A Very Simple One-Variable Flip-flop Model of the Belousov-Zhabotinskii Reaction

TORBEN SMITH SØRENSEN

Fysisk-Kemisk Institut, Technical University of Denmark, DK-2800 Lyngby, Denmark

On the basis of the socalled "Oregonator" model by Field and Noyes for the oscillating Belousov-Zhabotinskii reaction, a very simple one-variable model is proposed with virtually the same behaviour as the three-variable Oregonator model. The present model is inspired by the classical treatment of relaxation-oscillations by van der Pol.

The model involves quasi-stationarity assumptions for the intermediary compound $HBrO_2$ and for Br^-. Bromide is stationary except at two critical concentrations, where the concentration "flips" and "flops" almost instantaneously between two separate branches of the stationarity curve for Br^-. The limit cycle then involves a rapid movement in the phase plane along an "A-branch" triggered by a pulse of $HBrO_2$ followed by a slow restoring movement along a "B-branch". The time spent on the two branches can be calculated simply as two integrals (chronomals) in dimensionless units(θ_A and θ_B). The sum $\theta_A + \theta_B$ is equal to the dimensionless period of the limit cycle (θ_p). The period of the limit cycle in real time is determined exclusively by the inverse rate constant k_5 of the fifth reaction in the Oregonator-model: The oxydative decarboxylation reaction between Ce^{4+} and bromomalonic acid.
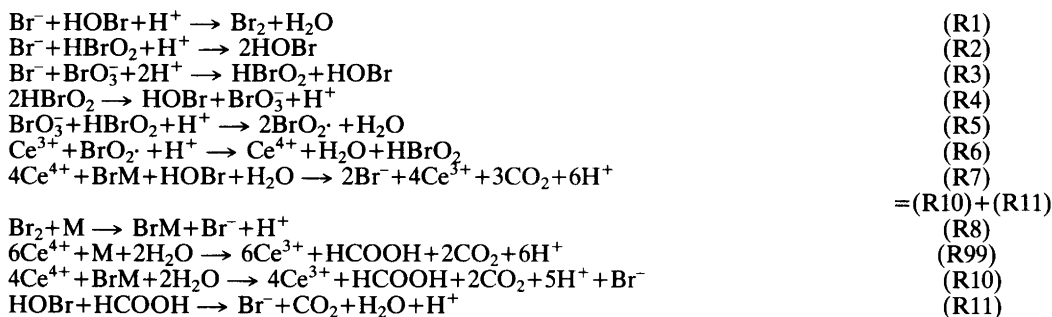
Experimentally, the influence of bromate concentration and temperature on the period and on the fraction of time spent on the A-branch (low bromide concentration) in the full cycle has been studied. Together with the experimental findings of Field, Körös and Noyes and the theoretical results of the present study we conclude from this that the value for parameter $q=2k_1k_4/k_2k_3$ should be in the interval $2.5 \cdot 10^{-2} - 7.6 \cdot 10^{-2}$.

The inverse period of the relaxation-oscillations has a simple Arrhenius dependence on the absolute temperature which is also explained by

the model. The activation energy for the oscillations is composed by the activation energy of k_5 and a term proportional to the activation energy of the q-parameter.

When chemical reactions occur outside the quite narrow range of applicability of the reciprocity relations of Onsager, numerous instabilities leading to spatial and/or temporal structures may occur induced by nonlinearities in the reaction system.[1] One of such possibilities is the appearance of *limit cycles* first discussed by Poincaré 100 years ago.[2] In 1958, Belousov reported on oscillations in the ratio of Ce^{4+} to Ce^{3+} ions during the cerium ion catalyzed oxidation of citric acid by bromate in aqueous sulfuric acid solution.[3] The study was some years later taken up by Zhabotinskii *et al.*[4-7] who elucidated the mechanism and showed that citric acid could be replaced by malonic acid or by another organic material with an active methylenic hydrogen and that Ce^{4+}/Ce^{3+} could be replaced with other redox couples as Mn^{3+}/Mn^{2+} or ferroin/ferriin indicator. It was also shown that spatial structures could appear in unstirred solution in the form of propagating chemical waves. Henceforth, the reaction system was called the Belousov-Zhabotinskii (BZ) system.

Further elucidation of the mechanism was made by Degn,[8] Kasperek and Bruice[9] and Busse.[10] However, it was the very careful experimental study and data collection of Field, Körös and Noyes[11] in 1972 which enabled Field and Noyes[12] from the University of Oregon to propose their socalled "Oregonator" model of the BZ-oscillator, a name chosen to match with

$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O$	(R1)
$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr$	(R2)
$Br^- + BrO_3^- + 2H^+ \rightarrow HBrO_2 + HOBr$	(R3)
$2HBrO_2 \rightarrow HOBr + BrO_3^- + H^+$	(R4)
$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2\cdot + H_2O$	(R5)
$Ce^{3+} + BrO_2\cdot + H^+ \rightarrow Ce^{4+} + H_2O + HBrO_2$	(R6)
$4Ce^{4+} + BrM + HOBr + H_2O \rightarrow 2Br^- + 4Ce^{3+} + 3CO_2 + 6H^+$	(R7)
	=(R10)+(R11)
$Br_2 + M \rightarrow BrM + Br^- + H^+$	(R8)
$6Ce^{4+} + M + 2H_2O \rightarrow 6Ce^{3+} + HCOOH + 2CO_2 + 6H^+$	(R99)
$4Ce^{4+} + BrM + 2H_2O \rightarrow 4Ce^{3+} + HCOOH + 2CO_2 + 5H^+ + Br^-$	(R10)
$HOBr + HCOOH \rightarrow Br^- + CO_2 + H_2O + H^+$	(R11)

Scheme 1. The 11 most important reactions in the BZ-reaction system. M=malonic acid; BrM=bromomalonic acid.

the well known "Brusselator" of the Brussels school of thermodynamics. The "Oregonator" is basically a five-reaction/three-variable model representing the oscillations very well. Therefore, in the light of the fact that there are at least 10 important reactions occurring simultaneously (see Scheme 1), the Oregonator constitutes a tremendous simplification and intellectual effort. However, the model is still not simple to explain pedagogically, and simulations have to be done by computer.
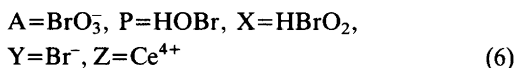
It has often been pointed out that the saw-tooth oscillations of the BZ-system are very like the relaxation-oscillations of the well known bistable multivibrators in electronics. Some time ago, I therefore started to speculate on the possibility of treating the BZ-system in analogy with the paradigm of relaxation-oscillations, *i.e.* the harmonic oscillator with negative and non-linear friction introduced by van der Pol in 1920 to describe relaxation-oscillations in electron tube oscillators, see Minorsky.[13] The present paper will show that it is indeed possible to give a very similar description of the BZ-reaction. Actually, the solution of the three-variable Oregonator system can be reduced − without any significant loss of precision − to the solution of a simple, one-variable kinetic equation along two quasi-stationarity branches with virtually instantaneous "jumps" from one branch to the other at critical positions on the two branches. The two branches are branches of a certain "H-curve", which has also a middle, unstable branch. The jumps occur at the maximum and the minimum of the H-curve, in precise analogy with the situation for the van der Pol oscillator.

THE OREGONATOR

The five reactions selected from the list in Scheme 1, which were considered by Field and Noyes to be the important "bottlenecks" in the reaction scheme, are the following:

$$A + Y \xrightarrow{k_1} X + P \qquad (1)$$

$$X + Y \xrightarrow{k_2} 2P \qquad (2)$$

$$A + X \xrightarrow{k_3} 2X + 2Z \qquad (3)$$

$$2X \xrightarrow{k_4} P + A \qquad (4)$$

$$Z \xrightarrow{k_5} f \cdot y \qquad (5)$$

The meaning of the symbols is given by eqns. (6):

$$A = BrO_3^-, \ P = HOBr, \ X = HBrO_2,$$
$$Y = Br^-, \ Z = Ce^{4+} \qquad (6)$$

It has been used that the ratio of ceri to cero-ions is always very small. Account has therefore only to be taken of the ceri-ions. In the following, the reaction labels (R1)−(R11) refer to Scheme 1. Concentrations of H^+ and H_2O have everywhere been built into the rate constants, since the reaction medium is about 1 mol/dm³ with respect to sulfuric acid, which is a much larger concentration than all the other concentrations.

By reaction (1) − which is identical to (R3) − the intermediate compounds $HBrO_2$ and $HOBr$ are formed by reaction between Br^- and BrO_3^-.

$HBrO_2$ is reacting further through reaction (2) with Br^- to form two moles of HOBr. Reaction (2) is identical to (R2). Reaction (3) is an *autocatalytic* reaction for formation of $HBrO_2$. It is equivalent with the reaction (R5)+2(R6)=(G) shown below. (R5) is the rate determining step.

$$2Ce^{3+}+BrO_3^-+HBrO_2+3H^+ \longrightarrow$$
$$2Ce^{4+}+H_2O+2HBrO_2 \qquad\qquad (G)$$
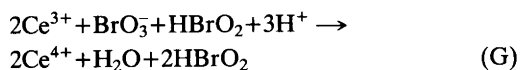
Reaction (4) is a sink for $HBrO_2$ which is equivalent to (R4). The last reaction (5) is a kind of pooled reaction representing the oxydation of organic matter by Ce^{4+} (formed in the autocatalytic reaction) and release of Br^- from bromomalonic acid (BrM). BrM is formed through Br_2 in reactions (R1) and (R8). In the original Oregonator model, reaction (5) was assumed to be a mixture of (R9) and (R10). The stoichiometric factor f for Br^- release would then vary between 0 (pure R9) and 1/4 (pure R10). The problem is, however, that f has to be between 0.25 and 1.206 in order to have possibility of oscillations in the Oregonator, see Murray.[14] (Note that we have followed the definition of f given in the book of Murray rather than the definition in the original Oregonator-model). Also, Bornmann et al.[15] failed to detect formic acid among the reaction products which should be the case if (R9) or (R10) was followed. In order to remedy this mismatch, Noyes and Jwo [16] postulated the reaction (R11) between HCOOH and HOBr. When (R10) is followed by (R11) with (R10) as the rate determining step, the kinetics is as given in reaction (5) and the net reaction is as (R7) where $f=0.5$. It has been assumed that the concentration of BrM is virtually constaant over a cycle, so that [BrM] can be built into k_5.

The more detailed kinetics of the oxidation of BrM by Ce^{4+} were elucidated by Jwo and Noyes.[17] They found the following dependence of k_5 on [BrM]:

$$k_5 = k_{05} \cdot [BrM]/(K_M+[BrM])$$
$$(k_{05} = 0.015\ s^{-1}) \qquad\qquad (7)$$

where k_{05} is a catalytic constant and K_M a "Michaelis-Menten" constant. The kinetics were really found to be first order with respect to Ce^{4+}. The value of K_M is dependent on the reaction time in an unexplained way. Before a

certain "break point" K_M is 0.107 mol/dm^3 and after K_M is 0.033 mol/dm^3. The "break point" seems to occur after a time of the order of magnitude of 10 min, so it is hardly reached with the normal oscillations of the BZ reaction of order of magnitude 1 min. We therefore conclude, that k_5 is varying between the value given in eqn. (8) for very low [BrM] to the value given in eqn. (9) for high values of [BrM], where the catalyst is saturated.

$$k_5 = 0.140\,[BrM]\ s^{-1},\ [BrM]\ll 0.1\ mol/dm^3 \qquad (8)$$

$$k_5 = 0.015\ s^{-1},\ [BrM]\gg 0.1\ mol/dm^3 \qquad\qquad (9)$$

In normal experimental cases for the BZ reaction, the condition given in eqn. (8) prevails. The activation energy found for k_{05}/K_M was the value given in eqn. (10) (before the "break point"):

$$E_5^{\neq} = 54.5 \pm 2.0\ kJ/mol \qquad\qquad (10)$$

We have been quite critical with k_5 here, since the present model will show that the period of the oscillations is largely determined by the rate constant k_5.

NONDIMENSIONALIZATION AND QUASI-STATIONARITY APPROXIMATION

Assuming that only X, Y and Z vary during a cycle, we obtain from the reactions (1)−(5) a set of three coupled differential equations in X, Y and Z:

$$dX/dt=(k_1A)\cdot Y-k_2\cdot X\cdot Y+(k_3A)\cdot X-2k_4\cdot X^2 \qquad (11)$$

$$dY/dt=-(k_1A)\cdot Y-k_2\cdot X\cdot Y+f\cdot k_5\cdot Z \qquad (12)$$

$$dZ/dt=2(k_3A)\cdot X-k_5\cdot Z \qquad\qquad (13)$$

Here, t is real time and X, Y and Z are the molar concentrations of X, Y and Z, where the square brackets have been left out for brevity. We can simplify the equations by introducing dimensionless concentrations:

$$x \equiv (k_2/k_1A)\cdot X \qquad\qquad (14)$$

$$\eta \equiv (k_2/k_3A)\cdot Y \qquad\qquad (15)$$

$$\zeta \equiv \{k_4 k_5/(k_3 A)^2\} \cdot Z \qquad (16)$$

Now, equations (11) to (13) transform to:

$$\varepsilon dx/d\tau = x + \eta - x \cdot \eta - qx^2 \qquad (17)$$

$$d\eta/d\tau = (2f/q) \cdot \zeta - \eta - x \cdot \eta \qquad (18)$$

$$(p/q)d\zeta/d\tau = x - (1/q) \cdot \zeta \qquad (19)$$

We have also introduced a dimensionless time given by (20) and three dimensionless parameters given by (21):

$$\tau \equiv k_1 A \cdot t \qquad (20)$$

$$\varepsilon \equiv k_1/k_3 \sim 2 \cdot 10^{-4}, \quad p \equiv k_1 A/k_5 \sim 3.1 \cdot 10^2,$$
$$q \equiv 2k_1 k_4/k_2 k_3 \sim 8.4 \cdot 10^{-6} \qquad (21)$$

The values given for ε, p and q are approximate values valid at 25 °C, see Refs. 12 and 14.

Since $\varepsilon \ll 1$ the approximation suggests itself to take the left hand side of eqn. (17) to be zero. This amounts to a quasi-stationarity approximation for $HBrO_2$, and the approximation has been discussed under the name "stiffly coupled approximation" by Field and Noyes.[12] In this manner we obtain a system of only two equations which we shall reformulate as eqns. (22) and (23):

$$d\eta/d\tau = (2f/q) \cdot \{\zeta - [H(\eta)/2f]\} \qquad (22)$$

$$d\zeta/d\tau = (1/p) \cdot \{U(\eta) - \zeta\} \qquad (23)$$

We have introduced two functions of η which become of crucial importance, $U(\eta)$ and $H(\eta)$, defined by eqns. (24) and (25):

$$U(\eta) \equiv \tfrac{1}{2}\{1 - \eta + \sqrt{(1-\eta)^2 + 4q\eta}\} \qquad (24)$$

$$H(\eta) \equiv [q + U(\eta)] \cdot \eta \qquad (25)$$

We have further a supplementary stationarity condition for x:

$$x = U(\eta)/q \qquad (26)$$

(The positive sign has to be chosen in the solution of the quadratic equation in order to obtain a positive x).

We shall further simplify eqn. (22) by taking $2f = 1$, since $f = 0.5$ seems to be a quite realistic

stoichiometric factor.[16] The functions $U(\eta)$ and $H(\eta)$ can now be seen to play the role of nullclines separating upward and downward motion or motion to the right and to the left of a phase point in the (η, ζ) phase plane. Indeed, we have:

$$d\zeta/d\tau \gtrless 0 \quad \text{for} \quad \zeta \lessgtr U(\eta) \qquad (27)$$

$$d\eta/d\tau \gtrless 0 \quad \text{for} \quad \zeta \gtrless H(\eta) \ (2f=1) \qquad (28)$$

Stationary points in the phase plane have to be intersections in the positive quadrant between the U and the H-curves.

A second stationarity approximation may be introduced. Since $q \ll 1$ and $p \gg 1$, the η-variable will equilibrate itself very rapidly according to eqn. (22) in comparison to the ζ-variable. We would therefore tend to have eqn. (29) satisfied whenever possible (we shall see that it is not always possible and then we have the "jumps"):

$$\zeta \cong H(\eta) \ (2f=1) \qquad (29)$$

The problem is then reduced to a one-variable problem, since the phase point just "slides" along the H-curve. It is now important to study the properties of the U and the H-curves, their intersection points and the stability of the intersection points. This will be the topic of the two next sections.

PROPERTIES OF THE U AND H FUNCTIONS

Fig. 1 exhibits some of the properties of the U and H functions for a q-value less than unity, but not much less. The U function decreases monotonously, but H has a maximum. In the case of Fig. 1, this maximum is positioned at a higher η-value than the intersection point. It is easy to see that the intersection point in that case is a *stable* stationary point since phase points in all directions around the intersection point will move towards that point due to the relative position of the nullclines. Basically, the slope of the H curve has to be negative in the intersection point in order to obtain instability, see the discussion in the next section.

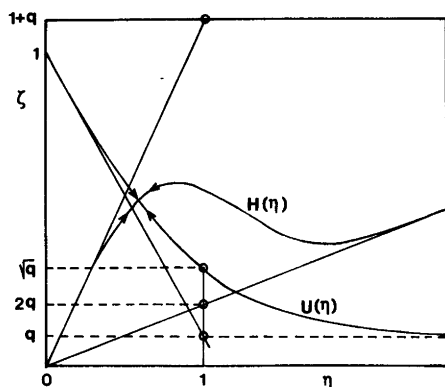The expression for U may be reformulated as eqn. (30):

Fig. 1. Phase plane with the *U*-nullcline between upwards and downwards motion and the *H*-nullcline between motion to the right and to the left. The *H*-curve is also the curve of quasi-stationarity for Br⁻. The dimensionless bromide concentration is η and the dimensionless Ce^{4+} concentration ζ. The intersection between the *U*- and *H*-curve is a stationary point. The stationary point is stable here, since the *U*- and *H*-curves cross at lower η than η_{max} corresponding to the maximum in the *H*-curve. For $q \ll 1$ this will not be the case.

$$U(\eta) = \tfrac{1}{2}(1-\eta) \cdot [1+\text{sign}(1-\eta) \cdot$$
$$\sqrt{1+4q\eta/(1-\eta)^2}] \tag{30}$$

If the condition (31) is satisfied, the square root can be Taylor-expanded, so that we obtain eqn. (32):

$$4q\eta/(1-\eta)^2 \ll 1 \tag{31}$$

$$U(\eta) \cong \tfrac{1}{2}(1-\eta) \cdot [1+\text{sign}(1-\eta) \cdot$$
$$\{1+[2q\eta/(1-\eta)^2]\}] \tag{32}$$

We therefore have two approximate equations for *U*, eqn. (33) for $\eta<1$ and eqn. (34) for $\eta>1$:

$$U(\eta) \cong (1-\eta) \cdot [1+\{q\eta/(1-\eta)^2\}] \cong 1-\eta \quad (\eta<1) \tag{33}$$

$$U(\eta) \cong q\eta/(\eta-1) \quad (\eta>1) \tag{34}$$

Condition (31) will be satisfied for any q with η close enough to zero, so the initial slope of the *U*-curve will be $-(1-q)$. If $q \ll 1$, condition (31) will be satisfied for all $\eta<1$ except for η-values

very close to 1, and in that case *U* will be $1-\eta$ in the interval $\eta \in [0|1-\delta]$, where δ is a small quantity. On the other hand, condition (31) will also be satisfied for any q and $\eta \gg 1$. In that case, approximation (34) is valid, and $U \to q$ for $\eta \to +\infty$.

For the function $H(\eta)$ we obtain under the same condition (31) the eqns. (35) and (36) for $\eta<1$ and $\eta>1$, respectively:

$$\frac{H}{\eta} \cong 1+q-[1-\{q/(1-\eta)\}]\eta$$
$$[\eta<1, \text{cond. (31)}] \tag{35}$$

$$\frac{H}{\eta} \cong \{(2\eta-1)/(\eta-1)\} \cdot q$$
$$[\eta>1, \text{cond. (31)}] \tag{36}$$

From eqn. (35) we see that the limiting slope for $\eta \to 0_+$ and any q for the *H*-function is $1+q$. For very small q-values *H* will be approximately equal to $(1-\eta) \cdot \eta$ in the interval $\eta \in [0|1-\delta]$ and the maximum in *H* will fall at $\eta_{max}=0.5$ with $H_{max}=0.25$. From eqn. (36) we see that the limiting value of *H* for very large η and any q will be $H=2q \cdot \eta$. The approximation (36) is also valid for all $\eta>1$ when q is very small, except for η-values very close to 1. The function in eqn. (36) has extrema at $\eta=1 \pm (\sqrt{2}/2)$, but only the plus sign yields an η in the correct range. The extremum is here a minimum. In summary we have for $q \ll 1$:

$$\eta_{max}=0.5; \quad H_{max}=0.25 \quad (q \ll 1) \tag{37}$$

$$\eta_{min}=1+\sqrt{2}/2=1.7071;$$
$$H_{min}=(2q/\sqrt{2})(1+\sqrt{2}/2)(1+\sqrt{2})=$$
$$5.828q \quad (q \ll 1) \tag{38}$$

Thus, for very small q (which is the case for the Oregonator), the maximum and the position of the minimum of the *H*-curve do not depend on the precise value of q. Only H_{min} depends proportionally on q.

The points of intersection between $H/2f$ and *U* are stationary points. Their η-values will be designated by η_o. The problem of finding roots of $H(\eta_o)/2f=U(\eta_o)$ can be recast into the problem of finding roots in eqn. (39):

$$U(\eta_o)=g(\eta_o) \equiv (q/2f) \cdot \eta_o/[1-(\eta_o/2f)] \tag{39}$$

(The relation (25) between U and H has been used). The function $g(\eta_o)$ grows up from 0 at $\eta_o=0$ to $+\infty$ at $\eta_o=2f$. From $2f+\delta$ to $+\infty$, g grows from $-\infty$ to $-q$. Therefore, there can only be one intersection point between $H/2f$ and U, and there *will* always be one which is positioned at $\eta_o<2f$. For $f=0.5$, the stationary point will always be positioned for $\eta_o<1$. For very small values of q, and $\eta<1$ we have $U=1-\eta$ and $H=(1-\eta)\cdot\eta$. U is 0.5 at η_{max} with $H_{max}=0.25$ and it is seen that H will continue to be less than U when η is growing towards 1. Therefore, the root η_o has to be positioned extremely close to 1, where the approximation breaks down.

LINEAR STABILITY OF STATIONARY POINT

The first step in the investigation of the stability of a stationary point will always be to investigate the *linear stability* of small perturbations from that point. We express the two variables as in eqn. (40) where δ signifies a small deviation:

$$\eta=\eta_o+\delta\eta \quad \zeta=\zeta_o+\delta\zeta \tag{40}$$

($\zeta_o=U(\eta_o)=H(\eta_o)/2f$). Introducing eqn. (40) into eqns. (22) and (23) throwing away all second and higher order terms in the perturbation, we obtain the linearised equations written in matrix form in eqn. (41):

$$\begin{bmatrix} \delta\dot{\eta} \\ \delta\dot{\zeta} \end{bmatrix} = \begin{bmatrix} -(H'_o/q) & (2f/q) \\ U'_o/p & -1/p \end{bmatrix} \begin{bmatrix} \delta\eta \\ \delta\zeta \end{bmatrix} \tag{41}$$

U'_o and H'_o are the derivates of the U and H functions with respect to η taken at $\eta=\eta_o$. The stability and the oscillatory behaviour in the region of validity of the linearisation is determined by the nature of the eigenvalues to the coefficient matrix of eqn. (41). The two eigenvalues are given by eqn. (42):

$$\lambda = \tfrac{1}{2}[-(H'_o/q+1/p) \pm$$
$$\sqrt{(H'_o/q-1/p)^2+(8f/qp)U'_o}] \tag{42}$$

The quadratic equation to which the eigenvalues n eqn. (42) are solutions is given by eqn. (43):

$$\lambda^2+a_1\cdot\lambda+a_o = 0 \tag{43}$$

The coefficients a_1 and a_2 are given in eqn. (44):

$$a_1 = (1/q)\cdot(H'_o+q/p)$$
$$a_o = (/q\cdot p)\cdot(H'_o-2fU'_o) \tag{44}$$

Using the Hurwitz stability criterion,[18] we find the conditions for having the real parts of $\lambda\geqq0$ (marginal stability or instability) as given in the conditions (45) and (46):

$$a_0\leqq0 \quad \text{(unstable node)} \tag{45}$$

$$a_1\leqq0 \quad \text{(unstable focus)} \tag{46}$$

The condition (45) corresponds to an unstable node (no oscillations) and (46) to an unstable focus (oscillations, complex eigenvalues). The stability behaviour according to eqn. (43) is summed up in Fig. 2.

Examining first the conditions (45) and using that

$$H' = q+U+U'\cdot\eta \tag{47}$$

we transform condition (45) to the form (48):

$$U'_o \geqq \frac{U_o+q}{2f-\eta_o} \tag{48}$$

This is clearly impossible, since U'_o is negative whereas the right hand side of (48) is positive since it was demonstrated in the previous section that $2f-\eta_o$ is always positive. Thus, the instability will always break out oscillatory, and condition (46) is the important one. Therefore, we have condition (49):

$$H'_o \leqq -q/p \tag{49}$$

The intersection point between the H-curve and the U-curve has to be positioned at $\eta_o>\eta_{max}$, where H'_o is negative, in order to have linear instability. With $q/p\ll1$, the critical slope $H'_o=-q/p$ will be close to zero. Therefore, the separation between stability and instability will be made by the value q_{max} with *coincidence* between η_o and η_{max} in the limit $p\to\infty$. One finds the value $q_{max}=7.62\cdot10^{-2}$. For $q>q_{max}$ it is not possible to have any oscillations with the present model.

The final point to be discussed in the framework of linear stability theory is the angular
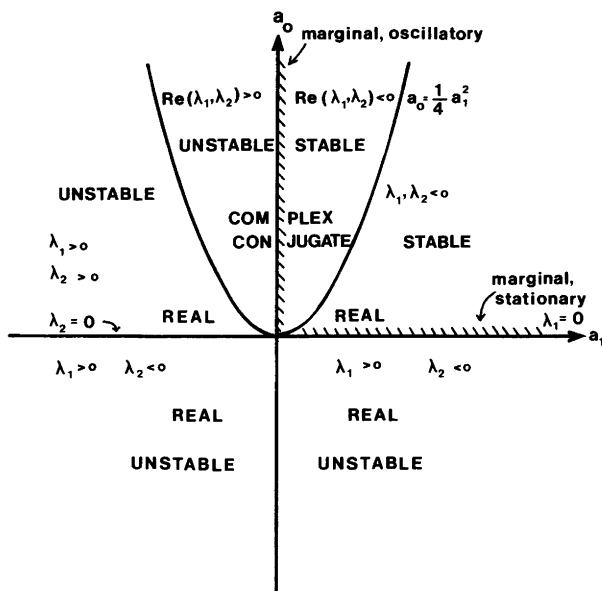
Fig. 2. Stability-instability diagram corresponding to the characteristic equation (43).

frequency (ω) for the marginally stable focus, *i.e.* $a_1 = 0$ or $H'_o = -q/p$. According to the bifurcation theorem of Hopf,[19] there will exist a *limit cycle* (stable or unstable) with the period $2\pi/\omega$ when we diminish the slope H'_o slightly below the critical value given by $-q/p$. This value is the only estimate for the period of the real limit cycle which we are able to extract from linear theory.

Inserting $\lambda = \pm i\omega$ in eqn. (43) we obtain $a_1 = 0$ and eqn. (50):

$$\omega = \sqrt{a_0} = \sqrt{\frac{H'_o - 2f \cdot U'_o}{qp}} \qquad (50)$$

Using the relation (47) we have:

$$H'_o - 2f \cdot U'_o = q + U_o + (1 - 2f) \, U'_o \qquad (51)$$

For $2f = 1$ we therefore have for the Hopf angular frequency:

$$\omega_{\text{Hopf}} = \sqrt{\frac{q + U_o}{q \cdot p}} = \sqrt{\frac{H_o}{\eta_o \cdot q \cdot p}} = \sqrt{\frac{U_o}{\eta_o \cdot q \cdot p}} \qquad (52)$$

From eqn. (39) and eqn. (52) we obtain for the dimensionless Hopf-period:

$$\tau_{\text{Hopf}} = 2\pi/\omega_{\text{Hopf}} = 2 \; \pi\sqrt{p(1-\eta_o)} \qquad (53)$$

Passing to real time through eqn. (20) we have:

$$t_{\text{Hopf}} = (2\pi/k_1 A)\sqrt{p} \cdot \sqrt{1-\eta_o} \qquad (54)$$

Using eqn. (21) for the parameter p we obtain:

$$t_{\text{Hopf}} = 2\pi\sqrt{1-\eta_o}/\sqrt{k_1 \cdot k_5 A} \qquad (55)$$

For comparison with experiments we write for the inverse period:

$$1/t_{\text{Hopf}} = \frac{\sqrt{k_1 k_5}}{2\pi\sqrt{1-\eta_o}} \cdot \sqrt{A} \qquad (56)$$

The value of $1-\eta_o$ depends solely on the value assumed for q. The rate constant k_1 has a value given in eqn. (57):[12,14]

$$k_1 \simeq 2.1 \; \text{s}^{-1} \cdot \text{dm}^3 \cdot \text{mol}^{-1} \quad (25 \; °C) \qquad (57)$$

The rate constant k_5 was given by the relation (7). It is independent of the bromate concentration (A) if either a) the concentration of BrM is much greater than $0.1 \; \text{mol}/\text{dm}^3$ or b) if BrM is only slightly dependent on BrO_3^-, so that k_5 in eqn. (56) may be replaced by k_5 (mean).

We shall indeed find a dependence of the experimental inverse period on the bromate concentration of the form (58):

$$1/t_p = \text{constant} \cdot [\text{BrO}_3^-]^{0.5} \qquad (58)$$

A more detailed comparison with experimental facts will be carried out in the final section. Here, I shall just warn the reader not to take the comparison between t_p (experimental) and t_{Hopf} too seriously. The experimentally observed relaxation-oscillations ("saw tooth" oscillations) are indeed far from the uniformly rotating Hopf cycle near the critical point. Therefore, the experimental conditions are probably too *supercritical* for the Hopf estimate to be more than an order of magnitude calculation. A better approximation to the period of the relaxation-oscillations will be derived in the next section.

THE CHRONOMALS OF THE RELAXATION-OSCILLATION

For the value $q=8.4 \cdot 10^{-6}$ given in eqn. (21), the H-curve has been drawn, see Fig. 3. The U-curve is also drawn, and they have an intersection point extremely close to $\eta=1$ as inferred also from the previous section. The slopes U_o' and H_o' are extremely large and negative. Actually, it is necessary to plot the (η,ζ) phase plane in logarithmic units as shown on Fig. 3. The intersection point will be unstable, but because of the enormous difference in magnitude of the rate of the two processes (22) and (23), the H-curve will be followed as far as possible according to eqn. (29). Then, the phase point will move up or down on the unstable C-branch of the H-curve according to the sign of the initial perturbation from stationary point O. Let us assume that it moves up. When H_{max} is reached, the phase point
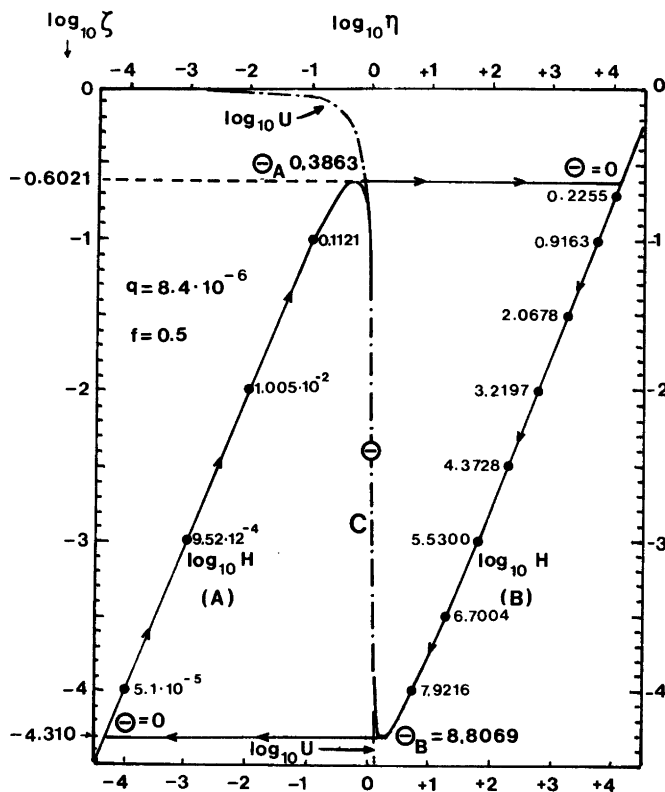

Fig. 3. Phase plane plot of relaxation oscillations for a very low value of q. The phase point is jumping back and forth between the A- and the B-branch of the H-curve at the two extrema. The C-branch with the stationary point (O) is unstable. The time consumed at some points along the A- and B-branches is indicated.

should still move upwards, since we are still below the U-nullcline (cf. conditions (27)). Thus, we have to leave the H-curve in the upwards direction. As soon as this happens, the very fast process (22) sets in, and a very rapid motion of the phase point in the η-direction starts. During the "jump", the "slow" ζ-variable does not change its value significantly. When we hit the B-branch we are above the U-nullcline, and we therefore move slowly downwards along the B-branch of the H-curve. When H_{min} is reached, the story repeats itself and we jump to the A-branch of the H-curve, where we move slowly upwards until H_{max} is reached. We are now in the relaxation-oscillation limit cycle and we never again follow the unstable branch C of the H-curve.

The situation here may be described as a *non-equilibrium phase transition:* The quasi-stationary curve for the Br^- concentration is followed smoothly up to an upper critical Br^- concentration ("superheating"). Another branch is followed smoothly down to a lower critical Br^- concentration ("supercooling").

The problem is now reduced solely to find the motion along the A and the B-branch of the H-curve, which is an almost trivial one parameter problem. In such cases, the concentration variable can be separated from the time variable. Then, the time consumption on each branch or the so called *chronomal* (a word introduced in connection with steady state kinetics by J. A. Christiansen [20]) can be calculated by analytic or numerical integration.

Thus, using eqn. (23) in connection with the inverse of eqn. (29) and introducing a new dimensionless time be eqn. (59), we obtain immediately eqn. (60) for the chronomal:

$$\theta \equiv \tau/p = k_5 \cdot t \qquad (59)$$

$$\theta = \int_{\zeta_{initial}}^{\zeta} \frac{dx}{U[H^{-1}(x)] - x} \qquad (60)$$

The inverse function $\eta = H^{-1}(\zeta)$ is not unique. In eqn. (60) it has to be chosen for the appropriate branch (A or B) of the H-curve. For the numerical integration to be more feasible, it is better to integrate in terms of $\log_{10}x$:

$$\theta = \int_{\log_{10}\zeta_{initial}}^{\log_{10}\zeta} F(u)\, du \qquad (61)$$

$$F(u) = \ln 10 \cdot [(1/10^u)\, U(H^{-1}(10^u)) - 1]^{-1} \qquad (62)$$

Since $q \ll 1$ we can use $U = 1 - \eta$ on branch A and $H = (1-\eta)\cdot\eta$ from which follows eqns. (63) and (64):

$$\eta_A = H_A^{-1}(\zeta_A) \simeq \tfrac{1}{2} \cdot (1 - \sqrt{1 - 4\zeta_A}) \qquad (63)$$

$$U[H_A^{-1}(\zeta_A)] \simeq \tfrac{1}{2} + \tfrac{1}{2}\sqrt{1 - 4\zeta_A} \qquad (64)$$

On the B-branch we can use the approximation (36) to which corresponds the inverse function (65):

$$\eta_B = H_B^{-1}(\zeta_B) \simeq (1/4q)[(\zeta_B + q) + \sqrt{(\zeta_B + q)^2 - 8q\zeta_B}] \qquad (65)$$

and we can use eqn. (34) as an approximation for U. However, we actually used the full expression for U in the numerical integration.

The numerical integrations were performed by a HP-41C microprocessor using a standard Simpson rule routine.[21] The precision of the chronomal values was checked by varying the step length. The results are given in Table 1. Some of the θ-values are also indicated on the phase plane plot, Fig. 2. For branch A, $\zeta_{initial} = H_{min} = 5.828q$ and $\zeta_{final} = H_{max} = 0.25$. For branch B, the values are in inverse order.

The time spent on branch A for $q = 8.4 \cdot 10^{-6}$ is $\theta_A = 0.3863$. In comparison, the time spent on branch B for the same q is $\theta_B = 8.8069$. Therefore, we shall call branch A the "fast branch" and branch B the "slow branch". The total period of the relaxation-oscillations is given by eqn. (66):

Table 1. Time consumption on A- and B-Branch of H-curve for $q = 8.4 \cdot 10^{-6}$.

$\log_{10}\zeta$	Branch A θ	Branch B θ
-4.31016	0	$8.8069 = \theta_B$
-4.00	$5.1050 \cdot 10^{-5}$	7.9216
-3.50	$2.6737 \cdot 10^{-4}$	6.7004
-3.00	$9.5204 \cdot 10^{-4}$	5.5300
-2.50	$3.1234 \cdot 10^{-3}$	4.3728
-2.00	$1.0053 \cdot 10^{-3}$	3.2197
-1.50	$3.2631 \cdot 10^{-2}$	2.0678
-1.00	$1.1208 \cdot 10^{-1}$	0.9163
-0.70	$-$	0.2255
-0.60206	$3.8626 \cdot 10^{-1} = \theta_A$	0

$$\theta_p = \theta_A + \theta_B = 9.1932 \qquad (66)$$

When q becomes even lower, H_{min} will be lower and both θ_A and θ_B will increase somewhat. Thus, the number corresponding to the dimensionless period will be greater than 9.1932 for smaller q and smaller for greater q than $8.4 \cdot 10^{-6}$. This, we have to remember when we want to discuss temperature dependence of the period of the BZ-reaction.

Fig. 4 shows the dimensionless concentration as a function of dimensionless time for the species Ce^{4+}, Br^- and $HBrO_2$. The concentrations are in logarithmic units and the curve form will be representative for the form of experimental curves of electromotive force of Pt and Br^- electrodes against a reference electrode (Nernst equation). The curves are remarkably similar to the experimental ones − though not in all details. They seem to be identical to the curves obtained by simulations on the full three-variable Oregonator.[12] It is interesting that even the sharp pulses of $HBrO_2$ seem to be well reproduced in spite of the fact that we used the quasi-stationary approximation for that species.

The mechanism of the pulses seems to be the following: Br^- is slowly consumed by reaction (1). Hereby, $HBrO_2$ is produced. This triggers the autocatalytic production of more $HBrO_2$ through process (3). At the same time Ce^{4+} is produced 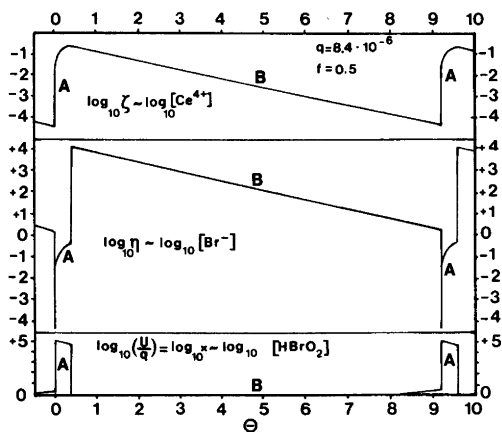and Br^- consumption is rapidly increased due to the reaction between Br^- and $HBrO_2$ in process (2). All this happens during the very short pulse of $HBrO_2$ (branch A) which terminates due to reaction (4). The Br^- concentration is then restored by reaction (5) and the play starts all over again at the upper critical Br^- concentration, where Br^- consumption again becomes dominating by reaction (1).

COMPARISON WITH EXPERIMENTAL DATA

The main purpose of the paper has been to demonstrate, that the simplified flip-flop model of the BZ-system yields results almost identical to the solutions to the full Oregonator-model. Another question is whether the Oregonator itself is a sensible model, and if it is, whether the values of the parameters used in the Oregonator are correct. Since the present model represents a much more simple picture of the situation than the Oregonator-model, one might hope that the parameters (especially the q-parameter) could be judged with greater reliability.

First, it should be noticed that the rate constant of the fifth Oregonator reaction according to our model should be directly evaluable from the real time consumption for a period (t_p):

$$k_5 = \theta_p / t_p \qquad (67)$$

θ_p is a *number* depending only on the parameter q. The smaller the value of q the lower is H_{min} (see eqn. (38)). Therefore, the chronomal integration paths are longer and θ_p increases. Fig. 5 shows that there is a linear relation between the dimensionless period and $log_{10}q$. Integrations have only been performed up to $q=10^{-2}$ since some of the approximations used for the inverse H-function do not work well at high q-values. However, the extrapolated linear part of the curve is probably a good approximation anyway. The intersection point for $\theta_p=0$ corresponds well to the value $q_{max}=7.62 \cdot 10^{-2}$ at which the maximum of the H-curve coincides with the intersection point between the U-curve and the H-curve. According to the linear stability analysis, this is the highest value q can have for oscillations to occur. Just below q_{max}, the flip-flop model will still be valid if only $p \gg q$. Fig. 5 also shows that the time consumption on the A-branch with low
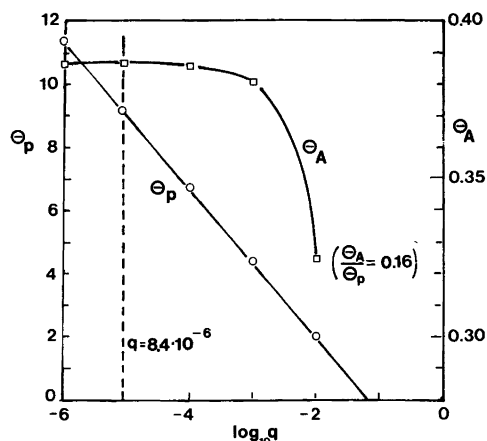

Fig. 4. The dimensionless concentrations of Ce^{4+}, Br^- and $HBrO_2$ as a function of dimensionless time for $q=8.4 \cdot 10^{-6}$ corresponding to the phase plane plot in Fig. 3.

Fig. 5. The dimensionless period and the dimensionless time consumption on the *A*-branch as a function of the dimensionless parameter q. No oscillations are possible above $q_{max}=7.62\cdot10^{-2}$ where the maximum in the *H*-curve and the intersection between the *H*-curve and the *U*-curve coincide.

bromide concentration is approximately constant for very low q-values but decreases with increasing q, when q_{max} is approached. The fraction θ_A/θ_p increases drastically when q_{max} is approached, see Table 2.

Some experimental findings are listed in Table 3. FKN refers to values estimated from Figs. 1–6 in the paper of Field, Körös and Noyes.[11] The other values have been determined for this paper, since it was found important to elucidate the influence of BrO_3^- and the temperature on the period t_p. In the FKN-paper no measures were apparently taken to thermostat the reaction vessel and only two bromate concentrations were used. The experimental conditions for the present measurements differ from the ones in the

Table 2. Relative duration of period with low Br^- to total period.

q	θ_p	θ_A/θ_p
10^{-6}	11.322	0.0341
$8.4\cdot10^{-6}$	9.193	0.0420
10^{-4}	6.716	0.0575
10^{-3}	4.404	0.0864
10^{-2}	2.004	0.1619

FKN-paper only with regard to the thermostating and the following (insignificant) details: Here, $Ce(SO_4)_2\cdot4H_2O$ was used as a catalyst (Ferak, Berlin, analytical grade) instead of $Ce(NH_4)_2(NO_3)_5$. The ratio Ce^{4+}/Ce^{3+} was monitored with a Pt-electrode instead of a tungsten electrode. The Br^- concentration was monitored by a third-order $Ag/Ag_2S/AgBr$ electrode.[22] Finally, the reference electrode was a $Hg/HgSO_4$ electrode with saturated K_2SO_4 as salt bridge.

It is evident from Table 3, that the ratio t_A/t_p is closer to 0.5 than the value 0.04 found theoretically for $q=8.4\cdot10^{-6}$, which is the q-value chosen in the Oregonator.[12,14] According to Fig. 5, the real q-value should therefore be in the region between 10^{-2} and $q_{max}=7.62\cdot10^{-2}$. The evidence from calculated values of k_5 points in the same direction. In Table 3, k_5 has been calculated from eqn. (67) using $\theta_p=9.19$ and 1, respectively. The former values (corresponding to $q=8.4\cdot10^{-6}$) are far too high, since the maximum value for k_5 at 25 °C should be 0.015 s^{-1} at saturating concentrations of BrM, see eqn. (9). For $\theta_p=1$ (corresponding to q around $2.5\cdot10^{-2}$), the values of k_5 are much better, although a few are too high. Therefore, q can be localized in the region between $2.5\cdot10^{-2}$ and $7.6\cdot10^{-2}$ by means of two independent criteria. If p can still be assumed to be of order of magnitude 10^2, the flip-flop model is still a reasonable approximation, though not as exact as before. Indeed, the "vertical" sections of the log c *vs.* time curves are found not to be completely vertical in the experiments. In other words, the "jumps" take some time.

In the experiments performed here, the inverse period was found to increase approximately as the square root of the bromate concentration, see Fig. 6. From the FKN-data, a dependence on the malonic acid concentration as [M] to the power 0.69 could be inferred. The "activation energy" $(E_p^{\neq})$ for $1/t_p$ was found to be practically independent on the level of bromate concentration, see Fig. 7, and equal to $8.8\cdot10^3\cdot R$. Assuming $E_p^{\neq}$ to be also independent of [M] (which is not proven by the present data), we may summarize the empirical findings in the formula (68):

$$1/t_p = k[BrO_3^-]^{0.48}\cdot[M]^{0.69}\cdot\exp[8.8\cdot10^3$$
$$(1/298.16-1/T)] \qquad (68)$$

Eqn. (68) is valid for [Ce]=0.001 mol/dm^3. From the data in Table 3, we can see that the influence

Table 3. Experimental data for the Belousov-Zhabotinskii reaction.[a]

Temp. °C	$[BrO_3^-]$	[M] mol/dm³	[Ce]	t_p s	t_A/t_p	$100/t_p$ s⁻¹	$(100/t_p)$ calcd.[b] s⁻¹	$(919/t_p)$ s⁻¹	Comments
Ambient	0.063	0.032	0.001	120	0.5	0.833	0.839	7.66	FKN,[c] Fig. 1
	0.063	0.013	0.001	215	0.4–0.6	0.465	0.451	4.27	FKN, Fig. 2
	0.063	0.500	0.001	18	0.5	5.55	5.59	51.0	FKN, Fig. 3
	0.016	0.130	0.001	93	0.2	1.075	1.143	9.88	FKN, Fig. 4
	0.063	0.130	0.005	66	0.5	1.515	–	13.9	FKN, Fig. 5
	0.063	0.130	0.0001	50	0.5	2.00	–	18.4	FKN, Fig. 6
15.0	0.040	0.0167	0.001	870	0.5	0.115	0.0910	–	Own experiments
	0.060			840	0.5	0.119	0.111	–	
	0.080			743	0.6	0.135	0.127	–	
	0.100			570	0.8	0.175	0.141	–	
	0.133			570	0.8	0.175	0.162	–	
20.0	0.060	0.0167	0.001	465	0.4	0.215	0.186	–	Own experiment
25.0	0.020	0.0167	0.001	450	0.5	0.222	0.182	2.04	Own experiments
	0.040			390	0.5	0.256	0.253	2.36	
	0.060			308	0.7	0.325	0.308	2.98	
	0.080			300	0.7	0.333	0.353	3.06	
	0.100			245	0.7	0.408	0.393	3.75	
	0.133			218	0.7	0.459	0.451	4.22	
	0.167			180	0.7	0.555	0.503	5.10	
30.0	0.060	0.0167	0.001	203	0.5	0.492	0.501	–	Own experiment
35.0	0.020	0.0167	0.001	240	0.3	0.417	0.473	–	Own experiments
	0.040			123	0.6	0.813	0.660	–	
	0.060			110	0.7	0.910	0.802	–	
	0.080			101	0.8	0.991	0.921	–	
	0.100			92	0.8	1.086	1.025	–	

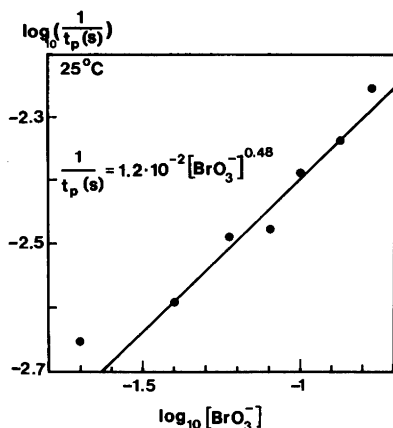[a] $[H_2SO_4]=0.8$ mol/dm³. [b] Calculated from eqns. (68) and (69). [c] Field, Körös and Noyes, Ref. 11.

Fig. 6. Dependence of the inverse period found in experiments on bromate concentration.

of [Ce] is very small. Increasing [Ce] from 0.0001 to 0.0050 mol/dm^3 (50 fold), the inverse period decreases only 25 % (from 2 s^{-1} to 1.5 s^{-1}). The values of k differ somewhat for the FKN experiments and the present experiments:

$$k = \begin{cases} 0.34 \text{ s}^{-1} & \text{(FKN)} \\ 0.20 \text{ s}^{-1} & \text{(TSS)} \end{cases} \tag{69}$$

The higher value found by FKN might be due to the exothermicity of the BZ-reaction and the apparent lack of thermostating in the FKN-investigation.
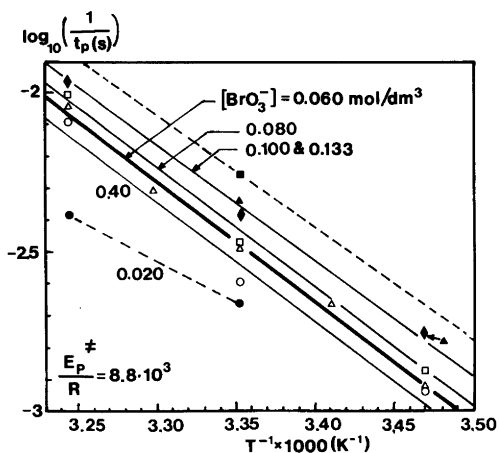

Fig. 7. Temperature dependence of inverse period at various levels of initial bromate concentrations. [BrO$_3^-$]: 0.020, 0.040, 0.060, 0.080, 0.100, 0.133, 0.167 mol/dm^3.

The dependence of $1/t_p$ on the bromate and the malonic acid concentration might well reflect the dependence of k_5 on the concentration of bromomalonic acid, see eqn. (7), indicating that we are somewhere in the transition region between the first and the zeroth order region of the Ce-catalyst in reaction (5).

In the section concerning the linear stability analysis it was mentioned, that the Hopf-estimate was able to produce an expression for $1/t_{Hopf}$ proportional to the square root of the bromate concentration, see eqn. (56). Since the constant in eqn. (58) is found to be $1.2 \cdot 10^{-2}$ (see Fig. 6), we should have:

$$\sqrt{k_1 \cdot k_5(\text{mean})}/(2\pi\sqrt{1-\eta_o}) \simeq 1.2 \cdot 10^{-2} \tag{70}$$

In Table 4, $1-\eta_o$ and values of $k_1 \cdot k_5(\text{mean})$ calculated from eqn. (70) are listed for various values of q. Taking the value of k_1 from eqn. (57), we can calculate approximate values of $k_5(\text{mean})$. Those values are all much lower than the maximum value of k_5. Therefore, a mean value of the concentration of bromomalonic acid can be estimated from eqn. (8) for all values of q. We are not able to say something about the correct value of q by this method. However, the bromomalonic acid concentration appears to be unrealistically low for $q=8.4 \cdot 10^{-6}$. For $q=q_{max}$, we still have [BrM] much less than [BrO$_3^-$] and [M]. If our conclusion from before (that we are in the transition region between first and zeroth order region for the Ce-catalyst) is correct, then the real values of [BrM] must be greater than the values in Table 4. Thus, if those greater values are used in eqn. (56) to calculate k_5, the values of $1/t_{Hopf}$ will be greater than the experimental values $1/t_p$. Most probably, the Hopf-periods will therefore be considerably shorter than the real periods of the relaxation-oscillations. Relaxation-oscillation is a highly nonlinear phenomenon, so it is no surprise that the (almost) linear Hopf limit cycle is a bad approximation. Nevertheless, the square root dependence on [BrO$_3^-$] of $1/t_{Hopf}$ as well as $1/t_p$ (exp) seems quite remarkable.

Finally, it is understandable that we obtain a straight line Arrhenius plot for the logarithm of the inverse period against $1/T$. Differentiating eqn. (67) we obtain:

$$E_p^{\neq}/R \equiv -d \ln(1/t_p)/d(1/T) =$$
$$E_5^{\neq}/R - (d \ln\theta_p/d \ln q) \cdot E_q^{\neq}/R \tag{71}$$

Table 4. Comparison between experimental data and the period of the Hopf limit cycle.

q	$1-\eta_0$	$k_1 \cdot k_5$(mean) [a] s^{-2} dm^3 mol^{-1}	k_5(mean) [b] s^{-1}	$[BrM]_{mean}$ [c] mol/dm^3
$8.4 \cdot 10^{-6}$	$2.05 \cdot 10^{-3}$	$1.16 \cdot 10^{-5}$	$5.53 \cdot 10^{-6}$	$3.95 \cdot 10^{-5}$
10^{-5}	$2.23 \cdot 10^{-3}$	$1.27 \cdot 10^{-5}$	$6.05 \cdot 10^{-6}$	$4.32 \cdot 10^{-5}$
10^{-4}	$7.05 \cdot 10^{-3}$	$4.00 \cdot 10^{-5}$	$1.905 \cdot 10^{-5}$	$1.36 \cdot 10^{-4}$
10^{-3}	$2.21 \cdot 10^{-2}$	$1.26 \cdot 10^{-4}$	$5.98 \cdot 10^{-5}$	$4.27 \cdot 10^{-4}$
10^{-2}	$6.83 \cdot 10^{-2}$	$3.88 \cdot 10^{-4}$	$1.85 \cdot 10^{-4}$	$1.32 \cdot 10^{-3}$
$2.5 \cdot 10^{-2}$	0.1057	$6.00 \cdot 10^{-4}$	$2.86 \cdot 10^{-4}$	$2.04 \cdot 10^{-3}$
$5 \cdot 10^{-2}$	0.1461	$8.29 \cdot 10^{-4}$	$3.95 \cdot 10^{-4}$	$2.82 \cdot 10^{-3}$
$7.62 \cdot 10^{-2}$ (q_{max})	0.1771	$1.007 \cdot 10^{-3}$	$4.80 \cdot 10^{-4}$	$3.43 \cdot 10^{-3}$ ($\ll 0.1$)

[a] Calculated from eqn. (56) with $t_{Hopf}=t_p$ (experimental), *i.e.* eqn. (70). [b] Assuming the value $k_1 = 2.1$ s^{-1} dm^3 mol^{-1}. [c] Calculated from eqn. (8).

We have used the following definition:

$$E_q^{\neq}/R \equiv -d \ln q/d(1/T) \qquad (72)$$

The value of d ln θ_p/d ln q can be obtained straightaway from Fig. 4:

$$d \ln \theta_p/d \ln q = -2.33 \qquad (73)$$

With $E_p^{\neq}/R = 8.8 \cdot 10^3$ and $E_5^{\neq}/R = 6.6 \cdot 10^3$ (see eqn. (10)), we therefore calculate the activation energy for q:

$$E_q^{\neq}/R = 9.4 \cdot 10^2 \qquad (74)$$

The activation energy for q is about an order of magnitude smaller than the activation energy for reaction (5) and it is positive. Both of those features are physically possible, since q is equal to $2k_1 k_4/k_2 k_3$ (see eqn. (21)). The activation energy for q is therefore given as eqn. (75):

$$E_q^{\neq} = E_1^{\neq} + E_4^{\neq} - (E_2^{\neq} + E_3^{\neq}) \qquad (75)$$

Since $E_q^{\neq}$ is a difference between the sum of two activation energies and the sum of two other activation energies, it should be small and it might be positive. The relations (74) and (75) should be tested by independent experiments in the future. For the present, we cannot push the comparison between the simple flip-flop version of the Oregonator and the real experiments any further. However, a considerable amount of clarification seems to have come with the investigation performed in this paper.

After the performance of the present calculations I have become aware, that J. J. Tyson [23-24] has made quite similar approximations to the relaxation-oscillations of the Oregonator (see especially Ref. 23 pp. 54–62). Tyson mostly stresses the importance of f (called h in his treatment). The parameter q is treated as a very small parameter and only the first terms in the power expansions in q of the various expressions are retained. However, it is hinted that q should perhaps be higher than $\sim 10^{-5}$. A value $q \sim 4 \cdot 10^{-3}$ is mentioned on p. 61. This value is based on comparison with the experimental value of the upper critical Br$^-$-concentration. I would not trust the absolute amplitudes of the bromide electrode so much. As already mentioned by Field, Körös and Noyes,[11] this electrode is in fact part of the time outside of its thermodynamic range of stability (too low Br$^-$-concentration).

Tyson also suggests, that p should rather be ~ 2 than ~ 300. For such a p-value there are significant deviations from simple flip-flop behaviour (Ref. 23, p. 64). However, the suggested value of p is estimated from the slope of the experimental $\log_{10}[Br^-]$ *vs.* time curve for the B-branch. In the experiments reported here, this curve is not a straight line and any estimation of p is very uncertain.

In a very recent paper by Edelson and Thomas,[25] a sensitivity analysis of the Oregonator has been performed. Those authors found that k_5 was of prime importance for the period time in complete agreement with the quasi-analytical results found in the present paper.

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