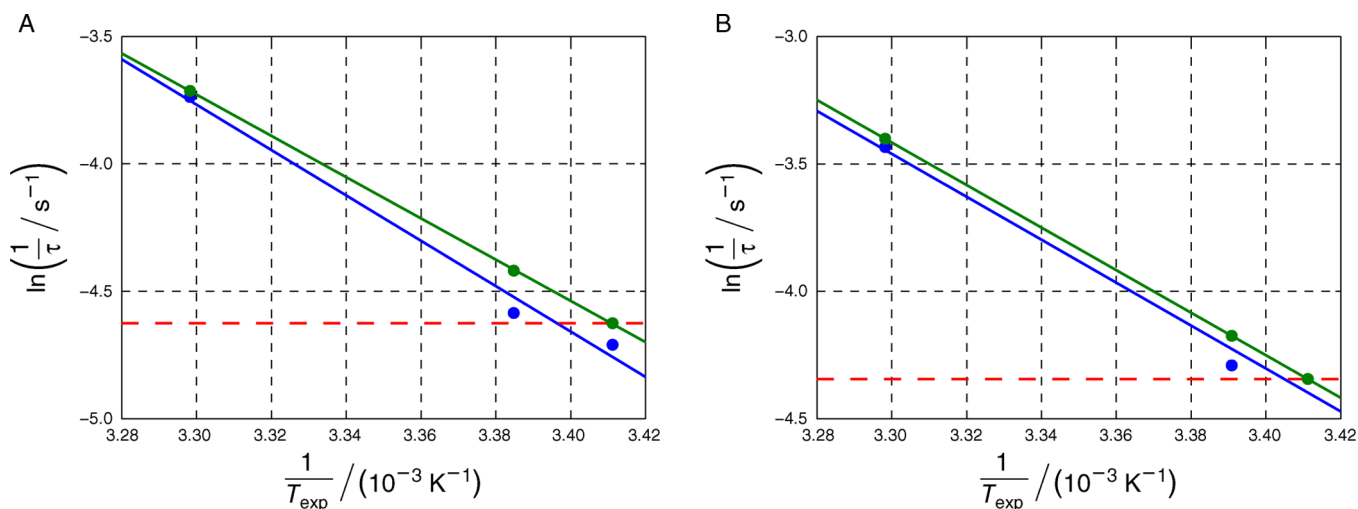


Figure 4. Arrhenius-type relationship between $\ln(\tau_{\text{exp}}^{-1})$ and T_{exp}^{-1} (blue dots and line) and $\ln(\tau_{\text{cal}}^{-1})$ and T_{exp}^{-1} (green dots and line): (A) set A (least-squares results for the calculated periods), slope = $-809(7)$ 10³ K, thus $E_a = 673(7)$ 10² J/mol ($r = -1.00$); and (B) set B (least-squares results for the calculated periods), slope = $-8346(4)$ K, thus $E_a = 6939(4)$ 10 J/mol ($r = -1.00$). Least-squares results for the experimental periods are shown in Figure 2.

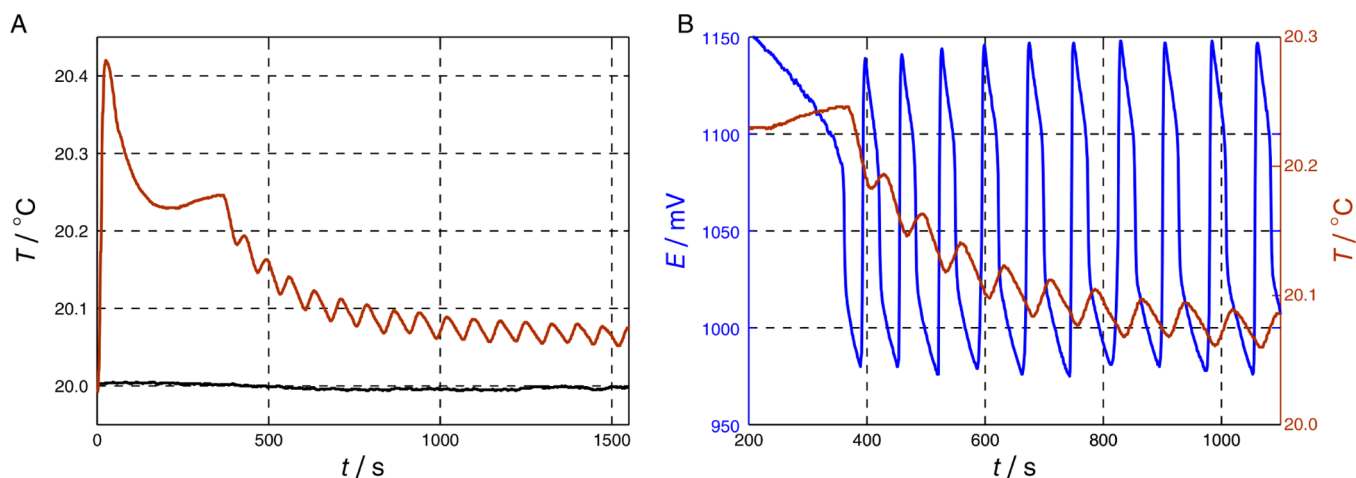


Figure 5. (A) Thermogram (black line, water bath; brown line, reaction beaker) for the following conditions: set B and $T_{\text{exp}} = 293.15(3)$ K (experiment 4). (B) The thermogram of the reaction beaker is superimposed on the oscillations of the redox potential (previously shown in Figure 1).

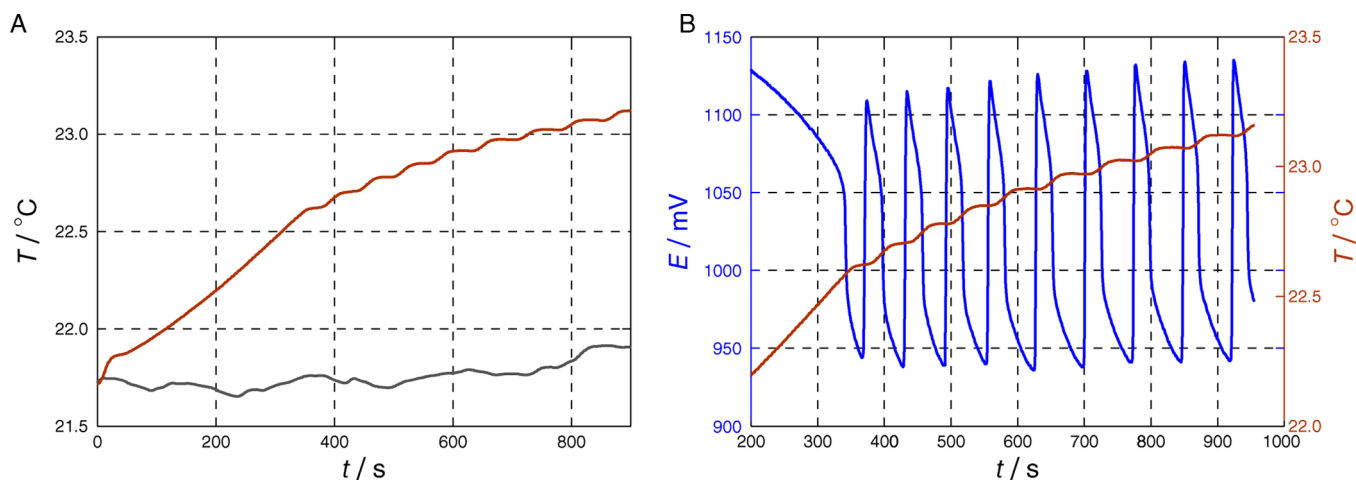


Figure 6. (A) Thermogram (black line, atmosphere; brown line, reaction beaker) for the following conditions: set B and $T_E = 294.91(3)$ K (experiment 5). (B) The thermogram of the reaction beaker is superimposed on the oscillations of the redox potential (not previously shown).

Oregonator (a model can never compete with a mechanism). However, this exercise shows that the Oregonator can be significantly improved by taking into account the effect of temperature with an equation as simple as the Arrhenius law. Students must grasp the critical significance of temperature on chemical kinetics and also how to take account of its effects using simple mathematical models. A detailed thermal track of the reaction shows the unavoidable presence of temperature fluctuations. This limits the quality of the data that the new combined model (Oregonator + Arrhenius) can generate as it assumes a strict invariance of the temperature. The development of an interactive simulator (*oregonatorg.m*) allows a quick comparison between the theoretical results of the new proposed model and the experimental data. There has also been established a clear recipe, simple and inexpensive, to measure accurately the oscillation period of the BZ reaction.

■ ASSOCIATED CONTENT

§ Supporting Information

Chemicals, hazards, stock solutions, instrumentation, uncertainty in the measurement of the temperature, uncertainty in the measurement of time, FKN mechanism, Oregonator model,

and MATLAB scripts (*oregonator.m* and *oregonatorg.m*). This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (12) There is no single criterion to make this decision. It has been arbitrarily decided to reject the first three peaks and use the next three to calculate the experimental oscillation periods. In the experiment 6, the first six peaks were rejected and the following three were used. The lack of regularity observed in this experiment, both in the amplitudes of the redox potential and in the oscillation periods, may be due to the response time of the redox electrode. The manufacturer ensures that the response time is not greater than 20 s, but may be insufficient because the oscillation period is quite similar. It is possible to use the Fourier Transform¹³ (FT) to calculate the experimental oscillation periods. Using the interval of the redox potential between the previously selected peaks, the results are practically the same: the differences never exceed 0.5 s. Although most current software automatically calculates FT, the underlying theoretical concepts (differences between continuous and discrete FT, stationary signal properties, etc.) are not so simple¹⁴ and their study would divert the attention of the students. In short, the simple average of the initial oscillation periods is more than enough for the purposes of this paper.
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- (36) The *oregonator.m* script can also be used to see the effect provoked by changes in the initial concentrations of other reagents (or the catalyst) different from bromate, or in the stoichiometric factor (and compare its predictions with new experimental results). The only thing to do is simply changing the appropriate variables in the script and re-execute it. It is possible to speed up the above process using the function *sliders* (MATLAB CENTRAL, Matthew Jones (matt_jones@fastmail.com), 2004), since then, the values of the variables can be changed interactively with the mouse. A new script (*oregonatorg.m*) has been written, also included in the Supporting Information, that recalculates the solution whenever there is a change.