Chapter 1

Introduction

1.1 Far-from-equilibrium self-organization and electrochemistry

> "Als ich den vorigen Versuch mit einem Antheil einer andersher bezogenen officinellen Silberauflösung anstellte, war die Ablenkung des Eisens ebenfalls anfangs positiv; sie ging aber bald in die entgegengesetzte negative über. Ich habe jedoch bei wiederholten Versuchen bemerkt, daß die Erscheinung hierbei gewöhnlich noch nicht stehen blieb, vielmehr das Auflösen des Eisens und sein Wiederblankwerden nebst Auflösung des gefällten Silbers wohl 4 bis 6 mal, oft sehr schnell hinter einander abwechselten, wobei jedesmal die Ablenkung der Magnetnadel auf das Entgegengesetzte übersprang, bis das Eisenstäbchen zuletzt jedesmal unwirksam liegen blieb."

M.G.Th. Fechner, Jahrbuch der Chemie und Physik, **53**II (**1828**) 141

The given quotation is taken from a remarkable publication which is usually cited as the very first report on spontaneous, periodic, self-organization phenomena in electrochemistry[1] [1]. Fechner made his memorable observations just four years after Carnot had verbally formulated the theoretical feasibility of a cyclic process for the production of work from heat. About another 40 years passed before Clausius was to introduce the notion of Entropy thereby opening up the triumphal march of equilibrium thermodynamics. Still, it was not until 150 years or so later that Fechner's surprising findings could entirely be explained.

Initially, the advent of classical thermodynamics made matters worse. While Fechner's contemporaries approached spontaneous dynamical phenomena in chemistry with a sense of puzzled admiration, many chemists during the second half of

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[1] Note, however, that Th. Fechner himself frequently refers to his own experiments as a mere confirmation of previous experiments conducted by the chemist Wetzlar in 1827.

the 19th century considered such reports as evidence for non-serious scientific work or, at best, as an irrelevant curiosity. At the heart of this uptight, dogmatic view lay doubtlessly the strict statements of the second law of thermodynamics regarding the immutable increase in entropy during irreversible processes in closed systems.

With the formulation of quantitative relations valid in near-equilibrium situations, the notion of fluxes, forces and stationary states eventually arrived in textbooks on thermodynamics during the first half of this century. Still, another rigid evolution criteria of "no return" - this time pertaining to the rate of entropy production - determined the fate of processes in the linear regime and left no room for sustained periodic rates.

Finally, De Groot, Prigogine and Glansdorff [2, 3], among other people, extended our view of thermodynamics to far-from-equilibrium processes introducing the notion of open systems with the ability to exchange mass and energy with their surroundings. In so doing, they could loosen the seemingly tight grip of the second law, but instead had to throw out most quantitative relations on state functions valid in the non-linear regime leaving behind a generalized evolution and a stability criterion only. These thermodynamic relations, however, usually are little instructive for an understanding or prediction of complex chemical reaction processes.

Meanwhile, scientific folk of various separated disciplines such as theoretical physics, hydrodynamics, bifurcation theory, laser physics, biomathematics, computer science, engineering or theoretical biology etc. started talking to each other realizing that the dynamics of their nonlinear systems under investigation had much more in common than they would have thought. Thus, certain scientific communities increasingly grew together thanks to the gradual usage of common mathematical tools and terminologies for the kinetic description of the complex spatial and temporal phenomena observed in models and experiments. This was the time when a sort of "Metadiscipline" was born referred to as "Complex Dynamical Systems Theory" or "Nonlinear Dynamics"; its goal has been to provide an interdisciplinary framework for the modeling of qualitatively similar natural phenomena. Yet the significance of this framework was not restricted to common mathematical tools, important though that is. Rather, the concepts of Nonlinear Dynamics evidence a certain inner functional relation between many natural processes which had been unknown until then. Needless to say that the emerging computer power catalyzed this development further providing the possibility of numerical solutions to equations previously too hard to tackle. The theory of nonlinear dynamical systems became finally appealing even for economists, social sciences and certain branches in humanities. Admittedly fascinating, though, it still remains to be seen whether or not the application of physical concepts in these areas will meet the expectations.

In the 1970s and 1980s, it was dawning on more and more chemists that it is the kinetic approach of Nonlinear Dynamics rather than pure thermodynamics which can possibly provide valuable help for understanding chemical self-organizing instabilities when the deviations from equilibrium became sufficiently marked. In this context the pioneering theoretical work by Meinhardt and Gierer [4, 5, 6] and O.E. Rössler [7, 8] is worth mentioning. At the same time, allegedly singular experimental findings, e.g. the oscillatory Belousov-Zhabotinskii reaction [9, 10] or aperiodic biochemical enzyme

reactions [11], were suddenly seen in the light of the new paradigm and fit smoothly in the theoretical framework. Sparked by ever more complex calculations of spatially extended reactive systems, spatial chemical phenomena increasingly came to the fore; they involved sustained, transient, propagating or stationary macroscopic inhomogeneities in concentrations, potential or temperature. The associated research field occasionally referred to as "chemical pattern formation" deals with the systematic hunt for novel spatiotemporal self-organizing structures in chemistry and gradually fascinated researchers of an increasing number of physico-chemical disciplines such as liquid-phase reactions, combustion chemistry or surface science and catalysis.

Recent years have seen nonlinear dynamicists focusing more and more on the deliberate control of chemical patterns rather than on merely evidencing their existence. "Chaos control" [12] had become the path-breaking paradigm of the early 1990s, and again, after the temporal taming of nonlinear behavior in certain systems, controlled spatial patterns are currently top on the research agenda.

The perception of nonlinear kinetic concepts in Electrochemistry pretty much followed a similar, slightly delayed pattern as pointed out above. At first, electrochemists gathered an enormous amount of experimental observations, data and mechanistic speculations on oscillatory electrochemical processes [13]. Naturally, electrodissolution rather than electrocatalytic systems were dominating the picture, since self-organizing systems of this kind have long been known and new ones were easy to find. This becomes comprehensible if one recalls that electrochemistry is usually conducted far from equilibrium and that the interplay of chemical reactions, mass transport and electrical quantities usually provides an appropriate number of different time scales. Both conditions are well known to be necessary for the occurrence of spontaneous temporal periodic behavior. Thus, electrochemistry offers ideal dynamical systems for the study of the spontaneous emergence of order. Very early, even spatial phenomena like propagating waves had been observed in electrodissolution systems [14]. Early dynamical modeling, though, still had to involve discontinuous chemical kinetics around the Flade potential in order to account for periodic behavior. In the early 1970s, Wojtowicz [15] surprised the electrochemical community with concepts on possible mechanistic origins of electrochemical oscillations such as a negative differential resistance which are partially still valid to date.

Until that time, prominent electrocatalytic reaction systems exhibiting kinetic oscillations involved the oxidation of small organic compounds which was discovered by E. Müller [16], as well as the reduction of certain anions like $S_2O_8^{2-}$ [17, 18, 19]. The latter reaction constitutes the most prominent example of a simple, one-reaction electrocatalysis and was thoroughly studied by Frumkin [17]. The former electrocatalytic reactions were known to be nontrivial electrocatalytic systems in the sense that they involved multiple and parallel reaction steps; they were intensively studied under both oscillatory and stationary conditions owing to their emerging technological importance for continuous energy conversion (direct methanol fuel cell). Consequently, a number of disputed mechanistic hypotheses pertaining to the oxidation of methanol and formic acid have been put forward [20]. Even though it was known that a successful kinetic description of far-from-equilibrium behavior provides meaningful conclusions as to the plausibility of a hypothetical mechanism, no one had ever

clearly shown by means of kinetic models that any of the proposed reaction schemes was actually able to account for the experimental nonlinear features.

Eventually, in the mid 1980s deterministic chaos had also been reported in experimental electrodissolution systems [21, 22]. Still, despite a great number of studies on electrochemical self-organization, the 1980s witnessed no significant progress in the mechanistic understanding of the origin of spontaneous instabilities.

Finally, it was Koper [23] who succeeded in giving stringent evidence for the crucial role of a negative differential resistance in the occurrence of temporal electrochemical instabilities such as bistability and oscillations. Using the methodology of Nonlinear Dynamics he impressively showed for electrochemical systems that operating with simple prototype models may suffice in order to account for complex self-organization. His work also included a refined categorization of electrochemical oscillators with respect to the operating conditions.

In the meantime, another non-trivial self-organizing electrocatalytic system had attracted considerable attention. The oxidation of hydrogen in the presence of anions and metal cations [24, 25, 26, 27] allowed for both potentiostatic and galvanostatic oscillations and, therefore, turned into a workhorse for galvanostatic oscillatory systems [28, 29]. Over the last few years more and more distinct electrochemical oscillatory phenomena have been reported in literature (e.g. [30] and [31] or see the review [32]). In order to gain a systematic understanding of these oscillators, a classification with respect to the mechanistic origin of the instability is a useful tool [33]. Still, an increasing number of chemical realizations of periodic instabilities requires ever more sophisticated methods for a unique experimental identification of the respective mechanistic category. Thus, a comprehensive mechanistic categorization scheme in combination with a ready identification procedure seemed presently to be appropriate.

Inhomogeneous spatial structures on electrode interfaces - though long ago observed in electrodissolution systems [14, 34] - had remained the last theoretical and experimental challenge where electrocatalytic processes were concerned. The major reason for this lies in the necessity for sophisticated imaging techniques for either potential or chemical surface species. Again, the simplest electrocatalysis, the $S_2O_8^{2-}$ reduction on Ag, was subjected first to a spatiotemporal investigation of the electrified interface employing both novel (plasmon microscopy [35]) and classical (potential microprobes [36]) imaging techniques. The principal experimental findings involved locally triggered, accelerated potential fronts under bistable conditions; importantly, the acceleration could be reproduced by a numerical model assuming a nonlocal migration coupling across the electrolyte [36, 37, 38, 39]. The model has recently been extended by J. Christoph to account for centro-symmetric electrode geometries and the effect of the range of the nonlocal coupling on the front velocity has theoretically been examined [40, 41]. However, the question of whether an electrocatalytic systems involving a more complex chemistry could lead to the observation of more complex spatiotemporal self-organization was still unclear. Also direct experimental evidence for the relations between certain model parameters and the nature of the migration coupling as suggested by theory [40] was missing. Thus, as far as spatial patterns are concerned, electrochemistry is still in the stage of collecting phenomenological data and matching them to models. The possibility of a practical leverage for

inhomogeneous electrocatalysis remains to be seen.

In summary, despite of over 150 years of complex dynamical phenomena, electrochemistry faces a number of ongoing, ever intriguing problems concerning spontaneous self-organization: (i) the mechanistic clarification of the temporal self-organization of individual important reaction systems, (ii) the physical and mechanistic origin and scope of spatial-pattern forming processes as well as (iii) the possibility of a practical leverage for self-organizing far-from-equilibrium structures.

1.2   Essentials of dynamical systems theory

This section will provide a brief introduction to some essential concepts of far-from equilibrium self-organization phenomena occurring in complex nonlinear (chemical) systems. Dynamical systems theory puts emphasis on the kinetic description of nonlinear phenomena where thermodynamics fails to provide a proper theoretical framework. The treatment is intentionally not an in-depth mathematical essay; rather it will focus on only those concepts which will be necessary for a comprehension of subsequent chapters; it will, therefore, remain incomplete. More complete treatments of this subject, especially with respect to chemical systems, can be found in ref. [42, 43, 44, 45, 46].

1.2.1   Temporal self-organization phenomena in chemistry

In the absence of any spatial inhomogeneity the temporal evolution of a chemical dynamical system can be described by coupled ordinary differential equations

$$\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x}, \mathbf{p}), \tag{1.1}$$

where $\mathbf{F}$ represents the set of nonlinear differential equations, the vector $\mathbf{x}$ consists of the individual state variables x_i, and $\mathbf{p}$ denotes the vector of system parameters. The number of state variables n defines the dimension of the phase space, while the parameters form a parameter space. Generally, there are many parameters involved in a nontrivial chemical system, but for practical reasons only a few of them can and will be varied experimentally.

It is useful to be very precise about the usage of the terms parameter and variable. Parameters are quantities which can usually be controlled by the experimenter (constraints). Examples are the externally applied potential U in electrochemistry, temperature, bulk concentrations of certain chemical species or pH etc. Variables, however, are typically time-dependent quantities which are chosen by the system, i.e. by its governing dynamical relations. Examples are the double layer potential ϕ or the electrical current in a potentiostatic experiment, the concentrations of surface species or, in general, of any intermediate. The total current in a galvanostatic experiment, however, changes back into a parameter as it is chosen prior to the experiment. In upcoming chapters, it will be seen that it is in general experimentally feasible to transform parameters into variables and vice versa by appropriately changing the experimental conditions.

Usually for given parameters, the dynamical system under consideration, i.e. the solution (trajectory) of eq. 1.1, autonomously evolves towards a *limit set* as time approaches infinity. In physically meaningful systems, there are always one or more limit sets in phase space exactly one of which is approached depending on the initial values of the variables. Time-independent limit sets, i.e. long-term solutions, are called *fixed points* or stationary states (steady states). It often occurs in complex systems that several steady states coexist in phase space. *Limit cycles* describe periodically oscillating limit sets, i.e. closed curves in phase space. Phenomenologically, oscillations can be characterized as harmonic, when involving smooth sinusoidal changes, or relaxation oscillations which exhibit sharp changes due to two very different time scales. *Mixed-mode oscillations* represent a limit set where two distinct modes of oscillations are periodically interwined: regular large-amplitude relaxation oscillations are interspersed by small-amplitude harmonic oscillations. Usually, experimental mixed-mode data are rarely strictly periodic owing to the narrow parameter ranges of mixed-mode regimes which leads to random jumps of the system trajectory between different mixed-mode states. Finally, the most complex limit set is referred to as *chaotic attractor* which leads to aperiodic trajectories with high sensitivity to initial conditions. Even though the system dynamics appears to be random, the unpredictable chaotic trajectory fulfills the deterministic equations at all times.

Limit sets can only be reached by the system if they are stable in all directions. Here, *stability* of a limit set means that nearby trajectories flow towards the limit set. Equally, the term stability is used for characterizing the current state of a dynamical system sitting on a stable limit set. There, the system shows an insensitivity to small perturbations (fluctuations): if a small perturbation takes the system away from the, for instance, steady state, the system will return to the stable state after the perturbation has died out. Conversely, instability implies that any fluctuation, no matter how small, will make the system leave that state. If there are trajectories in phase space that flow both towards and away from a limit set, this limit set solution is of a saddle-type, e.g. stationary saddles or saddle-orbits. Note that two coexisting stable steady states imply the existence of a third saddle-type state (*bistability*) the unstable direction of which separates the basins of attraction of the stable steady states. Also, in general, *spontaneous oscillations* in a physico-chemical system are related to the fact that a steady state has become unstable and imply its existence somewhere in phase space. Therefore, the question of why stable oscillations occur always involves the question of why a steady state has become unstable. Stability of simple limit sets, such as steady states or limit cycles, can be assessed by a linear stability analysis. This is a standard technique which studies the stability of the evolution equations in the linear neighborhood of a steady state where nonlinear term are negligible. Solving the linearized equations results in the calculations of the eigenvalues of the associated Jacobian matrix ($\frac{\partial \mathbf{F}}{\partial \mathbf{x}}\big|_{ss}$). (Linear) stability is determined by the signs of the eigenvalues: negative eigenvalues imply a damping out of fluctuations, while positive ones represent an exponential growth of perturbations, i.e. instability. According to their eigenvalues, steady states can be classified into nodes (only real eigenvalues) and foci (complex conjugate eigenvalues) which can be either stable or unstable. Similarly, the stability of the stationary intersection of a limit cycle with an
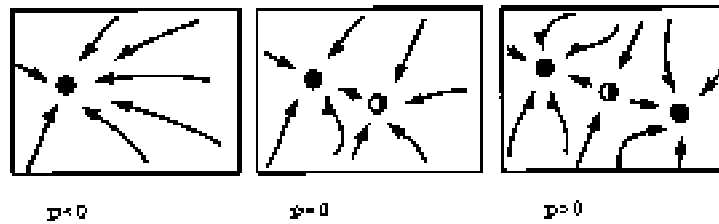
Figure 1-1: Schematic phase portrays near a saddle-node bifurcation at p=0.

$n - 1$ dimensional hyperplane determines the stability of the limit cycle. Since linear stability only looks at the immediate properties near a steady state, it represents the local nature of the trajectories. Global stability analysis, in contrast, requires more sophisticated non-linear stability tests.

Any significant qualitative change of the dynamical behavior of a system upon variation of a parameter is called a *bifurcation* and is caused by changes in stability of the limit set on which the system was sitting. Bifurcation theory seeks to provide a precise formalism in order to describe and predict when a certain bifurcation can occur in a set of differential equations. Bifurcation theory also teaches a lot on the universal and characteristic properties of bifurcations which helps experimentalists identify the occurrence of a certain bifurcation in experiments. Three bifurcations are of particular interest for the spontaneous temporal pattern formation in electrochemical systems. The saddle-node bifurcation and the Hopf bifurcation are both local in nature and can, therefore be identified by local stability analysis, whereas the homoclinic bifurcation represents a global bifurcation of a vector field. The homoclinic bifurcation can further be subdivided into a saddle-loop bifurcation and a saddle-node bifurcation on a limit cycle (SNIPER= saddle-node infinite period).

A *saddle-node bifurcation* is the simplest way of spontaneous temporal self-organization and occurs when one eigenvalue passes through zero. Here, a saddle and a steady state annihilate each other or are created out of the blue. Fig. 1-1 illustrates the characteristic changes in phase space as the parameter p passes through the saddle-node bifurcation at $p = 0$. Where the system will settle after the stable steady state and the saddle have annihilated each other, cannot be extracted be the linear analysis. In practice, however, the system will settle on another steady state or on periodic solutions. This is why this bifurcation is typically encountered at the boundaries of a bistable parameter region: in chemical systems, saddle-node bifurcations come in pairs and lead to S-shaped hysteresis which is observable as a parameter is swept back and forth across the bistable region.

Hopf bifurcations are the origin of spontaneous periodic self-organization. They constitute dynamical scenarios where a focus loses stability and a limit cycle with initially small amplitude is born. Here the real part of a pair of complex conjugate eigenvalues passes through zero. If the Hopf bifurcation is supercritical (soft transition), see Fig. 1-2, the oscillatory state is stable and oscillations will be observed with
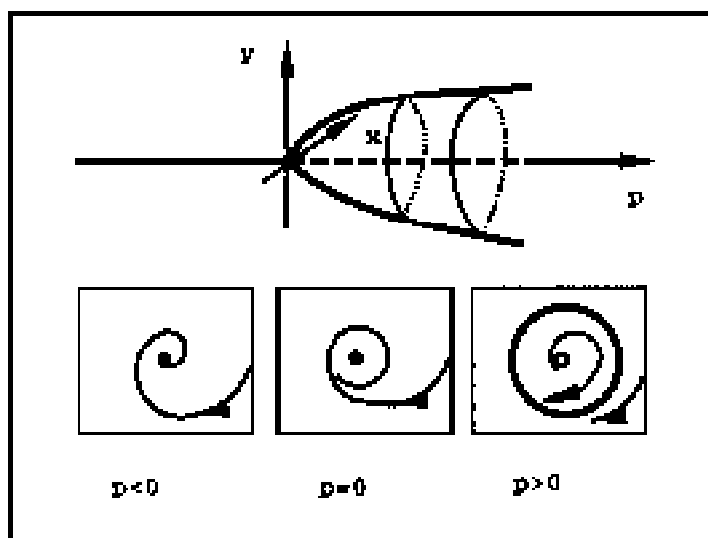
Figure 1-2: Schematic bifurcation diagram and phase space plots near a supercritical Hopf bifurcation.

the amplitude growing gradually as one moves away from the bifurcation point. If the Hopf bifurcation if subcritical (hard transition),see Fig. 1-3, oscillations of immediate finite amplitude may or may not be observed. The supercritical Hopf bifurcation is the most widespread way in which oscillations occur in chemical systems.

A generic homoclinic bifurcation in one parameter is the saddle-loop bifurcation; it appears when a limit cycle collides with a saddle (see Fig. 1-4). Upon collision the outset (unstable manifold) of the saddle is seen to be identical with its inset forming a closed loop called homoclinic orbit. Approaching this bifurcation the period of the oscillations exhibit a typical scaling behavior until it becomes infinite precisely at the bifurcation. In chemical practice, a saddle-loop bifurcation represents a typical way in which oscillatory behavior disappears after being born in a Hopf bifurcation given that bistability and oscillatory behavior coexist.

Finally, Fig. 1-5 illustrates briefly the most common bifurcations of co-dimension two, i.e. points where two or more bifurcations of the type discussed above coincide [42].

1.2.2 Spatial coupling and spatiotemporal patterns

Up to now it has been assumed that there are no spatial inhomogeneities present in the chemical system. In real systems, however, the state variables tend to exhibit some dependence on spatial coordinates due to incomplete rotation, heating etc. of the reaction vessel. Especially in heterogeneous catalysis, no simple way for avoiding
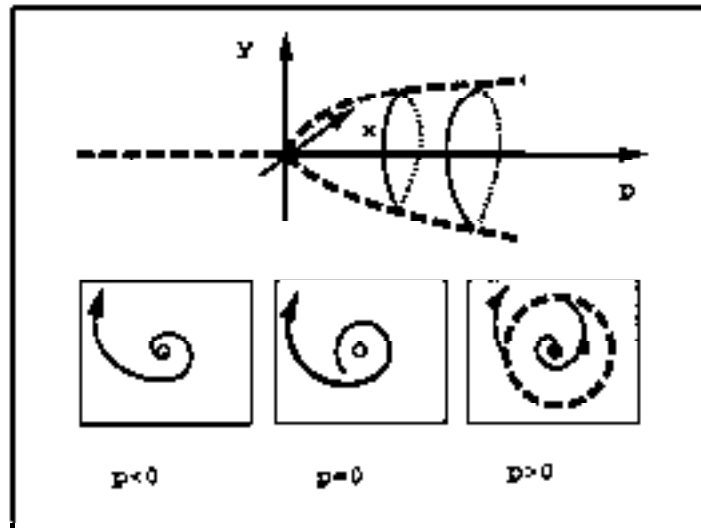
Figure 1-3: Schematic bifurcation diagram and phase space plots near a subcritical Hopf bifurcation.
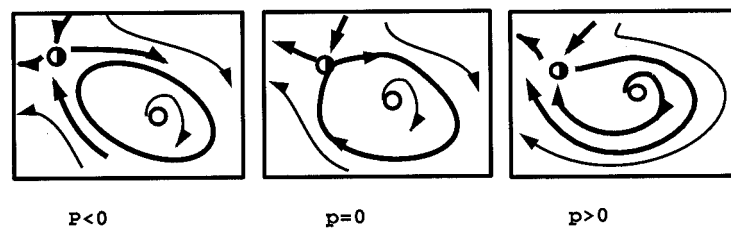

Figure 1-4: Schematic bifurcation diagram and phase space plots near a saddle-loop bifurcation.
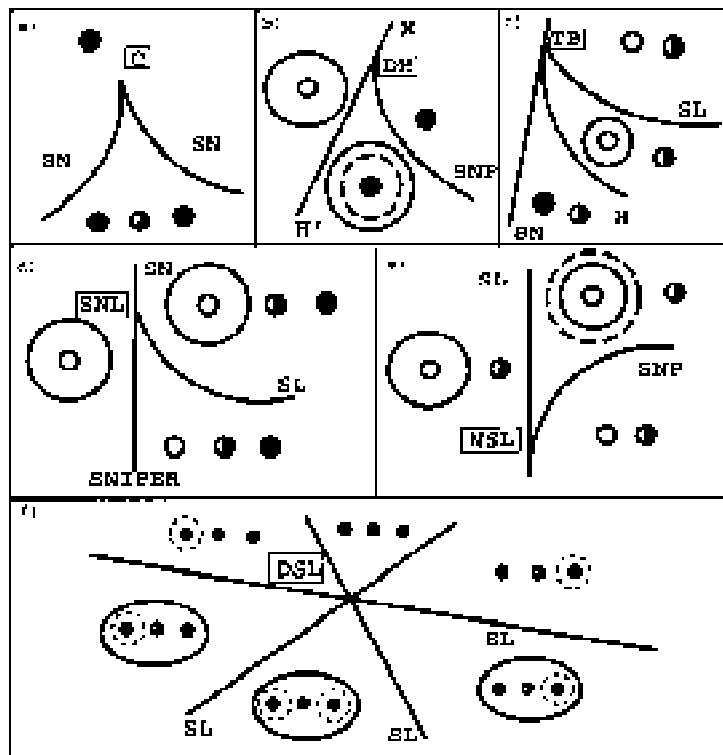
Figure 1-5: Examples of unfoldings of co-dimension 2 bifurcations: a) Cusp C, b) Degenerate Hopf DH, c) Takens-Bogdanov point TB, d) Saddle-node-loop SNL, e) Neutral saddle-loop NSL, f) Double saddle-loop bifurcation DSL (adapted from [47]).

spatial inhomogeneities of surface species exists. Spatial coupling of locally tempo-
ral reaction elements leads to the emergence of spatial patterns in extended systems
ranging from randomly distributed inhomogeneities (spatial fluctuations) to cooper-
atively emerging far-from equilibrium spatiotemporal structures (dissipative spatial
patterns).

Spatial coupling in chemical systems is generally based on gradients in certain
quantities leading to spontaneous transport (flux) of matter or energy; the fluxes
typically try to annihilate the gradients. Thus, depending on the range of the spatial
coupling one could say that neighboring or distant parts of the reactive chemical
system "feel" each other's presence. The most widespread entities transported across
chemical systems are heat due to a temperature gradient (*heat flux*) as well as mass
due to concentrations gradients (*diffusional flux*), velocity fields (*convective transport*)
or in electrochemistry due to potential gradients (*migration flux*).

All these types of coupling are *local couplings* in the sense that each infinitesimally
small location of the extended systems is coupled to the immediate neighboring region
only. It is further assumed that the time scale of the chemical reaction processes is
small ,i.e. fast, compared to the rate of spatial propagation of mass or heat. Following
textbooks [48, 49] one can write the evolution equation for a isothermal set of reactive
chemical species in one space dimension most generally as

$$\frac{\partial}{\partial t}\mathbf{x} = \mathbf{F}(\mathbf{x}, \mathbf{p}) - \operatorname{div}\mathbf{J} \tag{1.2}$$

$$J_i = -D_i\frac{\partial x_i}{\partial z} - \frac{z_i F}{RT}D_i x_i\frac{\partial \varphi}{\partial z} + x_i v_z \tag{1.3}$$

where the term $\mathbf{J}$ includes the spatial fluxes of all species x_i in the z direction, D_i
denotes the diffusion constant, φ the potential inside the electrolyte, v_z the velocity
component in z direction and z_i and F have their usual meaning. In the absence
of convection and migration one recovers the classical *reaction-diffusion equations*
applicable to homogeneous and heterogeneous reaction systems alike [50, 51, 52]

$$\frac{\partial}{\partial t}\mathbf{x} = \mathbf{F}(\mathbf{x}, \mathbf{p}) + \mathbf{D}\,\nabla^2\,\mathbf{x}. \tag{1.4}$$

Depending on the local dynamics and the spatial dimensionality spatiotemporal
patterns such as trigger waves (pulses or fronts), target patterns, spirals, chemical
turbulence etc. are possible solutions. If $\mathbf{F}$ exhibits bistable behavior, the most
common pattern consists of chemical *trigger fronts*, i.e. a moving interface between
domains of different stable steady states. The creation of a trigger front can be
rationalized as follows: Consider a system with an up and a down state. Sitting
initially in the down steady state the bistable system is locally perturbed at some point
to the up state. Subsequently, an interface (double front or circular wave, depending
on the spatial dimensionality) emerges and the up state domain starts invading the
domain of the down state until the entire system is in the up state. The front velocity
is a function of the diffusion constant as well as of the chemical reaction rates and,
therefore, is constant in reaction-diffusion systems at given parameters. The direction
in which the front moves is determined by the relative stability of the two steady

states. Since a one-variable nonlinear system allows the formulation of a kinetic potential, the relative stability is analytically well defined for each parameter value along the hysteresis. If two or more variables are involved, however, the assessment of the relative stability of steady states requires numerical methods. Fronts have been observed and successfully modelled by eq. 1.4 in numerous chemical systems such as catalytic surface reactions under UHV conditions [53, 52] or the Belousov-Zhabotinskii reaction [51]. Note that trigger fronts are transient spatial patterns. Stationary spatiotemporal patterns due to local coupling in eq. 1.4 are possible when certain experimental conditions are fulfilled: Turing structures [54] are characterized by a time-independent, periodic pattern in space, whereas standing waves [55] exhibit periodic behavior in space and time with one or more points along the system at rest (wave nodes). The number of locally coupled experimental systems exhibiting such structures is still rather limited [51, 53, 52].

In contrast to local coupling, nonlocal coupling implies that every location of the extended chemical system can immediately "feel" even remote changes in the reactive system. The strength with which remote events are influencing the local dynamics may vary with distance (global versus nonlocal coupling). Chemical nonlocality is often related to the small ratio of the time scales of chemical kinetics and spatial transport processes what makes perturbations appear immediately at a distant location. Thus, even a sufficiently rapid diffusion can in principal lead to a quai-nonlocal effect. Still, certain physical entities tend to be naturally transported on a time scale faster than chemical reaction kinetics and, therefore, can be considered as non-locally operating couplings. Nonlocal coupling can arise inherently in experimental reaction-diffusion systems when certain experimental conditions are applied. In surface reactions under UHV conditions a global mass coupling across the gas phase may be present for small pump rates as well as well-mixed gas phases, as local adsorption changes the partial pressure of the gaseous reactants immediately across the entire isothermal catalyst [52]. Moreover, in thermokinetic catalytic surface reactions involving an electrical heating of the catalyst implies a global coupling of the current, as any local change of the reaction rate leads to changes in the local electrical resistance and, in turn, immediately is followed by changes in the total current across the catalyst [56, 57, 58, 59]. In the latter system the presence of a negative nonlocal or global coupling across the systems resulted in the emergence of stationary spatiotemporal patterns such as standing fronts.

In general, stationary spatial patterns are easily obtained in reaction-diffusion systems when a negative long-range interaction is operating across the system. For nonlocal couplings, however, qualitatively new behavior can be expected.

1.3 Scope and outline of this thesis

The overriding objective of the present thesis is the contribution to our understanding of spontaneous self-organization phenomena in electrochemistry with an emphasis on electrocatalytic systems. The thesis deals with the experimental and theoretical investigation of certain self-organizing electrochemical reactions under far-from-equilibrium conditions in order to achieve a mechanistic understanding by means of

the conceptual machinery of Nonlinear Dynamics. In so doing, the present thesis seeks to give answers to several of the open problems in electrochemistry:

- Mechanistic analysis and clarification of temporal oscillatory self-organization in a number of electrocatalytic reactions is achieved using experiments and kinetic modeling,

- Spatiotemporal patterns in a complex electrocatalytic electrode process are investigated by means of an electrochemical imaging technique placing special emphasis on the clarification of the nature of the spatial coupling.

- A unifying categorization scheme for electrochemical oscillators is suggested including all relevant mechanistic information known so far. In addition, an operational procedure for a systematic classification of an unknown oscillator is provided.

The detailed outline of the thesis is as follows:

Chapter 2 and 3 cover the basic conceptual notions of the electrochemical interface and the general experimental details of methods applied in upcoming chapters.

The oscillatory electrocatalytic oxidation of formic acid on Pt single crystals is the primary subject of chapters 4 and 5. In chapter 4, the experimental characterization of temporal oscillatory regimes found on all three low-indexed Pt single crystals (100), (110) and (111) is reported. Chapter 5 deals with the development of a detailed kinetic model for the formic acid oxidation and gives exhaustive account of the mechanistic origin of the oscillations.

The experimental and theoretical investigation and mechanistic clarification of another class of oscillatory electrocatalytic reactions - the reduction of IO_3^- anions and related systems - is described in chapter 8.

Intriguing spatiotemporal patterns on polycrystalline Pt electrodes during the formic acid oxidation system are the subject of chapter 6. Here, the parameter dependence as well as the underlying spatial coupling of the spatial structures are examined

Chapters 7 and 9 focus on a general mechanistic classification of electrochemical oscillators. While chapter 7 stresses the leverage of feedback control methods for the purpose of a classifying distinction between oscillators exemplified in the experimental H_2 oxidation system, chapter 9 gives a detailed account of all relevant mechanistic categories of electrochemical oscillators and their experimental features along side with a practical experimental classification procedure.

Finally, chapters 10 and 11 conclude this thesis summarizing its important elements.