

EXPERIMENT 1: FOURIER TRANSFORM ANALYSIS OF OSCILLATING CHEMICAL REACTIONS

Introduction

This experiment serves as an introduction to the Fourier transform, which is used both in data analysis and in many forms of spectroscopy.¹ The text by Shoemaker *et al.* gives a discussion in Appendix F, pp. 756-757, on the use of Fourier transforms for data analysis. The Fourier transform is a mathematical operation which interconverts data in the time domain and data in the frequency domain. Two very widely employed applications for chemists is in modern NMR and infrared spectroscopy. A modern NMR instrument excites all regions of the frequency domain at once with a pulse; the response is then detected as the time dependence of the magnetization, as briefly described in Shoemaker *et al.*, pp. 456-459. The magnetization is found, as predicted theoretically, to oscillate in the time domain. By Fourier transformation of the time-domain data, one obtains the data in the frequency domain, and one finds that the time-dependent oscillations are made up of several different frequencies, each of which is the resonant frequency of a unique set of nuclei. The frequency-domain NMR spectrum can also be recorded directly by scanning the rf frequency slowly over the spectral region of interest. However, compared to such spectrometers based on steady-state measurements as a function of the frequency, pulsed Fourier-transform instruments result in substantial savings in the time required to record a spectrum and have displaced the older style of spectrometer.

Similarly, Fourier-transform infrared spectrometers have largely displaced conventional instruments which employ diffraction gratings to disperse light of different wavelengths (see Shoemaker *et al.*, pp. 679-680). In Fourier-transform spectrometers, the intensity is measured as a function of the displacement of one mirror of an interferometer, as described in Shoemaker *et al.*, pp. 680-683. The spectrum (intensity vs. wavelength) is obtained from the interferogram (signal vs. mirror displacement) by a Fourier transform.

In the present experiment, time-domain data (absorbance at one wavelength) on an oscillating chemical reaction will be collected and will be converted to the frequency-domain by the Fourier transformation. The frequency-domain information will be inspected, and high-frequency components (due mainly to "noise" on the signal, from the evolution of gas bubbles in the reaction mixture) will be removed by truncating the frequency-domain data. An inverse Fourier transformation of the truncated frequency-domain data will then be used to obtain a filtered time-domain plot of the slowly oscillating component.

Theory

The reaction to be studied is the Belousov-Zhabotinskii (BZ) reaction. It is one of many oscillating reactions and is described by Eastman *et al.*² Oscillating reactions are a fascinating area of theoretical and experimental chemical kinetics.^{3,4} In our experiment, the chemical oscillations are coupled to an oxidation-reduction couple that is colored. The reaction solution oscillates between red and blue. Absorbance of red light by the reaction mixture is measured using a helium-neon laser. The absorbance should change as a function of the state of the reaction in an oscillatory nature. Once these data are Fourier

transformed, the period of oscillation can be determined, and some of the "noise" can be eliminated from the time-domain spectrum by truncation and inverse Fourier transformation.

Experimental

The reaction will be set up as described by Eastman *et al.*² **SAFETY NOTE:**
When adding sulfuric acid, make sure the addition is done very slowly and into water.

The program for data acquisition is in the folder "ADC for PChemLab" on the Power Macintosh. To run program, double click on "ADC". You will need to specify the number of times the signal received by the detector is recorded (0.2 sec between samples). The program will give instructions for the collection and storage of the data. The data should be stored in a file called "xxx.expt.dat" (where xxx represents your initials).

Once the data are collected, the program "newerfourier" can be used do the Fourier transform, truncation, and inverse transformation. This program has been installed on the Macintoshes in MacChemLab on the 3rd floor of Remsen Hall. The program will give instructions for its operation. The files will be stored under "FFT.dat" and "InvFFT.dat." To plot, these data files must be transformed from MPW files to Kaleidagraph files (Kaleidagraph is a convenient graphing program for the Macintosh). This can be done by opening Kaleidagraph and then opening the MPW data files. A window entitled "Text file input format" will then appear. The proper setting are Tab ≥ 1 , and Lines Skipped = 0 for the "xxx.expt.dat" and Space ≥ 1 , Line Skipped = 1, and Read Titles for the files you will generate during Fourier transformation. The data can then be plotted in the usual way.

Note the time when the sulfuric acid is added to the solution and the times when the data collection begins and ends. This will allow you to see if the frequency of the reaction is related to the time between the addition of sulfuric acid and the beginning of data collection. You also need to know the length of time T required to collect $N = 2048$ data points so that you can determine the time per point, $\Delta t = T/N$. This value is needed to assign units of frequency (sec^{-1}) to the frequency scale when you get a FT plot. The basis for the frequency calibration of your FT plot is given as follows: The Fourier transform

$$g(f) = c \int_{-\infty}^{+\infty} e^{-i2\pi ft} f(t) dt , \quad (1)$$

for a function $f(t)$ which is sampled at discrete times $t_n = n \Delta t$, where $n = 0$ to $N - 1$, is approximated by the function $g(f_m)$ at discrete frequencies $f_m = m \Delta f$:

$$g(f_m) = c \sum_{n=0}^{N-1} e^{-i2\pi f_m t_n} f(t_n) = \sum_{n=0}^{N-1} e^{-i2\pi mn/N} f(t_n) , \quad (2)$$

From comparison of the 2 expressions in Eq. (2), the frequency sampling interval may be seen to be $\Delta f = 1/T$.

Discussion and Calculations

Use the FFT program to truncate at 4 or 5 different frequencies and back transform to the time domain. Use the *Formula* in Kaleidagraph to add constants to all but one of the columns of intensity data so that they can be plotted on a single graph as a function of time. The frequency scale should be changed from counters to actual frequency units as outlined above. For the final report, make a table of the major frequencies found. Refer to the plots and time- and frequency-domain data in the article by Eastman *et al.*² to get a sense of the relation of the two. Discuss how different frequency components contribute to the shape of the time domain oscillations. How did truncation help you understand this?

In your lab report also include the full balanced equation of the BZ reaction. This equation should include the metal and its oxidation states. The lab report should also contain the full balanced equation for at least one other common oscillating reaction.

Error Analysis

If any significant deviation from the results described in Fig. 4 of Reference 1 was observed, include an explanation of why. Determine the average period of oscillation. Also develop a method of expressing the uncertainty of the measured frequency of oscillation. (*Hint*: If you analyze the original data by hand, do you get different periods of oscillation at the beginning and end of the experiments?)

FOURIER TRANSFORM EXERCISE (Turn in as part of Preliminary Report)

Start with the time domain function (square pulse):

$$\begin{aligned} h(t) &= A, & |t| < T_0, \\ h(t) &= 0, & |t| > T_0. \end{aligned}$$

Transform into the frequency domain by multiplying by $e^{-i2\pi ft}$ and integrating from $-\infty$ to $+\infty$. (*Hint*: Is the integrand nonzero over this entire range?) This will give:

$$h(f) = (A/\pi f) \sin(2\pi f T_0).$$

Some examples of Fourier transforms from the book by Brigham⁵ are presented in this manual.

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An Introduction to Fast Fourier Transforms through the Study of Oscillating Reactions

M. P. Eastman, G. Kostal, and T. Mayhew
University of Texas at El Paso, El Paso, TX 79968

Fourier transform (FT) techniques are routinely used in NMR, IR, mass spectrometry and a variety of other applications. One reason for this usage is the improvement in the spectral signal-to-noise ratio that can be achieved through the use of fast Fourier transforms (FFT) (1-3). Unfortunately, FT spectrometers of any type are expensive and not always available for undergraduate instruction. The purpose of the experiment described here is to introduce students to the basic principles of the FFT and Fourier smoothing through the transformation of time-dependent optical absorption data obtained from an oscillating reaction. The equipment employed is relatively inexpensive and is useful in a variety of experiments.

The importance of the Fourier transform lies in its ability to transform time domain data into the frequency domain (3). Typically this is done by means of a discrete Fourier transform of a time-dependent signal $A(t)$, which is band limited. Signals of this type are considered to have no spectral components in the frequency domain above a maximum frequency f_m . In a typical experiment digital data are accumulated by a computer at time intervals, Δt , where

$$\Delta t = 1/(2f_m)$$

The use of longer time intervals can result in distortion of the Fourier transform of the data. The number of time intervals accumulated, N , is related to the desired resolution of the spectrum in the frequency domain Δf by the relation

$$N = 1/(\Delta t \Delta f)$$

Thus,

$$N = 2f_m/\Delta f$$

The resulting discrete Fourier transform is

$$X(n/N \Delta t) = \sum_{k=0}^{N-1} A(k\Delta t) \exp(-i2\pi nk/N)$$

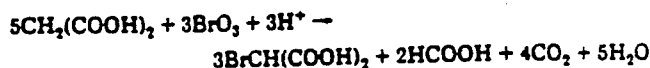
where

$$n = 0, 1, \dots, N - 1,$$

$X(n/N\Delta t)$ represents the amplitude of the components in the frequency domain, and $A(k\Delta t)$ represents the amplitude of the signal in the time domain. The FFT is an algorithm that can rapidly compute this discrete Fourier transform. A detailed description of the FFT problem and some straightforward FFT programs can be found in the text by Brigham (4).

Phenomena periodic in time have been experimentally observed in a variety of systems including colloidal clay suspensions, artificial membranes, and homogeneous reaction mixtures (5-7). It has often been pointed out that studies of these experimental systems may increase the understanding of periodic processes in living systems. Lotka was the first to present a reaction mechanism capable of producing periodic concentration changes for species participating in a homogeneous chemical reaction; since Lotka's work the understanding of periodic phenomena has benefited from work in irreversible thermodynamics and nonlinear systems (8-10).

The Belousov-Zhabotinskii (BZ) reaction is perhaps the best known oscillating homogeneous chemical reaction (11). It is easy to prepare, the cost of the reactants is low, and the oscillations persist for long periods. In the BZ reaction malonic acid is brominated in the presence of the oxidation-reduction couple Ce(III)-Ce(IV) according to the reaction



The chemistry of this reaction has been extensively reviewed (12, 13).

Experimental

Figure 1 shows the general arrangement of the experimental apparatus. A Metrologic ML-669 He-Ne laser is employed as a light source, a Metrologic 60-530 radiometer as a detector and a HP-3438A voltmeter as a digitizer. The HP-85 computer is a convenient choice for this project because of its display and plotting capabilities, but a variety of other systems could be used.

The reaction mixture consists of 4.3 g of malonic acid, 1.6 g of potassium bromate, 0.1626 g of ceric ammonium nitrate, and 2 ml of ferroin indicator in 135 ml of water. These reactants are combined in a 250-ml beaker, and the reaction is initiated by the addition of 12.5 ml of concentrated sulfuric acid. Appropriate safety conditions are maintained during the potentially dangerous acid addition step. The reaction is vigorously stirred to prevent the appearance of spatial periodicity. Oscillations in the Ce(III)-Ce(IV) concentrations are made visible using the ferroin indicator. This indicator is blue in an oxidizing solution and red in a reducing solution. The 632.8-nm output of the laser is more strongly absorbed by the blue solution than the red; thus, the oscillations in the Ce(III)-Ce(IV) concentrations are reflected in the radiometer output.

In a typical experiment 512 points were taken over a 200-s period. Conversion of the time-dependent signal to the frequency domain was accomplished using an FFT program similar to the Fortran program presented by Brigham or using the Hewlett Packard Waveform Analysis package available for HP Series 80 computers (4).

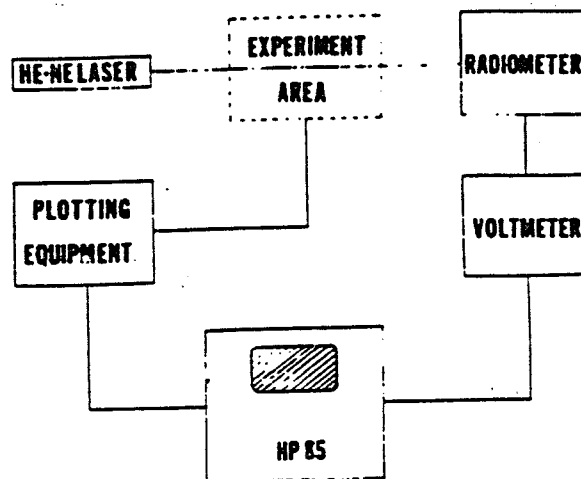


Figure 1. A block diagram of the experimental apparatus.

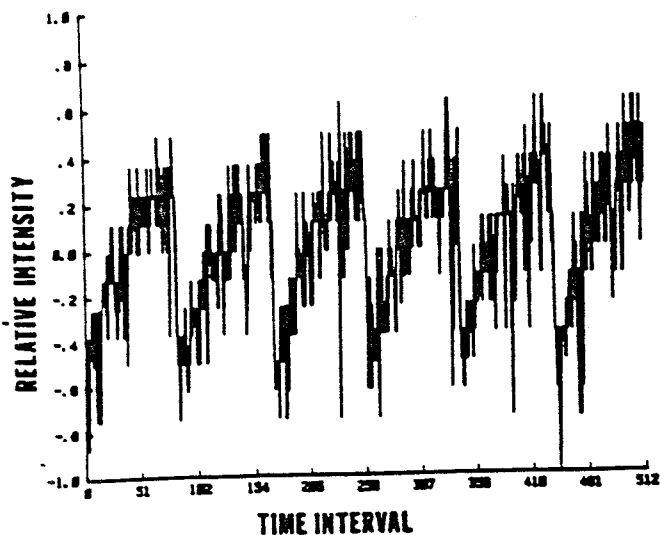


Figure 2. A plot of the digitized time-domain data. The time interval for this plot is 0.395 s.

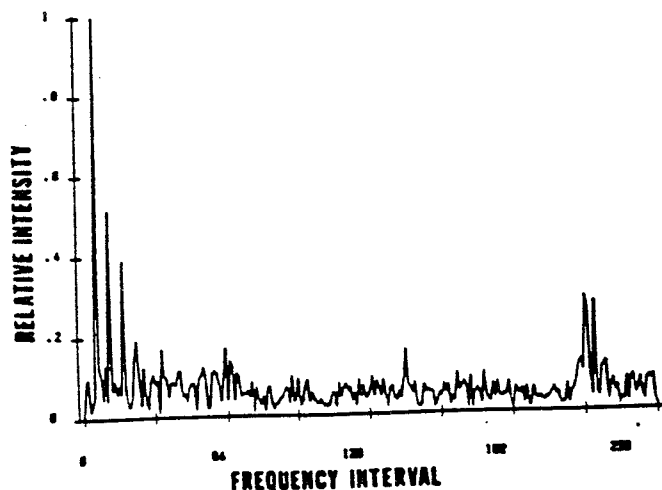


Figure 3. The frequency domain data obtained by carrying out a FFT on the data in Figure 2. The frequency interval for this plot is 4.94×10^{-3} Hz.

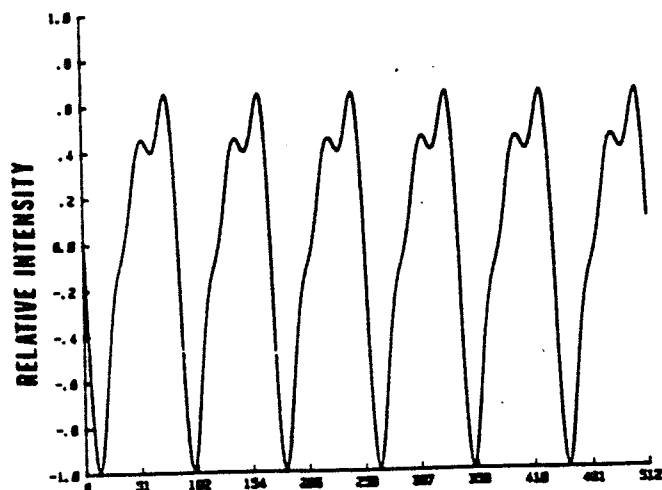


Figure 4. A plot of the results of removing the portion of the frequency spectrum assigned to noise in Figure 3 and transforming the remaining frequencies into the time domain using an inverse FT. The time interval for this plot is 0.395 s.

Discussion

Figure 2 shows a reconstruction of an absorption signal at 632.8 nm as a function of time. This reconstruction derives from the digital data stored by the computer; it is quite noisy due primarily to the scattering of the laser beam by small bubbles of CO_2 produced in the reaction. Calculations show that $f_m \approx 1.3$ Hz, $\Delta t \approx 0.39$ s, and $\Delta f \approx 5 \times 10^{-3}$ Hz. Transformation of the time domain data is quickly accomplished using the FFT algorithm. Figure 3 shows a plot of the FT coefficients in the frequency domain spectrum. This spectrum is interpreted as showing a major low-frequency peak at 30 mHz and harmonics at 60 and 90 mHz, random or stochastic noise throughout the frequency range covered and two significant stochastic noise peaks at ~ 1.1 Hz. The assignment of the high-frequency components in Figure 3 to stochastic processes is based on a number of experiments in which the high-frequency components were either reduced in intensity or totally absent.

The next step in the experiment is to remove those frequency spectrum components assigned to stochastic processes. There are a variety of sophisticated approaches to this problem; however, here a simple point of view is adopted. Based on the assignment of the frequency domain discussed above, a base line noise level of 15% is subtracted from all of the spectral components, and all spectral components above 0.16 Hz are attributed to random processes and removed from the frequency spectrum. Because the original signal is a real function of time, a single computer program can be used to compute both the discrete transform and its inverse (4). Thus, it is easy to transform the data back into the time domain. Figure 4 shows the results of removing the portion of the frequency spectrum assigned to random processes and the transformation of the remaining frequencies into the time domain. Students can readily explore the consequences of different truncation schemes including the use of frequency-weighting functions (2). Alternate approaches to Fourier smoothing have recently appeared and could also be applied to the problem (14).

The BZ reaction, when carried out in a stirred-flow reactor, provides evidence for a series of periodic and chaotic states, with experimental conditions determining which state is observed (15). Chaotic behavior can arise as a natural property of nonlinear systems and is to be distinguished from stochastic noise. Time-domain data from nonlinear systems when Fourier-transformed provide an important component in discussion of chaos (10, 15).

The experiment offers a variety of interesting options for the ambitious student. For example, students in our laboratory have failed to confirm the observations of Dutt and Banerjee who reported that, at low temperatures, the oscillation period of the BZ reaction itself shows periodicity (16). The experiment described here can also be carried out using the Briggs-Rauscher reaction (17). It should be noted that the experimental equipment in Figure 1 can be used for a variety of other experiments including the study of diffraction phenomena and response times in liquid-crystal systems (18).

Acknowledgment

This work was greatly aided by an equipment grant from the Hewlett-Packard Corporation to The University of Texas at El Paso. The experimental work was supported by the Robert A. Welch Foundation of Houston, Texas.

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Mechanisms of Chemical Oscillators: Experimental Examples¹

Richard M. Noyes*

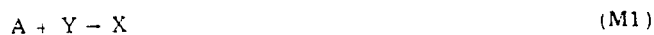
Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Richard J. Field*

Department of Chemistry, University of Montana, Missoula, Montana 59801, and Radiation Research Laboratories and Department of Chemistry, Mellon Institute of Science, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

Received February 25, 1977

In a previous Account,¹ we discussed the possibilities for concentration oscillations in closed chemical systems and illustrated the principles by means of the Oregonator³ model consisting of the following five steps.



If [X] is always small compared to the other concentrations, the first four steps can be combined in pairs to generate the stoichiometries of processes Mi and Mii.



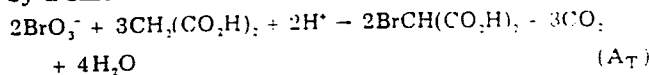
As we discussed before,¹ certain combinations of values for the rate constants and the stoichiometric factor *f* permit the concentrations of X, Y, and Z to undergo repetitive oscillations while processes Mi, Mii, and M5 cause A and B to be converted irreversibly to P and Q.

We discuss here a number of chemical systems that exhibit temporal or spatial periodicities. Whenever appropriate, these discussions of mechanism will be numbered to emphasize how the detailed chemistry relates to the Oregonator model.

The Belousov-Zhabotinsky Reaction

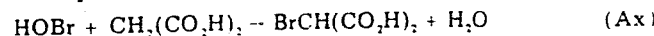
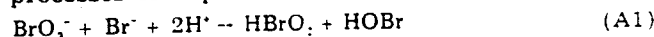
An acidic bromate solution can oxidize various organic compounds, and the reaction is catalyzed by species like cerous and manganous ions that can generate 1-equiv oxidants with quite positive reduction potentials. Belousov⁴ first observed oscillations in [Ce^{IV}]/[Ce^{III}] in such a system, and Zhabotinsky made extensive studies of both temporal⁵ and spatial⁶ oscillations. This system is by far the most studied and best understood of any chemical oscillator.

Basic Mechanism. The chemical mechanism of the temporal oscillations has been elucidated by Field, Körös, and Noyes.⁷ If an acidic solution of potassium bromate contains a comparable amount of malonic acid, a plausible stoichiometry for net chemical change is given by process A_T. That stoichiometry is not affected by a small amount of cerium ion catalyst.

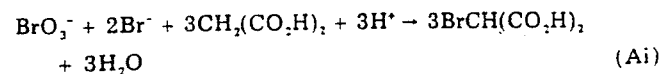


Although eq A_T represents the change of major reactants whose free-energy difference drives the chemical processes, bromate ion attacks organic substrates only very slowly by direct reaction. However, thermodynamic considerations show that it can also oxidize both bromide ion and cerium(III).

If reduction of bromate is initiated by bromide, the processes of importance are A₁, A₂, and A_x. If we



assume that proton transfer equilibria are rapidly established and make the assignment A = BrO₃⁻, X = HBrO₂, and Y = Br⁻, the analogy to steps M1 and M2 of the Oregonator is obvious. Step A_x has no analogue in the Oregonator and serves merely to consume the product HOBr from the first two steps; the stoichiometry is the same whether A_x takes place directly or through intermediate Br₂ formed from HOBr and Br⁻. Then overall reaction A_i is a direct analogue of Mi.



(1) Paper No. 19 in the series Oscillations in Chemical Systems. Paper No. 18 is R. J. Field and R. M. Noyes, *Acc. Chem. Res.*, 10, 214 (1977).

(2) Present address is University of Montana.

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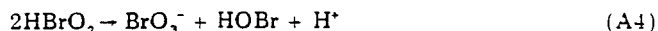
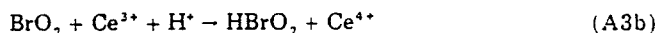
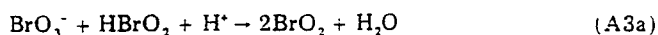
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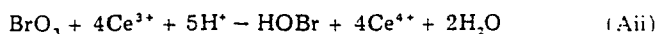
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Although thermodynamic data indicate that cerium(III) can reduce bromate either to HOBr or to Br_2 , Ce(III) is a 1-equiv reductant, and bromate is such a weak 1-equiv oxidant it cannot initiate the reaction. However, BrO_2 radicals are strong enough 1-equiv oxidants to attack Ce(III) directly. The mechanism of cerium oxidation is then given by processes A3a, A3b, and A4⁸. If we make the additional assignments B =

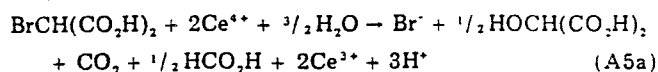


BrO_3^- and $\text{Z} = 2\text{Ce}^{4+}$, then step M3 of the Oregonator is equivalent to the sequence A3a + 2(A3b), with step A3a rate determining, and step M4 is equivalent to step A4. The stoichiometry of process Aii differs from a

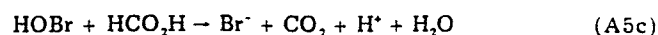
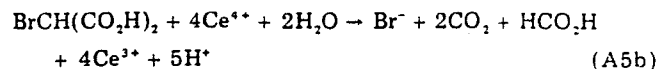


simple interpretation of process Mii because half the bromate that reacts by step A3a is regenerated by step A4 while the Oregonator model made no effort to include this kinetically unimportant refinement. Of course step Ax can easily be added to the stoichiometry of process Aii.

Ce(IV) is a strong oxidant that can attack various of the organic species in the system. Studies by Jwo⁹ show that the overall chemistry is very complex, but the reactions are kinetically first order in Ce(IV). If malonic acid is present in large excess over other organic species, it reacts preferentially with cerium(IV) to produce malonyl radicals which abstract hydrogen from bromomalonic acid to initiate a complicated sequence whose overall stoichiometry is approximated by process A5a.



If malonic acid is present in stoichiometric deficiency with respect to bromate, the brominated form becomes the chief organic species. More elementary bromine then builds up during the time when cerium(IV) is present, and the overall stoichiometry can be approximated by processes A5b and A5c. Either A5a or



A5b + A5c produces one bromide ion for each two Ce(IV) consumed and generates the stoichiometry of step M5 of the Oregonator with $f = 1$; this is precisely the stoichiometry of maximum susceptibility to oscillation. Of course only the sequence A5b + A5c generates the stoichiometry of process A_T. Figure 1 may help the reader to grasp the stoichiometric relationships for this particular overall result.

The above discussion shows that the Oregonator does indeed model the essential features of the chemical mechanism, although the chemistry presented here is much oversimplified. Edelson¹⁰ has shown that a model

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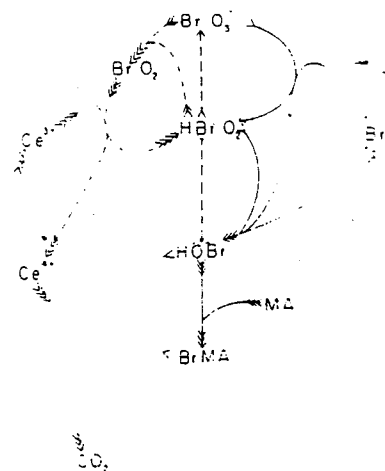


Figure 1. Schematic representation of chemical mechanism of Belousov-Zhabotinsky reaction. Barbs approaching or leaving each species indicate numbers of molecules formed or destroyed to generate process A_T. Solid paths generate stoichiometry of nonradical process A_i; dashed paths generate stoichiometry of partly radical process A_{ii}; dotted paths generate stoichiometry of process A₅.

much like this chemistry does reproduce many experimental features. Unfortunately, the model equations presented in that paper are not precisely the same as those for which calculations are shown. We are now attempting to refine the chemical detail further to reproduce the wide range of experimental observation. Although this work is not yet complete, it is clear that the main chemical features of this remarkable system are understood.

Modifications in Closed Systems. Reactions A₁, A₂, A_{3a}, and A₄ are confined specifically to oxybromine chemistry, and it is not surprising bromate appears to be an essential component in any Belousov-Zhabotinsky system. However, all the other components are subject to substitution. The following comments are suggestive, but should not be considered a thorough review.

The cerium(III) catalyst discussed above is a weak 1-equiv reducing agent. Körös et al.¹¹ have shown that Mn^{2+} , $\text{Fe}(\text{phen})_3^{2+}$, and $\text{Ru}(\text{bpy})_3^{2+}$ also serve as catalysts. An effective catalyst couple must apparently have a reduction potential roughly between 1.0 and 1.1 Volt/equiv. It is not yet clear to what extent kinetics as well as thermodynamic factors contribute to determining catalyst efficacy.

Kasperek and Bruce¹² list a number of organic acids that did and did not generate oscillations in their hand. Although specific requirements are not entirely clear, a satisfactory organic substrate should be easily brominated, and the resulting bromo compound should react with the oxidized form of the catalyst with liberation of bromide ion. The species that gave oscillations for Kasperek and Bruce¹² are acids that also produce carbon dioxide during oxidation, but Bower et al.¹³ observed oscillations with 2,4-pentanedion ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) which generates no gaseous products during the oscillatory reaction. Stroot and

(11) (a) E. Körös, L. Ladányi, V. Friedrich, Zs. Nagy, and Á. Kis, *React. Kinet. Catal. Lett.*, **1**, 455 (1974); (b) E. Körös, M. Burger, V. Friedrich, L. Ladányi, Zs. Nagy, and M. Orban, *Faraday Symp. Chem. Soc.*, **9**, 2 (1974).

(12) G. J. Kasperek and T. C. Bruce, *Inorg. Chem.*, **10**, 382 (1971).

(13) P. G. Bowers, K. E. Caldwell, and D. F. Prendergast, *J. Phys. Chem.*, **76**, 2185 (1972).

Janjic¹⁴ report other ketone substrates that exhibit oscillations.

The Belousov-Zhabotinsky reaction requires a strong acid, and H₂SO₄ has usually been used. At least in our hands, HClO₄ is an unsatisfactory acid with cerium catalyst, apparently because Ce³⁺ is too weak a reducing agent in this medium. There is no obvious reason why HClO₄ could not be used with some catalyst couples having smaller reduction potentials. Körös¹⁵ reports that nitric acid can be substituted for sulfuric and that the frequency of oscillation is thereby increased; nitrogen oxide radicals may be involved with this enhanced behavior. Even the weaker acid H₃PO₄ can generate oscillations.¹⁶ Of course HCl is also a strong acid, but it is unsatisfactory because chloride ion inhibits the oscillations; Jacobs and Epstein¹⁷ have elucidated the mechanism of that inhibition.

Periods observed for oscillation are usually about a minute to within a factor of ten, but Dayantis and Sturm¹⁸ report some concentrated solutions that oscillate with periods as small as about a tenth of a second.

Spatial Periodicities. Belousov-Zhabotinsky systems certainly provide the best known examples of spatial structures. The phenomenon was first reported by Busse¹⁹ and by Zhabotinsky.⁶ Winfree²⁰ developed a particularly effective set of concentrations for illustrating this behavior. Regions of oxidation where process Aii is dominant move by reaction and diffusion into reducing regions of excess bromide ion where Ai is dominant, and the reactions of A5 in the trailing edge serve to accomplish the transition from oxidized catalyst to excess bromide. The distinctions between phase and trigger waves and the peculiar spiral and scroll phenomena were discussed briefly with references in the previous Account.¹ Recent applications include the observation of Showalter²¹ that trigger waves of oxidation can be generated electrolytically at will and a report by Jessen et al.²² that the manganese pentanedione system can generate trigger waves without the accompanying carbon dioxide evolution that sometimes disturbed Winfree.²⁰

Flow Systems. Chemical engineers have long known that reactions which exhibit only stable steady states and monotonic behavior in a stirred batch reactor may exhibit unstable steady states and nonmonotonic behavior in a stirred-flow reactor.²³ Often the necessary feedback arises because the rate of a strongly exothermic reaction increases rapidly with temperature, and linking of this effect with the flow kinetic terms can destabilize the steady state.²⁴ The Belousov-Zhabotinsky reaction exhibits other more complex features when it is run in a stirred-flow reactor. Papers are

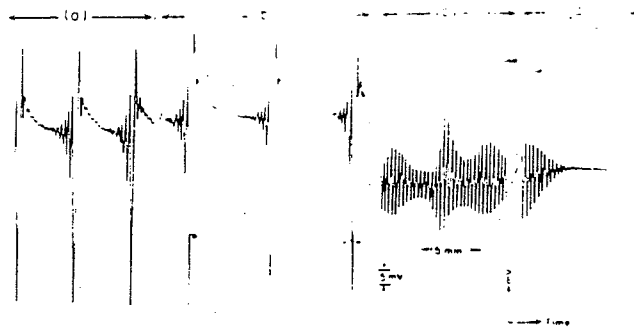


Figure 2. Effect of different sodium bromate feed rates on Belousov-Zhabotinsky oscillations in a stirred-flow reactor. Total flow rate was 4.7 mL min⁻¹. Bromate flow rates during different periods were (a) 1.28 mL min⁻¹, (b) 1.32 mL min⁻¹, (c) 1.33 mL min⁻¹, (d) 1.36 mL min⁻¹. Reproduced with permission from K. R. Graziani, J. L. Hudson and R. A. Schmitz, *Chem. Eng. J.*, 12, 9 (1976).

appearing frequently, and the following discussion is suggestive rather than complete.

If flow rates are adjusted properly, the system may exhibit repetitive pulses of a few oscillations separated by periods of steady reaction. This phenomenon has been observed apparently independently by workers in Russia,²⁵ Denmark,²⁶ Germany,²⁷ Czechoslovakia,²⁸ France,²⁹ and U.S.A.³⁰ Figure 2 illustrates the sharpness with which the effect can be produced by changes in flow rate, and the phenomenon apparently is restricted to a narrow range of conditions between those for limit cycle oscillations and steady reaction. Noyes³¹ has rationalized the observations by noting that bromomalonic acid (BrMA) is produced more rapidly during steady reaction in the oxidized condition (process Aii dominant) than the average rate during oscillation. A proper flow rate may remove BrMA more rapidly than it is produced during oscillation but less rapidly than during steady reaction, and the system may alternate between the two conditions.

Graziani et al.³⁰ point out that the above observations suggest the possibility of hysteresis and of bistability with two different states stable to small perturbations at the same flow rate. They also show that such a conclusion is consistent with the FKN mechanism,⁷ but they did not obtain convincing experimental evidence. More conclusive evidence has been reported by de Kepper et al.²⁹ and by Marek and Svobodová.²⁸

The latter authors²⁸ also report some interesting observations of phase linking by using a short tube to connect two stirred-flow reactors oscillating at the same frequency but in different phase. Both reactors approached a single new frequency one-quarter of the original one. Such behavior is expected from the theory of synchronized oscillators.³² Marek and Stucil³³ have carried out a more complete study of the synchroni-

(14) P. Stroot and D. Janjic, *Helv. Chim. Acta*, 58, 116 (1976).

(15) E. Körös, private communication.

(16) K. Prasad and R. B. Rai as reported by P. Rastogi, Ph.D. Thesis, University of Gorakhpur, 1976.

(17) S. S. Jacobs and I. R. Epstein, *J. Am. Chem. Soc.*, 98, 1721 (1976).

(18) J. Dayantis and J. Sturm, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 280, 1447 (1975).

(19) H. G. Busse, *J. Phys. Chem.*, 73, 750 (1969).

(20) A. T. Winfree, *Science*, 175, 634 (1972).

(21) K. Showalter and R. M. Noyes, *J. Am. Chem. Soc.*, 98, 3730 (1976).

(22) W. Jessen, H. Busse, and B. H. Havstein, *Angew. Chem.*, 88, 728 (1976); *Angew. Chem., Int. Ed. Engl.*, 15, 689 (1976).

(23) Perlmutter, "The Stability of Chemical Reactors", Prentice-Hall, Englewood Cliffs, N.J., 1972.

(24) S. F. Bush, *Proc. R. Soc. London, Ser. A*, 309, 1 (1964).

(25) V. A. Vavilin, A. M. Zhabotinsky and A. N. Zaikin, *Russ. J. Phys. Chem.*, 42, 1649 (1968).

(26) P. G. Sørensen, *Faraday Symp. Chem. Soc.*, 9, 88 (1974).

(27) G. Junkers, Diploma Thesis, University of Aachen, 1969, as reported by O. E. Rössler, *Faraday Symp. Chem. Soc.*, 9, 91 (1974).

(28) M. Marek and E. Svobodová, *Biophys. Chem.*, 3, 263 (1975).

(29) P. de Kepper, A. Rossi, and A. Pacault, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 283, 371 (1976).

(30) K. R. Graziani, J. L. Hudson, and R. A. Schmitz, *Chem. Eng. J.*, 12, 9 (1976).

(31) R. M. Noyes, *Faraday Symp. Chem. Soc.*, 9, 89 (1974).

(32) D. Ruelle, *Trans. N.Y. Acad. Sci.*, 70, 66 (1973).

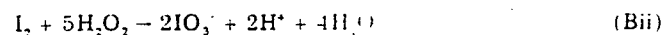
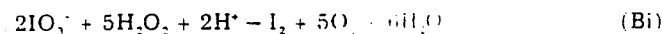
(33) M. Marek and I. Stucil, *Biophys. Chem.*, 3, 274 (1975).

zation of oscillating Belousov-Zhabontinsky systems.

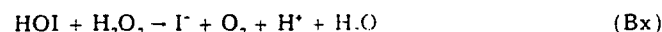
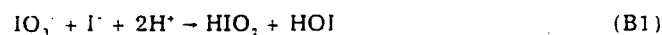
Other Oscillating Solution Reactions

The Bray-Liebhafsky Reaction. Over 50 years ago, Bray³⁴ concluded from thermodynamic considerations that the iodate-iodine couple should be almost ideal to catalyze the decomposition of hydrogen peroxide. He found the anticipated catalysis but also discovered it was not always smooth and that bursts in oxygen evolution were sometimes accompanied by alternating destruction and formation of iodine. Spectrophotometric measurements of iodine can be coupled with potentiometric measurements of iodide and of oxygen.³⁵ The reaction was studied extensively by Liebhafsky³⁶ at two widely separated periods during his career, and the mechanism has now been elucidated by Sharma and Noyes.³⁷

Thermodynamic considerations indicate that reactions Bi and Bii are both almost irreversible.



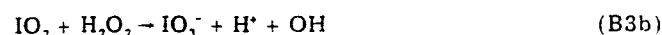
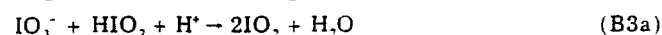
The steps B1, B2, and Bx exhibit obvious similarities



to the analogously numbered A reactions except that step Bx regenerates the iodide ion consumed in steps B1 and B2. If these steps are combined with the reversible hydrolysis of elementary iodine, the stoichiometry of process Bi can be generated with kinetic behavior resembling steps M1 and M2 of the Oregonator.

Process Bi results from direct 2-equiv oxidation of a hydrogen peroxide molecule. Although iodide ion is also thermodynamically capable of reducing hydrogen peroxide by a 2-equiv process, the reaction is too slow to be significant in this system. On the other hand, thermodynamic considerations indicate that the radicals I and IO₂ are incapable of oxidizing hydrogen peroxide by hydrogen atom abstraction but are capable of reducing it with hydroxyl radical formation. It therefore appears that process Bii is at least partly radical in nature.

The situation is further complicated because HOI will not be oxidized by a direct 1-equiv radical reaction. A mechanism that seems to be consistent with everything that is known about the system and its component parts is given by steps B3a-g and B4. Of course B3a is an



exact analogue of A3a, and the sequence B3a + 2(B3b)

(34) W. C. Bray, *J. Am. Chem. Soc.*, 43, 1262 (1921).

(35) K. R. Sharma and R. M. Noyes, *J. Am. Chem. Soc.*, 97, 202 (1975).

(36) References 4-23 in reference 37.

(37) K. R. Sharma and R. M. Noyes, *J. Am. Chem. Soc.*, 98, 4345 (1976).

consumes one HIO₂ while producing two OH radicals. The sequence B3c to B3g is a hydroxyl radical catalyzed oxidation of iodine. (Of course the IOO peroxy radical is a different species from the IO₂ radical derived from iodic or iodous acid.) Whenever the average chain length exceeds 0.5, occurrence of step B3a initiates autocatalytic generation of HIO₂ in a mechanism very similar to the sequence A3a + A3b in the Belousov reaction or the step M3 in the Oregonator. Autocatalysis does not lead to indefinite buildup of [HIO₂] because of higher order step B4 just like steps A4 and M4 in the other mechanisms.

The radical mechanism developed here does not generate the stoichiometry of process Bii. The HO₂ produced in steps B3f and B4 will react by Bx. A careful analysis leads to the conclusion that the mechanism generates the approximate stoichiometry of process Bii' which differs from that of process Bii:

$$\text{I}_2 + 11\text{H}_2\text{O}_2 \rightarrow 2\text{IO}_3^- + 3\text{O}_2 + 2\text{H}^+ + 10\text{H}_2\text{O} \quad (\text{Bii}')$$

the additional catalytic decomposition of six molecules of hydrogen peroxide. If chains are terminated by reactions of the sluggish HO₂ radicals, an apparent accidental combination of circumstances generates the stoichiometry of Bii' regardless of the length of the radical chains! This revised stoichiometry explains the well-known but previously puzzling fact that the rate of oxygen evolution increases greatly when iodine is being oxidized by iodate even though the stoichiometry of Bii produces no oxygen whatsoever.

The average length of the chain B3c-g is increased by increasing amounts of both I₂ and O₂. At low concentrations of iodine, the chain length will be less than 0.5 and net process Bi will dominate. When enough iodine has been formed, the chain length reaches the critical value, and the system switches to dominance by process Bii'. After this switch, the solution becomes grossly supersaturated with dissolved oxygen, and the chain length increases because of the effect on steps B3e and B3f. Therefore, the concentration of iodine must fall significantly before the system switches back to dominance by process Bi. The relief of supersaturation by dissolved oxygen introduces the slow restoration step analogous to M5 in the Oregonator; the system would otherwise go to a stable steady state.

The simple Oregonator model is not strictly applicable to the Bray reaction, but many features are still valid. Edelson³⁸ is attempting to model the experimental observations by means of the proposed mechanism.

The Briggs-Rauscher Reaction. Briggs and Rauscher³⁹ added manganous ion and malonic acid to a Bray system of acidic iodate and hydrogen peroxide. They discovered dramatically enhanced oscillation with a period of only a few seconds. Cooke⁴⁰ has begun to obtain the sort of information necessary to elucidate the mechanism, and Pacault et al.⁴¹ have reported

(38) D. Edelson, private communication.

(39) T. S. Briggs and W. C. Rauscher, *J. Chem. Educ.*, 50, 496 (1973).

(40) (a) D. O. Cooke; (b) *React. Kinet. Catal. Lett.*, 3, 377 (1975); *J. Chem. Soc., Chem. Commun.*, 27 (1976); (d) *React. Kinet. Catal. Lett.*, 4, 329 (1976).

(41) (a) A. Pacault, P. Hanusse, P. de Kepper, C. Vidal, and Boissonade, *Acc. Chem. Res.*, 9, 438 (1976); (b) A. Pacault, P. de Kepper, P. Hanusse, and A. Rossi, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 28, 215 (1975); (c) P. de Kepper, A. Pacault, and A. Rossi, *ibid.*, 282, 199 (1976); (d) P. de Kepper, *ibid.*, 283, 25 (1976).

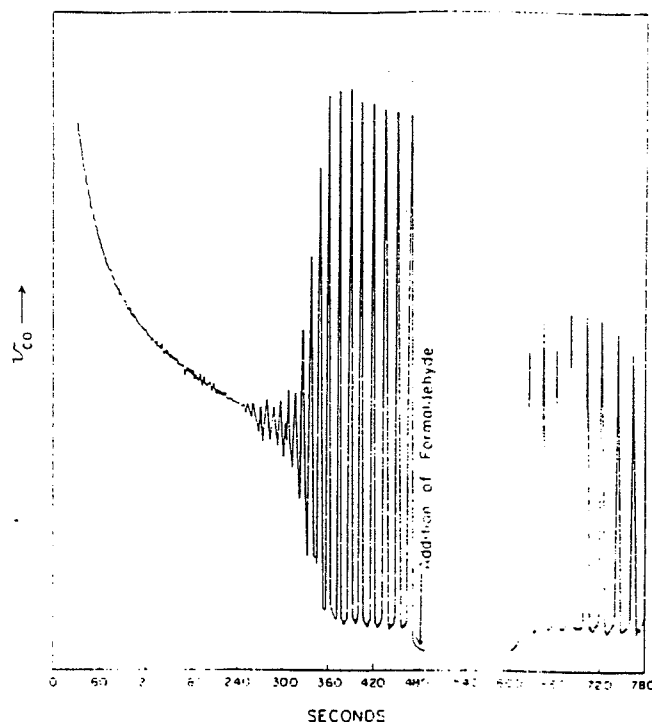


Figure 3. Rate of carbon monoxide production (in arbitrary units) at 55 °C by a stirred solution prepared from 4.0 mL of 88% aqueous formic acid and 10.0 mL of concentrated (ca. 97%) sulfuric acid. An addition of 0.3 mL of 37% formaldehyde solution was made at the time indicated.

interesting observations of multiple stationary states in a stirred-flow reactor. It appears that iodate is reduced and malonic acid is oxidized during the reaction, but it is not even clear whether hydrogen peroxide is a net oxidant or reductant or whether only its catalyzed decomposition contributes free energy as it does in the Bray-Liebafsky reaction. Much more work will be needed before the mechanism is understood.

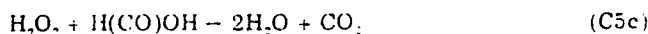
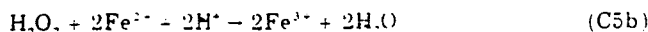
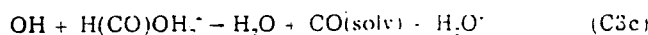
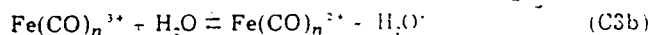
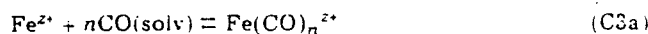
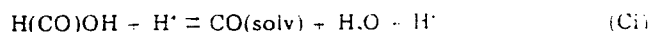
The Morgan Reaction. Formic acid could conceivably decompose either by $C\alpha$ or by $C\beta$. Standard



free-energy changes for both are negative by a few kilocalories/mole, with $C\beta$ slightly favored.

In concentrated sulfuric acid medium, virtually all of the observed products correspond to $C\alpha$. Over 60 years ago, Morgan⁴² reported an oscillatory evolution of gas. Although these observations precede all other reports of homogeneous condensed-phase oscillators, the system has been generally ignored. Showalter⁴³ has recently reexamined it and has established that the basis of the oscillations is indeed chemical. The kinetic behavior may be grossly affected by small additions of species like formaldehyde, sodium nitrite, or ferrous sulfate, and the mechanism appears to be free radical rather than the acid catalysis that might have been expected. A typical experiment is shown in Figure 3.

Further mechanistic studies⁴³ have implicated iron salts and perhaps nitrates, always present at the part per million level in sulfuric acid. Reactions with C prefixes summarize the mechanism presently favored. Those equations do not specifically note rapid protolytic equilibria between species like OH and H_2O^+ or



$\text{H}(\text{CO})\text{OH}$ and $\text{H}(\text{CO})\text{OH}_2^+$.

Reaction C1 is a general-acid-catalyzed dehydration that slowly produces CO without any radical component. As iron ions become carbonylated, Fe(III) becomes a stronger oxidizing agent and the equilibrium of C3b becomes more favored—although the equilibrium constant will always be many orders of magnitude less than unity. Of course H_3O^+ is a protonated hydroxyl radical, and the sequence of the C3 steps provides autocatalysis resembling step M3 of the Oregonator.

As radicals are destroyed by second-order step C4 rather than by first-order step C3b, the concentration of Fe(II) increases until equilibrium C3b becomes so unfavorable that radical-catalyzed reaction C3c is suppressed.

If step C5a is faster than C5b, carbon monoxide is then effectively removed before $[\text{Fe}^{\text{III}}]/[\text{Fe}^{\text{II}}]$ becomes large enough for the autocatalytic radical C3 sequence to again become significant.

This mechanism resembles the Oregonator in many ways if the hydroxyl radical is equated with intermediate X while Fe(II) and dissolved carbon monoxide are regarded as phase-determining intermediates. However, this mechanism exhibits an interesting variation from the Oregonator in that the nonradical reaction C1 and steps C3a–C5b (equivalent to process Mii + M5 of the Oregonator) both generate the same stoichiometry expressed by process $C\alpha$.

A pathway alternative to step C5b is the combination C5c + C5d which generates the stoichiometry of steps C5b + C β . Arguments in favor of this general mechanism for the Morgan reaction are being developed in another manuscript to be submitted soon.

An important potential application of the Morgan reaction arises because at elevated carbon monoxide pressure the system reaches a true equilibrium with a significant concentration of formic acid still present. If the pressure is then lowered, the system can be driven far enough from equilibrium to generate renewed oscillations. It is generally recognized that a system must be sufficiently far removed from equilibrium before oscillations are possible, but nobody has really established how far is sufficient. Preliminary very crude measurements⁴³ suggest that oscillations will not occur unless the system differs from equilibrium by at least $RT \ln 3$ for the $-\Delta G$ of process $C\alpha$.

Ammonium Nitrite Decomposition. It has long been known that aqueous solutions of ammonium nitrite, NH_4NO_2 , decompose when heated and produce elementary nitrogen. Degn⁴⁴ has reported that the gas

(42) J. S. Morgan, *J. Chem. Soc., Trans.*, 109, 274 (1916).

(43) K. Showalter and R. M. Noyes, unpublished observations.

(44) H. Degn, informal report at European Molecular Biology Organization Workshop, Dortmund, Oct 4–6, 1976.

may be evolved in oscillatory pulses with a period of tens of seconds. Smith⁴⁵ has confirmed this claim and has observed similar behavior from solutions of methylammonium nitrite, $\text{CH}_3\text{NH}_3\text{NO}_2$. It is too early to say much about the probable mechanism, but a radical component is suggested by the visual observation of nitrogen dioxide in the evolved gas. It appears doubtful that nitrogen gas itself is a chemically reactive product the way the evolved gas is in the Bray-Liebhafsky and Morgan reactions.

The Mason Reaction. DePoy and Mason⁴⁶ have reported oscillations of up to 15% in the concentration of aqueous dithionite, $\text{S}_2\text{O}_4^{2-}$, during its autocatalytic disproportionation. The analytical method involved measurements at different times rather than a continuous recording of some property. It may be that massive concentrations of some intermediate build up and then break down with regeneration of some of the original dithionite. It may also be that the analytical method is measuring some intermediate species in addition to dithionite. It seems difficult in any other way to reconcile the observations with the thermodynamic requirement¹ that concentrations of reactant species can not oscillate.

Photochemically Driven Oscillators. In all of the above examples, oscillations are driven by the free-energy change of an irreversible chemical reaction. Nitzan and Ross⁴⁷ showed theoretically that continuous illumination of a homogeneous system could initiate oscillations, hysteresis, and similar instabilities. Yamazaki et al.⁴⁸ have reported photochemically driven oscillations during irreversible chemical processes arising from ultraviolet irradiation of 1,5-naphthyridine. Turro⁴⁹ has reported oscillations in the photostationary state sometimes attained when the peroxide of 9,10-diphenylanthracene is simultaneously being formed photochemically and destroyed thermally. Such a phenomenon could be accommodated⁵⁰ to an Oregonator type of mechanism involving singlet oxygen as an intermediate. If such a system does undergo no net chemical change while concentrations of species oscillate during continuous radiation, the observation may have practical implications.

Oscillations in Heterogeneous Condensed Systems

Oscillatory Electrode Reactions. It has long been known that electrochemical systems may oscillate as changing electrode surfaces affect conductivity and/or potentiometric behavior⁵¹. No effort will be made to review the field here.

The "beating mercury heart" phenomenon involves pulsation of a mercury globule near a corroding electrode not necessarily touching the mercury. Surface charge density changes the surface tension of the mercury and hence the shape of the globule; the shape change alters capacity and/or conductivity of the

system. Lin, Keizer, et al.⁵² have recently explained oscillations driven by the solution of aluminum in aqueous alkali.

Periodic Precipitation Phenomena. If silver nitrate solution is added at one point to a sheet of gel impregnated with potassium chromate, silver chromate precipitates in concentric rings. The phenomenon was discovered by Liesegang⁵³ and has been observed with several sparingly soluble salts. The subject was reviewed by Stern,⁵⁴ and the theory has been extended by Flicker and Ross.⁵⁵ When crystallization is initiated in a supersaturated region, ions diffuse from the surroundings to the growing crystals. Silver ions diffusing outward beyond those crystals must traverse a region of depleted chromate before the medium again becomes sufficiently supersaturated for nucleation to occur.

A similar banding with periods up to 2 m has been observed in igneous rocks that formed from large bodies of magma cooling at great depths. Most geologists since Darwin have attempted to invoke gravitational field effects to explain differentiation in such magmas. McBirney and Noyes⁵⁶ have shown that the non-Newtonian viscosities of the fluid magmas would not permit gravitational differentiations, and the effect has been explained by a molecular model based on supersaturation and diffusion much as occurs with Liesegang rings.

Oscillations During Gas Reactions

Heat capacities of dilute gases are much less per unit volume than are those of liquids, and temperatures can be greatly altered by sudden changes in reaction rate. Because reaction rates are strongly dependent upon temperature, various reactions can be accelerated or retarded by the thermal consequences of their occurrence, and the possibilities for oscillatory behavior are thereby enhanced.

Explosions due to chain branching autocatalytic oxidations have been known for centuries. Oscillations have also been reported during oxidation and chlorination of some hydrocarbons. Appropriate references are provided by Gray et al.⁵⁷ who also report their own observations of propane oxidation. It is not yet clear whether any of these systems generate unstable steady states under truly isothermal conditions.

Dickens et al.⁵⁸ report oscillatory flames during the oxidation of "dry" carbon monoxide. The system is very complicated, and about a part per million of water could accelerate the rate by orders of magnitude. Yang⁵⁹ has suggested an isothermal model that generates an unstable steady state. However, that model requires an unidentified excited electronic state of carbon dioxide with peculiar kinetic properties. Pilling and Noyes⁶⁰ have argued that the Yang model is im-

(45) K. Smith and R. M. Noyes, preliminary observations.

(46) P. E. DePoy and D. M. Mason, *Faraday Symp. Chem. Soc.*, 9, 47 (1974).

(47) A. Nitzan and J. Ross, *J. Chem. Phys.*, 59, 241 (1973).

(48) I. Yamazaki, M. Fujita, and H. Baba, *Photochem. Photobiol.*, 23, 69 (1976).

(49) N. J. Turro, private communication.

(50) R. M. Noyes, unpublished.

(51) K. S. Indira, S. K. Rangarajan, and K. S. G. Doss, *J. Electroanal. Chem.*, 21, 57 (1969).

(52) S. W. Lin, J. Keizer, P. A. Rock, and H. Stenschke, *Proc. Natl. Acad. Sci. U.S.A.*, 71, 4477 (1974).

(53) R. E. Liesegang, *Naturwiss. Wochenschr.*, 11, 353 (1896).

(54) K. H. Stern, *Chem. Rev.*, 54, 79 (1954).

(55) M. Flicker and J. Ross, *J. Chem. Phys.*, 60, 3458 (1974).

(56) A. R. McBirney and R. M. Noyes, *Am. J. Sci.*, submitted for publication.

(57) P. Gray, J. F. Griffiths, and R. J. Moule, *Faraday Symp. Chem. Soc.*, 9, 103 (1974).

(58) P. G. Dickens, J. E. Dove, and J. W. Linnett, *Trans. Faraday Soc.*, 60, 539 (1964).

(59) (a) C. H. Yang, *Combust. Flame*, 23, 97 (1974); (b) C. H. Yang and A. L. Berlad, *J. Chem. Soc., Faraday Trans. 1*, 70, 1661 (1974); (c) C. H. Yang, *Faraday Symp. Chem. Soc.*, 9, 114 (1974).

plausible and have shown the isothermal steady state must be stable if only known reactions of species in ground electronic states are considered. Explosions can be modeled if thermal gradients due to conduction are added, but turbulence apparently must be invoked also if oscillations are to be explained. A recent paper by McCafrey and Berlad⁶¹ suggests that heterogeneous effects may also be necessary in order to account for oscillations.

Oscillations in Biological Systems

Living organisms are open chemical systems constantly subject to external influences and invariably far from equilibrium! Numerous oscillatory responses have been observed with periods ranging from seconds to at least a year.⁶² Some of these responses are undoubtedly initiated by external stimuli, but others like human "jet lag" are in opposition to those stimuli and must originate in the chemistry of the individual concerned.

No effort will be made to review the field. None of the chemical mechanisms has been elucidated in detail, but glycolysis has been studied extensively. Boiteux and Hess⁶³ have summarized the evidence that the key step contributing to instability involves the conversion of fructose 6-phosphate to fructose 1,6-bisphosphate catalyzed by phosphofructokinase. The activity of this enzyme is strongly influenced by the product of the reaction it catalyzes. A model that leads to an unstable steady state has been proposed by Goldbeter and Lefever.⁶⁴ That model involves a process third order in reactive intermediates as invoked for the Brusselator model of Prigogine and Lefever.⁶⁵ It is not clear whether or not existing experimental data could also be accommodated to an Oregonator model³ based on switching between pseudo steady states.

The dynamics of populations of individual species introduce still more complexities, especially when those populations are not uniformly distributed through the space of interest.⁶⁶ Although some oscillations in predator-prey populations bear superficial resemblances to the chemical oscillators discussed here, the systems involved are so different that any comparisons should be handled with great caution.

Characteristics of Known Chemical Oscillators

The above discussion illustrates that chemical instabilities may arise for several different reasons. Thus periodic precipitation phenomena involve kinetics of nucleation in supersaturated systems. Electrode reactions and localized trigger wave initiation require a heterogeneity in the system, and phase waves require a gradient in a system that would be oscillatory even if uniform. All presently known gas-phase oscillators seem to require a coupling with the thermal effects associated with very exothermic processes, although there is no reason why isothermal gas oscillators could not occur. Probably enzyme kinetics are not yet well enough established to determine whether biological

oscillations involve switching between pseudo steady states (Oregonator) or third order in intermediates (Brusselator) types of mechanisms.

At the present time, the best understood homogeneous oscillators involve ionic reactions in aqueous solution. It is interesting that many of the best established examples include gas evolution as one of the processes. In the Bray-Liebhaftsky³⁷ and Morgan reactions, the evolved gas is chemically reactive and rate of evolution is critical to the possibility of oscillations. In the Belousov-Zhabotinsky⁷ reaction, evolved gas seems to be inert chemically, and completely gas-free systems can exhibit both temporal¹³ and spatial²² periodicities. It is too early to say whether or not gas evolution is chemically significant for ammonium nitrite⁴⁵ and photochemically driven oscillators.

So few mechanisms are yet understood that it is not possible to generalize. However, enough homogeneous solution mechanisms have been elucidated that we can suggest a few features that are probably worth looking for when studying other oscillators:

(a) The major reactants must undergo at least two key processes (like M_i and M_{ii}) that produce or consume phase-determining intermediates. Both processes must be strongly favored thermodynamically.

(b) The rate of one of the key processes can be switched on or off relative to the other. This switch is a kinetic effect free of thermodynamic constraints. For the systems whose mechanisms are understood, only one of the two key processes involves radicals in its mechanism.

Unless d-orbital shells are only partially filled, transition metal molecules have an even number of electrons. The difference of two even numbers is always even, the sum or difference of an even and an odd number is always odd. Therefore radical and nonradical processes can take place independently of each other and a radical seems to be required for processes M_i and M_{ii}.

Most organic free radicals tend to be high-energy species that react rather indiscriminantly and should be avoided in biological processes. This argument suggests that transition elements in the third row of the periodic table may be involved in the 1-equiv oxidation and reductions that are required for one of the key processes; such reactions might be coupled to transition between S-H and S-S bonds in proteins. Many of those transition elements are essential to life but are needed only in trace amounts. It is tempting to suggest they may be incorporated in some of the enzyme systems needed for biological control mechanisms.

(c) The switching between the two key processes involves a stiffly coupled intermediate (X in the Oregonator) that is formed and destroyed by processes of the same order in its concentration. Small dominance in either formation or destruction can greatly alter the concentration of that intermediate and switch the system to major dominance by one or the other of the key processes.

(d) A final process must overcome the effects of the two key processes on the concentrations of the intermediates. This final process (such as step M5 in the Oregonator) must have a sufficiently small time constant that the system will repeatedly overshoot its mathematical steady state. Whenever the rate constant for

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(64) A. Goldbeter and R. Lefever, *Biophys. J.*, **12**, 1302 (1972).

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restoration process exceeds a certain value, the system will go to that steady state. Such a steady state may be only marginally stable, so that the system can still be excited by a suitable perturbation.

In many of the known solution oscillators, this final process is escape of a gas. Many metabolic processes in living organisms produce carbon dioxide, which then affects cytoplasmic pH. If pH is important to the processes leading to oscillation, diffusive escape of carbon dioxide through cell walls could be the slow process permitting the delayed feedback necessary for oscillation.

We wish to emphasize the biological suggestions we have made above are purely speculative without any experimental justification. However, they arise from direct analogies with now established mechanisms in simpler chemical systems. We make no claim they are valid, but we believe they are provocative. We hope they will suggest further tests by which these crude

ideas may be substantiated or rejected.

Notes Added in Proof

Bowers and Rawji⁶⁷ have also studied the Morgan reaction^{42,43} of formic acid dehydration. They believe the oscillations are caused by physical rather than by chemical effects.

Bose, Ross, and Wrighton⁶⁸ have independently observed photochemically induced oscillations in the fluorescence of anthracene and of dimethylanthracene similar to those found by Turro⁴⁹ for the diphenyl derivative.

Much of the work described here was supported either by the National Science Foundation or by the Atomic Energy Commission.

(67) P. G. Bowers and G. Rawji, *J. Phys. Chem.*, submitted for publication.

(68) R. L. Bose, J. Ross, and M. S. Wrighton, *J. Am. Chem. Soc.*, submitted for publication.

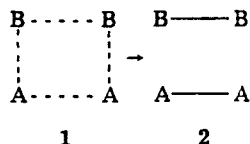
A Transition-State Probe

Dudley H. Williams

University Chemical Laboratory, Cambridge, United Kingdom

Received February 2, 1977

A central problem in chemistry is that of increasing our knowledge of transition states. The lifetime of the transition state is so short relative to the time scale of the majority of our investigative techniques that direct observations are normally not possible. Thus, in solution chemistry, conclusions regarding transition-state geometry may be inferred from calculation following kinetic studies; the possibility of the *direct* measurement of a transition-state property is lost due to collisions which precede the determination of the experimental parameter (e.g., rate of product formation). Clearly, if we wish to obtain information about transition-state geometry, then it would be extremely useful to know what happens to the electronic energy stored in the stretched bonds of the transition state (e.g., 1) as it passes to more stable products (e.g., 2).



Let us consider first a hypothetical and extreme case where the geometry of 1 was such that the A-A and B-B bond lengths were close to their equilibrium values in the products 2, and the excess electronic energy of

1 over 2 could then be regarded as lying in the form of a potentially repulsive interaction along the two A-B bonds in 1. Thus, as the transition state was converted to products, a quantity of energy close to the reverse activation energy would appear as kinetic energy (mutual repulsion) of the products. In the reverse process (2 → 1), such a model would correspond to an activation energy being supplied by collision of A-A and B-B due to relative translation along the A → B directions, without the requirement of vibrational excitation of A-A and B-B.

As a second and opposite extreme, we might envisage a situation where the A-A and B-B bond lengths in 1 were far from their equilibrium values in the products 2, such that the excess electronic energy of 1 over 2 would appear as vibrational energy of the products 2 which would drift apart without mutual repulsion. Here, in the reverse process (2 → 1), the activation energy would be supplied almost exclusively as vibrational energy of A-A and B-B, a large relative translational (collisional) energy of the two molecules not being required.

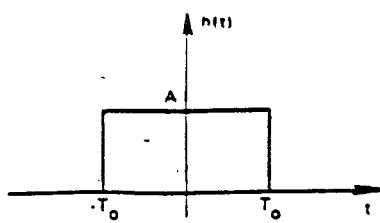
Information on the presence or absence of large mutual repulsions of A-A and B-B as a transition state 1 collapses to products in a period comparable to vibrational frequencies (10^{-13} s) can only be obtained by direct observation of the behavior of isolated 1, i.e., in the absence of collisions. Such conditions can be found in a molecular beam. The measurement of mutual repulsion of two particles formed by the collapse of transition state is facilitated if the transition state itself carries a charge and the products correspond to a charged molecule and a neutral molecule. The ionic product can then be passed through a magnetic field

Dudley H. Williams was born in Leeds, England, in 1937, and studied for his undergraduate and doctoral degrees at the University of Leeds. He subsequently worked at Stanford University as a postdoctoral fellow, and then returned to the U.K. to carry out research and teaching at Cambridge University. He is a Fellow of Churchill College and Reader in Organic Chemistry at the University of Cambridge. His research interests cover the general areas of structure elucidation and synthesis in organic chemistry, with special interest in the development and application of new techniques in mass spectrometry and nuclear magnetic resonance. He is a past recipient of the Meldola Medal of the Royal Institute of Chemistry and the Corday-Morgan Medal of the Chemical Society.

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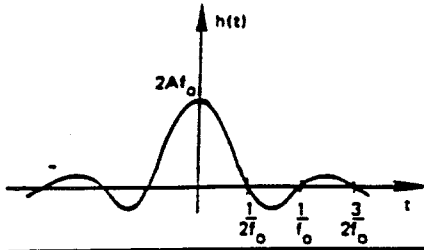
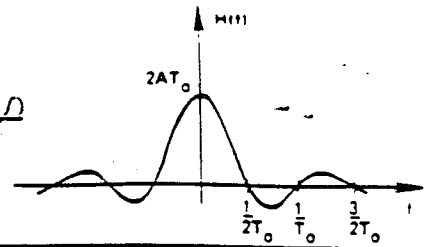
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$$h(t) = \begin{cases} A & |t| < T_0 \\ \frac{A}{2} & |t| = T_0 \\ 0 & |t| > T_0 \end{cases}$$



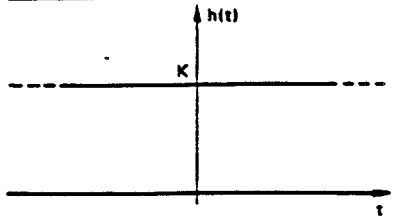
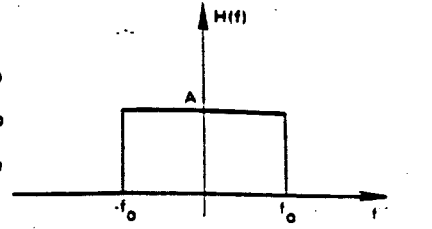
$$H(f) = 2AT_0 \frac{\sin(2\pi T_0 f)}{2\pi T_0 f}$$



$$h(t) = 2A f_0 \frac{\sin(2\pi f_0 t)}{2\pi f_0 t}$$



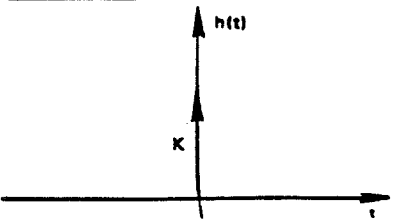
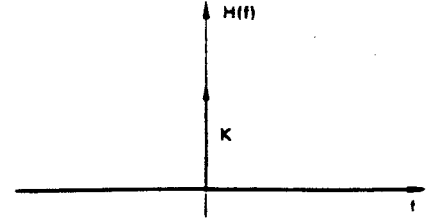
$$H(f) = \begin{cases} A & |f| < f_0 \\ \frac{A}{2} & |f| = f_0 \\ 0 & |f| > f_0 \end{cases}$$



$$h(t) = K$$



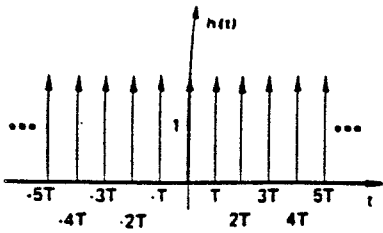
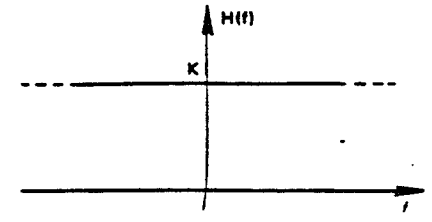
$$H(f) = K\delta(f)$$



$$h(t) = K\delta(t)$$



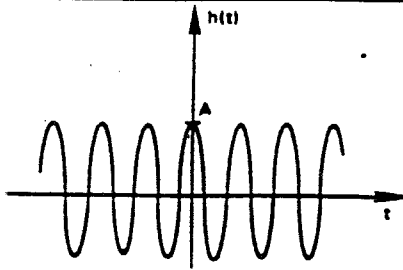
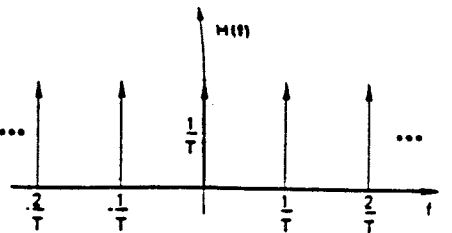
$$H(f) = K$$



$$h(t) = \sum \delta(t - nT)$$



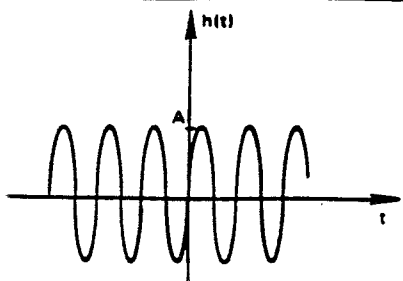
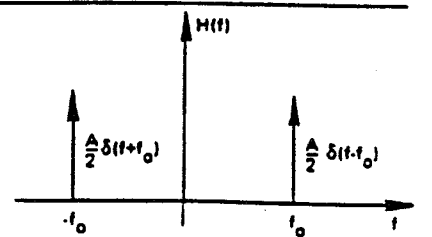
$$H(f) = \frac{1}{T} \sum \delta(f - \frac{n}{T})$$



$$h(t) = A \cos(2\pi f_0 t)$$



$$H(f) = \frac{A}{2} \delta(f - f_0) + \frac{A}{2} \delta(f + f_0)$$



$$h(t) = A \sin(2\pi f_0 t)$$



$$H(f) = -j\frac{A}{2} \delta(f - f_0) + j\frac{A}{2} \delta(f + f_0)$$

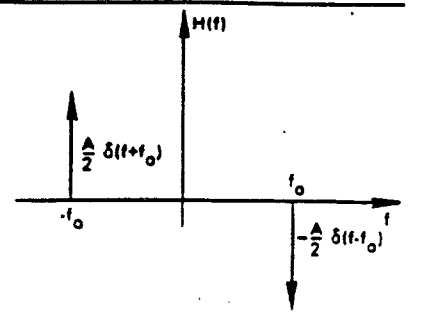
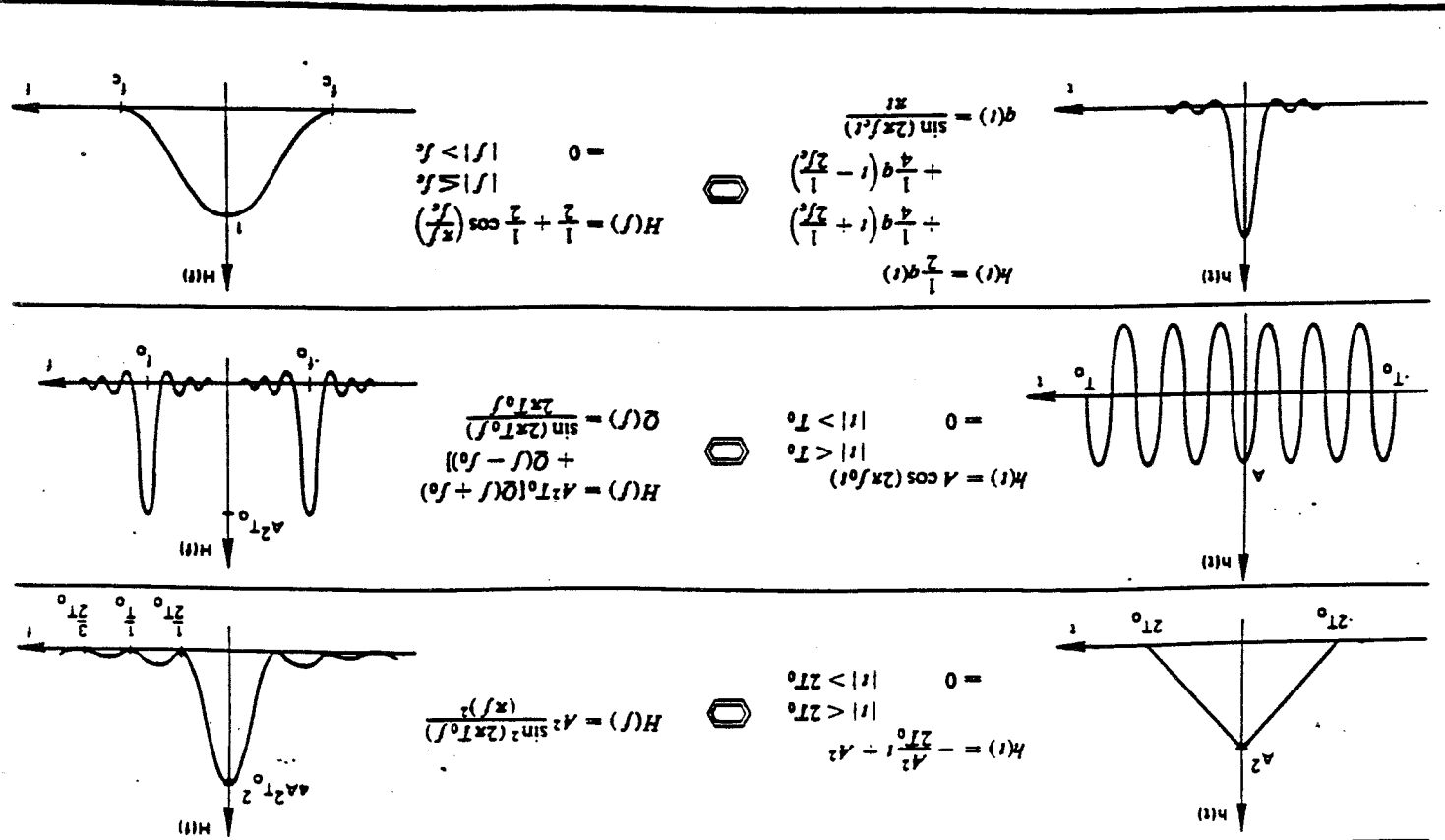
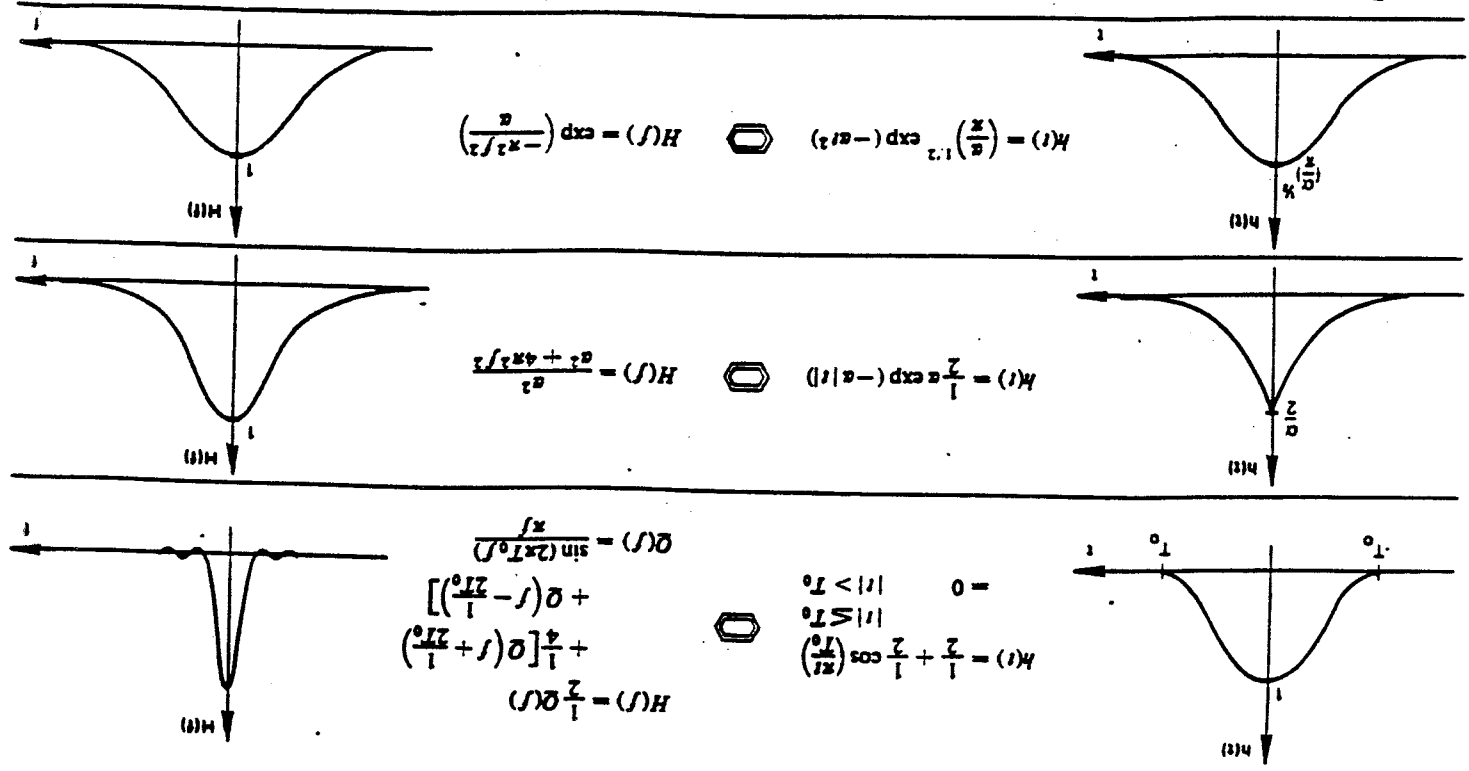


Figure 2-11. Fourier transform pairs.

Figure 2-11 (continued)



Frequency domain

Time domain