

**Slow Invariant Manifold  
and its approximations  
in kinetics of catalytic reactions**

Department of Mathematics

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presented by

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**To my  
Mother and  
Memories of my Father.**

*All praises for almighty **Allah**, the most beneficial, compassionate, the creator of the universe who blessed me with the knowledge and enabled me to complete this research work, without the blessing of whom, I could not be able to complete all my work and to be at such a place.*

*All respect to holy prophet **Muhammad** (PBUH), who appeared and blossomed as model for whole humanity.*

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# Abstract

Equations of chemical kinetics typically include several distinct time scales. There exist many methods which allow to exclude fast variables and reduce equations to the slow manifold. In this thesis, we start by studying the background of the quasi equilibrium approximation, main approaches to this approximation, its consequences and other related topics.

We present the general formalism of the quasi equilibrium (QE) approximation with the proof of the persistence of entropy production in the QE approximation. We demonstrate how to apply this formalism to chemical kinetics and describe the difference between QE and quasi steady state (QSS) approximations. In 1913 Michaelis and Menten used the QE assumption that all intermediate complexes are in fast equilibrium with free substrates and enzymes. Similar approach was developed by Stuekelberg (1952) for the Boltzmann kinetics. Following them, we combine the QE (fast equilibria) and the QSS (small amounts) approaches and study the general kinetics with fast intermediates present in small amounts. We prove the representation of the rate of an elementary reaction as a product of the Boltzmann factor (purely thermodynamic) and the kinetic factor, and find the basic relations between kinetic factors. In the practice of modeling, a kinetic model may initially not respect thermodynamic conditions. For these cases, we solved a problem: is it possible to **deform (linearly) the entropy** and provide agreement with the given kinetic model and deformed thermodynamics ?

We demonstrate how to modify the QE approximation for **stiffness removal** in an example of the CO oxidation on Pt. QSSA was applied in order to get an approximation to the **One dimensional Invariant Grid** for oxidation of CO over Pt. The method of **intrinsic low dimension manifold (ILDm)** was implemented over the same example (CO oxidation on Pt) in order to automate the process of reduction and provide more accurate simplified mechanism (for one-dimension), yet at the cost of a significantly more complicated implementation.

## CHAPTER 1

# Thesis Outline

In this thesis, we discuss in detail the application of the quasiequilibrium (QE) and quasi steady state (QSS) approximation in physical and chemical kinetics with exposition of some new results.

### Structure of the Thesis

The thesis is organized as follows:

- **Chapter 2**

The main ideas of slow (positively) invariant manifold (SIM), invariance equation, invariant grid and thermodynamic projector are reviewed. Relevant properties of the thermodynamic projector are discussed and the method of invariant grid (MIG) illustrated in the form of the Newton method with incomplete linearization. Considering an example of the Michaelis Menten mechanism various approximations of one-dimensional reduced description are constructed and refined by the Newton method.

We start with the formal description of the general idea of QE and its possible extensions. In Section 2.3, we briefly introduce main notations and some general formulas for exclusion of fast variables by the QE approximation.

Section 2.6 clears the idea of QE and QSSA and describes these approximations for general kinetic systems.

Roughly speaking, this approximation states that any reaction goes through

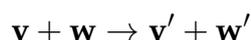
the transformation of fast intermediate complexes (compounds), which have two important properties:

- They are equilibrium with the correspondent input reagents.
- They exist in a very small amount compared to other components.

One of the most important benefits from this approach is the exclusion of kinetics of compounds production: they are in fast equilibrium and equilibrium is ruled by thermodynamics. For example, when Michaelis and Menten discussed the production of the enzyme–substrate complex  $ES$  from enzyme  $E$  and substrate  $S$ , they did not discuss reaction rates. These rates may be unknown. They just assume that the reaction  $E+S\rightleftharpoons ES$  is in equilibrium. Briggs and Haldane included this reaction into a kinetic model. This approach is more general but for this new model we need more information, not only equilibrium of  $E + S \rightleftharpoons ES$  but also reaction rates and constants.

Transformation of compounds is a linear first order kinetics, there is no need to include interactions between them because they are present in very small amounts in the same volume, and their concentrations are also small. (By the way, this argument is not always applicable to the heterogeneous catalytic reactions, because the intermediates there are in small amounts but in a small volume as well, i.e. in the surface layer. The concentration of intermediates in this volume is not small, and their interaction does not vanish when their amount decreases [70]. Therefore, kinetics of intermediates in heterogeneous catalysis may be nonlinear and demonstrate bifurcations, oscillations and other complex behavior.)

In 1952, Stückelberg [59] used similar approach in his seminal paper "*H*-theorem and unitarity of the *S*-matrix". He studied elastic collisions of particles as the quasi-chemical reactions



( $\mathbf{v}, \mathbf{w}, \mathbf{v}', \mathbf{w}'$  are velocities of particles) and demonstrated that for the Boltzmann equation the linear Markov kinetics of the intermediate compounds results in the special relations for the kinetic coefficients. These relations are sufficient for the *H* theorem.

- **Chapter 3**

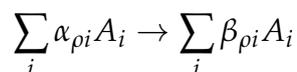
Here we discuss the general idea of elementary reactions, stoichiometry of the reaction, mass action law, principle of detail balance and thermodynamic Lyapunov functions, to measure the behavior of chemical species and model reduction (discussed in next chapters). The classical formulation of the principle of detailed balance deals not with the thermodynamic and global forms we use but just with equilibria: in equilibrium each process must be equilibrated with its reverse process as explained it in next chapter.

- **Chapter 4**

We present the role of thermodynamics, entropy maximum, stoichiometry of complex's and compounds, relations between the kinetic factors and how to recover them during the entropy deformation. Later, these relations for the chemical mass action kinetics were called the *complex balance conditions* [25, 50]. Also we generalize the Michaelis–Menten–Stückelberg approach and study (Section 4.1) the general kinetics with fast intermediates present in small amount.

The result of the general kinetics of systems with intermediate compounds can be used wider than this specific model of elementary reactions: the intermediate complexes with fast equilibria and the Markov kinetics can be considered as the "construction staging" for general kinetics. In Section 4.2, we delete this construction staging and start from the general forms of the obtained kinetic equations as from the basic laws.

For each reaction



a nonnegative quantity, reaction rate  $r_\rho$  is defined. It consists of two factors (4.2.2), the kinetic factor  $\varphi_\rho > 0$  and the Boltzmann factor  $\exp(\alpha_\rho, \check{\mu})$ :

$$r_\rho = \varphi_\rho \exp(\alpha_\rho, \check{\mu}),$$

where  $(\alpha_\rho, \check{\mu}) = \sum_i \alpha_{\rho i} \check{\mu}_i$  and  $\check{\mu}_i$  are (minus) partial derivatives of the Kulback–Leubler entropy (i.e. chemical potentials  $\mu$  w.r.t concentration divided on  $RT$ ).

We study relation between these forms and thermodynamics. For example, two identities guarantee the entropy growth: the detailed balance (4.2.15)

$$\varphi_{\rho}^{+} = \varphi_{\rho}^{-}$$

for all  $\rho$  and the complex balance conditions (4.2.17),

$$\sum_{\rho} \varphi_{\rho} \exp(\check{\mu}, \alpha_{\rho}) = \sum_{\rho} \varphi_{\rho} \exp(\check{\mu}, \beta_{\rho})$$

for all admissible values of  $\check{\mu}$  and given  $\varphi_{\rho}$  which may vary independently.

The Boltzmann factors  $\exp(\mu, \nu)$  are independent for any set of different vectors  $\nu$ . Therefore, we can collect all terms with the same Boltzmann factors together and simplify this condition (4.2.18).

We also develop another, less restrictive sufficient conditions for accordance between thermodynamics and kinetics. For example, we demonstrate that the  $G$ -inequality

$$\sum_{\rho} \varphi_{\rho} \exp(\check{\mu}, \alpha_{\rho}) \geq \sum_{\rho} \varphi_{\rho} \exp(\check{\mu}, \beta_{\rho})$$

is sufficient for the entropy growth and, at the same time, weaker than the condition of complex balance.

Sometimes the kinetic equations may not respect thermodynamics from the beginning. To repair this discrepancy, deformation of the entropy may help. In Section 4.3 we solved the problem: when is it possible to deform the entropy by adding a linear function in order to provide agreement between given kinetic equations and the deformed thermodynamics? As a particular case, we obtain the "deficiency zero theorem" [50].

Section 4.3 confirms that for the general kinetic law the existence of a point of detailed balance is equivalent to the existence of such linear deformation of the entropy that the global conditions (4.2.15) hold. Analogously, the existence of a point of complex balance is equivalent to the global condition of complex balance after some linear deformation of the entropy.

- Chapter 5

Stiffness of equations often causes more problems than the large dimension of the space. The formalism of the QE approximation with all the necessary notations and examples for chemical kinetics is presented in Section 5.2. In Section 5.3 we reformulate the aim of the QE approximation. It can be used for removing the stiffness from the kinetic equations instead of model reduction.

We develop the general formalism and give an example of its application to the catalytic oxidation reaction.

We apply the methods of QE and QSS to a chemical kinetics (CO oxidation over Pt) and construct an approximated one-dimension invariant manifold. Using different parameters for testing and considering higher dimensional cases.

- **Chapter 6**

Here we apply an Intrinsic Low-Dimensional Manifold (ILDm) over the same system CO oxidation over Pt and obtain a slow trajectory of one-dimensional ILDM. Comparison between different methods of model reduction are given along with stiffness measures. In contrast to the above reduction methods i.e QSSA and partial equilibrium assumptions, the ILDM method (introduced by Maas and Pope) automatically reduces the reaction mechanisms.

- **Chapter 7**

We conclude with the overview of our results and literature review. Further generalization, its implementation of the methods are discussed.

## CHAPTER 1. THESIS OUTLINE

A part of our work has been published as an e-print and submitted for the publication.

- Gorban A.N, Shahzad M, QE+QSS for Derivation of Kinetic Equations and Stiffness Removing, arXiv:1008.3296v1 [physics.chem-ph],2010.

<http://arxiv.org/abs/1008.3296>

- Gorban A.N, Shahzad M, The Michaelis-Menten-Stueckelberg Theorem, submitted to Entropy (January 20, 2011) for open access under the terms and conditions of the Creative Commons Attribution license

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# Slow Invariant Manifold for Kinetic Equations

In kinetic theory the idea of slow invariant manifold is considered as a cornerstone for the discussion of micro to macro model reduction. In the physical and in chemical problems, the problem of reduced description is considered as the problem of constructing a Slow Invariant Manifold (SIM) for it.

The dissipative dynamical system whether finite or infinite dimensional arises in many kinetics problems. Here we consider some methods and their application, which are useful not only for dissipative systems but also for conservative systems. Non-equilibrium statistical physics gives a number of ideas and methods how to construct the slow invariant manifold. There exist a number of methods used to compute the slow invariant manifold but those considered to be better approximations are discussed in detail. To make understanding of the idea clearer it is implemented on a simple example with a setting of several parameters [2.8.1](#).

## 2.1 Slow Invariant Manifold

In chemical kinetics, dissipative reaction while solving with respect to fast and slow motion their solution trajectories in a phase space move fast toward the lower dimensional manifold during the relaxation and after reaching a small vicinity of this manifold they move slowly along it (Figure [2.1](#)). We call such a manifold SIM.

It is not difficult to find a slow manifold for the two variables in the ODE model of a chemical reactions with a single equilibrium point, where the slow manifold is a unique trajectory corresponding to slow relaxation of the system towards the equilibrium point. More than two variables make the system complex and need special approach (as in the case of fast relaxation of the intermediate in a chemical reactions).

There exist several methods used to calculate SIM

- Method of Invariant Manifolds (MIM) gives iterative process for SIM approximation.
- Method of Invariant Grids (MIG) gives iterative process for construction of discrete approximation of SIM.
- Computational Singular Perturbation (CSP) gives iterative process for approximation of SIM and fast foliation.
- Intrinsic Low Dimensional Manifold (ILDm) gives promising first-order approximation of SIM.

These methods are discussed in detail in [57]. Various methods can be used to construct the SIM at non-trivial test-case [22], the most common of them are essentially different iterative algorithms:

- MIG-approach (based on the Newton method), ([54],[55],[57]);
- MIG-approach (based on the relaxation method), ([54],[55],[57])
- CSP-approach ([61],[20]).

Each iterative procedure starts from an initial approximation that can be refined through an iteration towards the solution. For that purpose one can take different **initial approximations methods** :

- Quasi-Equilibrium-Manifold (QEM), ([54],[55]),
- Spectral-Quasi-Equilibrium-Manifold (SQEM),
- Intrinsic-Low-Dimensional-Manifold (ILDm) ([65],[67]),
- Symmetric-Entropic-Intrinsic-Low-Dimensional-Manifold (SEILDm)([54], [55]).

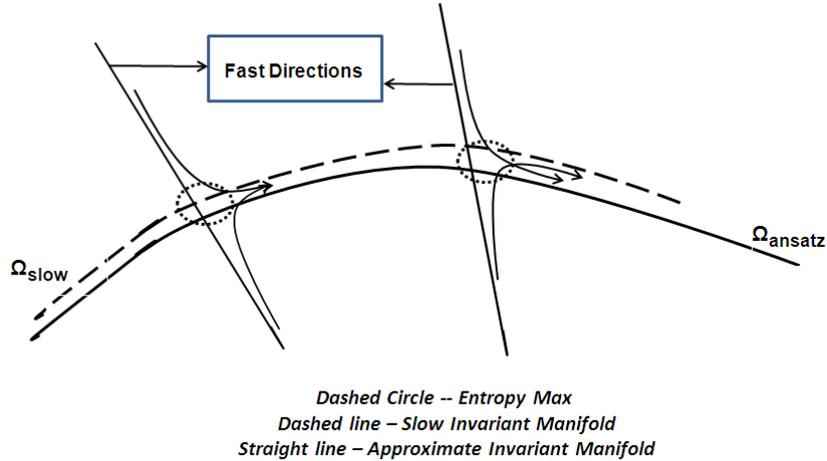


Figure 2.1: Decomposition of motion into Fast-slow trajectories.

## 2.2 SIM for kinetics

Let  $\Omega_{slow}$  be the slow manifold such that trajectories of the system starting at different initial condition converge to a small neighborhood of the manifold(ansatz) and after that start to move along it. It is said to be a positive invariant manifold if the trajectories starting on it never leave the manifold for all  $t > t_0$ , the fast motion can also be define in a neighborhood of the slow manifold. Thermodynamics is useful for the model reduction in dissipative system. The idea behind its application is [57] that during the fast motion the entropy (or the correspondent *free entropy*, if the system is not isolated) should increase, hence, the point of entropy maximum on the plane of rapid motion is not far from the slow manifold, in the area where fast and slow motion have comparable velocities (Figure 2.1, inside dashed circles). This implies that differential of the entropy at points near the slow manifold almost annuls the planes of fast motions (i.e. entropy gradient is almost orthogonal to these planes) discuss in detail in Chapter 4. For sufficiently strong fast-slow time separation the fast invariant subspace of a Jacobian near the slow manifold approximates the plane of fast motions, hence, this invariant subspace is also nearly orthogonal to the entropy gradient.

The idea of the fast and slow decomposition becomes more clear by considering its motion toward and along the manifold in which fast construction is selected in the transversal directions (in directions of projector kernel) and relatively slow change of vector field tangent component along manifold. In our

case, the slow invariant manifold is a stable fixed point which can be calculated by the following processes:

If the **Newton method with incomplete linearization** converge the initial approximation, then it leads to the slow manifold in the usual sense, while the standard Newton method does not. (This is very convenient because the standard method is also much more complicated). For sufficiently strong fast-slow time separation, most of the numerous definitions of the slow invariant manifold give the same result (exactly the same, or up to higher order terms, depending on the required regularity of the manifolds).

There is another iterative procedure, **relaxation method** using to a film extension of dynamics [57], that is defined by the equation for immersed manifold motion

$F : W \rightarrow D, F(W) = \Omega$  with velocity  $J_{\perp}(c)$ , where  $J(c) = J_{\perp}(c) + J_{\parallel}(c)$ :

$$\frac{dF(y)}{dt} = (1 - P)J \quad (2.2.1)$$

If we are able to approximate the slow invariant manifold  $\Omega_{slow}$  then the slow reduced system is the system on the manifold  $\Omega$  defined by the projected vector space

$$\dot{c} = PJ(c), \quad (2.2.2)$$

Where  $c \in \Omega$  and projector  $P : R^n \rightarrow T_c\Omega$  depends both on the point  $c$  and on the tangent space  $T_c\Omega$ . Because  $F$  is immersion, differential of  $F(y)$ ,  $DF(y)$ , is reversible on its image,  $TF(y)(\Omega)$ . Hence, reduced system ( 2.2.2) defines dynamics in the parameter space:

$$\dot{y} = (DF(y))^{-1}(PJ(F(y))). \quad (2.2.3)$$

### 2.2.1 Chemical Kinetics

In this Section, we introduce the basic notations of the chemical kinetics formalism. For more details see, for example, [70].

The list of components is a finite set of symbols  $A_1, \dots, A_n$ .

A reaction mechanism is a finite set of *stoichiometric equations* of elementary

reactions:



where  $\rho = 1, \dots, m$  is the reaction number and the *stoichiometric coefficients*  $\alpha_{\rho i}, \beta_{\rho i}$  are nonnegative integers.

A *stoichiometric vector*  $\gamma_\rho$  of the reaction (2.2.4) is a  $n$ -dimensional vector with coordinates

$$\gamma_{\rho i} = \beta_{\rho i} - \alpha_{\rho i}, \quad (2.2.5)$$

that is, 'gain minus loss' in the  $\rho$ th elementary reaction.

A nonnegative extensive variable  $N_i$ , the amount of  $A_i$ , corresponds to each component. We call the vector  $N$  with coordinates  $N_i$  'the composition vector'. The concentration of  $A_i$  is an intensive variable  $c_i = N_i/V$ , where  $V > 0$  is the volume, the vector  $c = N/V$  with coordinates  $c_i$  is the vector of concentrations.

A non-negative intensive quantity,  $r_\rho$ , (or  $W_\rho$ ), the reaction rate, corresponds to each reaction (2.2.4). The kinetic equations in the absence of external fluxes are

$$\begin{aligned} \frac{dN}{dt} &= V \sum_\rho r_\rho \gamma_\rho, \quad \text{or} \\ \dot{N} &= VJ(c), \quad J(c) = \sum_\rho \gamma_\rho W_\rho(c). \end{aligned} \quad (2.2.6)$$

If the volume is not constant then equations for concentrations include  $\dot{V}$  and have different form (this is typical for the combustion reactions, for example).

How can we find the reaction rates? For perfect systems and not very fast reactions the reaction rates are functions of concentrations and temperature given by the *mass action law* for the dependence on concentrations and by the generalized Arrhenius equation for the dependence on temperature  $T$ .

The mass action law:

$$r_\rho(c, T) = k_\rho(T) \prod_i c_i^{\alpha_{\rho i}}, \quad (2.2.7)$$

where  $k_\rho(T)$  is the reaction rate constant.

The generalized Arrhenius equation:

$$k_\rho(T) = A_\rho \left( \frac{T}{T_0} \right)^{\frac{S_{a\rho}}{R}} \exp \left( -\frac{E_{a\rho}}{RT} \right), \quad (2.2.8)$$

where  $R = 8.314472 \frac{\text{J}}{\text{K mol}}$  is the universal, or ideal gas constant,  $E_{a\rho}$  is the activation energy,  $S_{a\rho}$  is the activation entropy (i.e.  $E_{a\rho} - TS_{a\rho}$  is the activation free energy),  $A_\rho$  is the constant pre-exponential factor. Some authors neglect the  $S_{a\rho}$  term because it may be less important than the activation energy but it is necessary to stress that without this term it may be impossible to reconcile the kinetic equations with the classical thermodynamics.

In general, the constants for different reactions are not independent. They are connected by various conditions that follow from thermodynamics (the second law, the entropy growth for isolated systems) or microreversibility assumption (the detailed balance and the Onsager reciprocal relations). In Section 4.2.2 we discuss these conditions in more general settings.

For nonideal systems, a more general kinetic law is needed. In Section 4.1 we produce such a general law following the ideas of the original Michaelis and Menten paper (this is not the same as the famous "Michaelis–Menten kinetics"). For this work we need a general formalism of QE approximation for chemical kinetics. The principle of detailed balance gives a relation between these quantities:

$$W_\rho^+(c^{eq}) = W_\rho^-(c^{eq}), \quad \rho = 1\dots m. \quad (2.2.9)$$

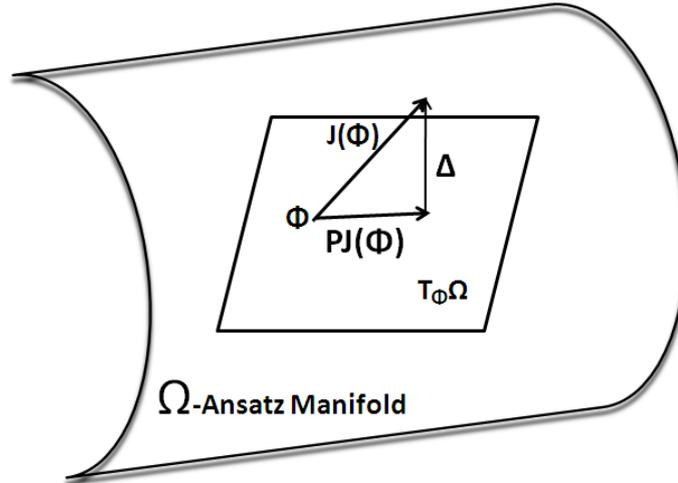
Where the positive vector  $c^{eq}(T)$  is the equilibrium of the system ( 2.2.6). In order to obtain a closed system of equations, one should supply an equation for the volume  $V$ . For an isolated system the extra-equations are  $U, V = \text{const}$  (where  $U$  is the internal energy), for an isochoric isothermal system we get  $V, T = \text{const}$ , and so forth. For example, Eq.( 2.2.6) in the latter case simply takes the form:

$$\dot{c} = \sum_\rho \gamma_\rho W_\rho(c) = J(c). \quad (2.2.10)$$

Finally, also other linear constraints, related to the conservation of atoms, must be considered. In general, such conservation laws can have the following form:

$$Dc = \text{Const.}, \quad (2.2.11)$$

Where  $l$  fixed and linearly independent vectors  $d_i$  are the rows of the  $l \times n$  matrix  $D$ , and  $\text{Const}$  is a constant vector. Once the thermodynamic features of the system have been defined, equations ( 2.2.6) and ( 2.2.11) constitute the kind



**Figure 2.2:**  $\Phi'(t) = J(\Phi)$ ,  $PJ(\Phi)$  is the projection of the vector  $J(\Phi)$  onto tangent space  $T_\Phi$ , in order to measure the defect of invariance  $\Delta = (1 - P)J(\Phi)$ .

of dissipative systems which we are interested in.

## 2.2.2 Invariant Manifold and Condition of Invariance

A manifold is said to be invariant in a phase space under some flow, if orbits that start out in the manifold remain in it. The phase space of many dynamical systems has embedded in them invariant manifolds whose dimensions are smaller than the dimensions of the entire phase space. Let us consider a general system of autonomous ordinary differential equations in a domain  $D$

$$\dot{c} = J(c). \quad (2.2.12)$$

For the above system a sub manifold  $\Omega \subset D$  is a positively invariant manifold if, for any solution  $c(t)$ , inclusion  $c(t_0) \in \Omega$  implies that  $c(t) \in \Omega$  for  $t > t_0$ . Such a set  $\Omega$  is an invariant manifold. If  $T_c\Omega$  is a tangent space at a point  $c$ , then gives a necessary differential condition of invariance.

$$J(c) \in T_c\Omega. \quad (2.2.13)$$

To transform the condition into an equation, split the  $J(c)$  into two component and proceed as follow:

- take a complement to  $T_c$  in  $R^n$ ,  $R^n = T_c \oplus E_c$ ,
- split  $J(c)$  into two components:  $J(c) = J_{\perp}(c) + J_{\parallel}(c)$ ,  
 $J_{\perp}(c) \in E_c$ ,  $J_{\parallel}(c) \in T_c$ .
- write down an equation,  $J_{\perp}(c) = 0$ .

Operator  $P$  called thermodynamic projector, clearly define this operation. If a projector  $P$  on  $T_c$  is defined with image  $imP = T_c$  and kernel  $kerP = E_c$ , then the differential condition of invariance will become

$$(1 - P)J = 0. \quad (2.2.14)$$

The component  $J_{\perp}$  represents the defect of invariance :  $J_{\perp} = (1 - P)J = \Delta$ . In the invariance equation ( 2.2.14) an unknown is the manifold  $\Omega$ . This manifold has to be represented in a parametric form, as an immersion  $F : W \rightarrow D$  of a domain  $W$  in the parameter space into the domain  $D$ ;  $\Omega$  is the image of this immersion:  $\Omega = F(W)$ . There exists a natural method for projector field  $P$  construction, if for any  $c$  a positive definite inner product  $\langle x, y \rangle_c$  (a Riemannian structure) is defined, then we can choose  $P$  as  $\langle , \rangle_c$ -orthogonal projector, and  $J(c) = J_{\perp}(c) + J_{\parallel}(c)$  is h, orthogonal splitting. Careful analysis shows that this idea is absolutely right and after some changes leads to the thermodynamic projector [[53], [4]]. The relevant Riemannian structure is generated by the second differential of the entropy. In a majority of applications, we are looking not for an approximation to an invariant manifold that definitely exists, but rather for an approximate invariant manifold with sufficiently small defect of invariance ( $\|\Delta\| \ll \|J\|$ , for example). When the manifold is not invariant, it is not able to satisfy the invariance condition so that

$$c_o : \Delta = [1 - P]J(c_o) \neq 0, \quad (2.2.15)$$

where  $\Delta$  is the defect of invariance

### 2.2.3 Thermodynamic Potential and Thermodynamic Projector

Due to the dissipative property of our system, it has a thermodynamic potential which is the Lyapunov function, and this function implements the 2nd law

of thermodynamics: This means that during the motion from the initial to the equilibrium state, the Lyapunov function must decrease monotonically. So if  $G(c)$  is the Lyapunov function,  $c^{eq}$  (equilibrium state) is its point of global minimum in the phase space. A simple example of a function  $G$  is given by the free energy of perfect gas in a constant volume and at a constant temperature[22]:

$$G = \sum_{i=1}^n c_i [\ln(c_i/c_i^{eq}) - 1]. \quad (2.2.16)$$

When the function  $G$  is known, also its gradient  $\nabla G$  and the second derivatives matrix, where

$$H = |\partial^2 G / \partial c_i \partial c_j| \quad (2.2.17)$$

so we introduce the thermodynamic scalar product as follows:

$$\langle x, y \rangle = (x, Hy), \quad (2.2.18)$$

where  $(, )$  implies Euclidean scalar product. Thermodynamic projector is an operator which projects the vector field at each point of the manifold into the tangent space to give the induced vector field  $PJ(c)$  [53]. Now a differential of  $G$ , is a linear functional

$$DG(x) = (\nabla G(c), x). \quad (2.2.19)$$

The induced vector field respects the dissipation inequality:

$$DG(PJ) \leq 0, \quad \text{for all } c \in \Omega. \quad (2.2.20)$$

Where the projector  $P$  respects the above condition if and only if :

$$\ker(P) \subset \ker(DG), \quad \text{for all } c \in \Omega \quad (2.2.21)$$

where  $\ker$  denotes the null space of an operator. The thermodynamic projector is also important to induce the dynamics on a given manifold and in constructing corrections, where the projector participating in the invariance condition is arbitrary. It is convenient to make use of this point where the thermodynamic projector, which is also used in MIG procedure, depends on the concentration point  $c$  and on the tangent space to the manifold  $\Omega$ . After a reduced description form our SIM will be a  $q$ -dimensional SIM. Let  $\mathbf{g}$  be a discrete subset of  $q$

dimensional parameter space and let  $F|_{\mathbf{g}}$  be a mapping of  $\mathbf{g}$  into the concentration space. If we select an approximation procedure to restore the smooth map  $F$  from the discrete map  $F|_{\mathbf{g}}$  (we need a very small part of  $F$ , derivatives of  $F$  at the grid points only), then the derivatives  $f_i = \partial F / \partial y_i$  are available, and for each grid point the tangent space is:

$$T_y = \text{Lin}(f_i), \quad i = 1 \cdots n. \quad (2.2.22)$$

We assume that one of the points,  $y \in \mathbf{g}$ , maps into equilibrium, and at other points intersection of the manifold with  $G$  levels is transversal (i.e.  $(DG)_{F(y)}(x) \neq 0$  for some  $x \in T_y$ ). Let us consider the subspace  $T_{0y} = T_y \cap \ker(DG)$ . In order to define the thermodynamic projector it is required, if  $T_{0y} \neq T_y$ , to introduce the vector  $e_y$  which satisfies the following conditions

$$e_y \in T_y, \quad \langle e_y, x \rangle = 0 \quad \text{for all } x \in T_{0y} \quad DG(e_y) = 1. \quad (2.2.23)$$

Let  $P_0$  be the orthogonal projector on  $T_{0y}$  with respect to the entropic scalar product (2.2.18), then the thermodynamic projection of vector  $x$  is defined as:

$$\begin{aligned} T_{0y} \neq T_y &\Rightarrow P_x + P_{0x} + e_y DG(x) \\ T_{0y} = T_y &\Rightarrow P_x + P_{0x} \end{aligned} \quad (2.2.24)$$

## 2.2.4 Newton method with incomplete linearization

There are several methods used to approximate the slow invariant manifolds. The Newton method with incomplete linearization is one of them which is an efficient method for the invariance equation. It is the basis of an iterative construction of the manifolds of slow motions. We will try to obtain such a manifold through the MIG method whose defect of invariance is small and, if  $\Omega$  is such a manifold, then initially  $\Omega_0$  it can not satisfy the invariance equation. Due to that reason we can change its position from  $c_0$  of  $\Omega_0$  to a new position  $(c_0 + \delta c)$  with a lower defect of invariance  $\Delta = [1 - P](c_0 + \delta c)$ . If the initial node is 'not far' from the invariant manifold, a reasonable way to get the node correction  $\delta c$  is to solve the linearized invariance equation for which the vector field  $J$

is expanded to the first order and the projector  $P$  to the zeroth order

$$[1 - P(c)][J(c) + L(c)\delta c] = 0. \quad (2.2.25)$$

Where  $L$  (Jacobian matrix) is the matrix of first derivatives of  $J$  and the Newton method with in-complete linearization consists of Eq.( 2.2.25) supplied by the extra condition [53]:

$$P\delta c = 0. \quad (2.2.26)$$

The additional condition ( 2.2.26) and the atoms balances ( 2.2.11) automatically can be taken into account choosing a basis  $b_i$  in the subspace  $S = (\ker P \cap \ker D)$ . Let  $h = \dim(S)$ , then the correction can be cast in the form  $\delta c = \sum_{i=1}^h \delta_i b_i$ , so that the linearized invariance equation ( 2.2.25) becomes the linear algebraic system in terms of  $\delta_i$ :

$$\sum_{i=1}^h \delta_i \langle (1 - P)Lb_i, b_k \rangle = -\langle (1 - P)J, b_k \rangle \quad k = 1, \dots, h \quad (2.2.27)$$

In the case of the thermodynamic projector, it proves convenient to choose the basis  $b_i$  orthonormal with respect to the entropic scalar product ( 2.2.16) and write the ( 2.2.27) as

$$\sum_{i=1}^h \delta_i \langle (1 - P)Lb_i, b_k \rangle = -\langle (1 - P)J, b_k \rangle \quad k = 1, \dots, h \quad (2.2.28)$$

The projector ( 2.2.22) is "almost"  $\langle , \rangle$ -orthogonal ( $\langle imP, \ker P \rangle \cong 0$ ) close to the SIM Because of that special feature, Eq( 2.2.28) can be approximated and simplified as follows:

$$\sum_{i=1}^h \delta_i \langle Lb_i, b_k \rangle = -\langle J, b_k \rangle \quad k = 1, \dots, h \quad (2.2.29)$$

The refinement carried out by Eq. ( 2.2.29) leaves a residual defect ( 2.2.15) in the grid nodes which cannot be annihilated even if we continue to refine it through iteration. Therefore, when a higher accuracy in the SIM description is required, Eq.( 2.2.27) is recommended.

## 2.3 Quasi Equilibrium Manifold

Let us consider a system in a domain  $U$  of a real vector space  $E$  given by differential equations

$$\frac{dx}{dt} = F(x). \quad (2.3.1)$$

We assume that for any  $x_0 \in U$  solution  $x(t; x_0)$  to the initial problem  $x(0) = x_0$  for (2.3.1) exists for all  $t > 0$  and belongs to  $U$ . Shifts in time,  $x_0 \mapsto x(t; x_0)$  ( $t > 0$ ), form a semigroup in  $U$ .

We do not specify the space  $E$  now. In general, it may be any Banach or even more general space. For nonlinear operators we will use the Fréchet differentials: for an operator  $\Psi(x)$  the differential at point  $x$  is a linear operator  $(D\Psi)|_x$ :

$$(D\Psi)|_x y = \left. \frac{d\Psi(x + \alpha y)}{d\alpha} \right|_{\alpha=0}.$$

We use notation  $(D_x \Psi)$  when the choice of variables is not obvious.

The QE approximation for (2.3.1) uses two basic entities: entropy and slow variables.

*Entropy*  $S$  is a concave Lyapunov functional for (2.3.1) which increases in time:

$$\frac{dS}{dt} \geq 0. \quad (2.3.2)$$

In this approach, the only property of entropy that is exploited is its increase in time (the Second Law in the form (2.3.2)).

Formally, any Lyapunov function may be used. Nevertheless, most of famous entropies, like the Boltzmann–Gibbs–Shannon entropy, the Rényi entropy, the Burg entropy, the Cressie–Read and the Tsallis entropies could be defined as *universal* Lyapunov functionals for Markov chains which satisfy some natural additivity conditions [31].

‘Universal’ means that they do not depend on kinetic coefficients directly but only on the equilibrium point. The ‘natural additivity conditions’ require that these entropies can be represented as sums (or integrals) over states, maybe after some monotonic transformation of the entropy scale, and, at the same time, are additive with respect to the joining of statistically independent sys-

tems (maybe, after some monotonic rescaling as well).

*Slow variables*  $M$  are defined as some differentiable functions of variables  $x$ :  $M = m(x)$ . Selection of the slow variables implies a hypothesis about separation of fast and slow motion. In its strongest form it consists of two assumptions: the slaving assumption and the assumption of small fast–slow projection.

**The slaving assumption.** For any admissible initial state  $x_0 \in U$  after some relatively small time  $\tau$  (*initial layer*) solution  $x(t; x_0)$  becomes a function of  $M$  (up to a given accuracy  $\epsilon$ ) and can be represented in a slaving form:

$$x(t) = x_{M(t)}^* + \delta(t) \text{ for } t > \tau, \text{ where } M(t) = m(x(t)), \|\delta(t)\| < \epsilon. \quad (2.3.3)$$

This means that everything is a function of slow variables, after some initial time and up to a given accuracy.

The smallness of  $\tau$  is essential. If there is no restriction on  $\tau$  then every globally stable system will satisfy this assumption because after some time it will arrive into a small vicinity of equilibrium.

The second assumption requires that the slow variables (almost) do not change during the fast motion: during the initial layer  $\tau$ , the state  $x$  can change significantly because of fast motion, but the changes in  $M = m(x)$  during  $\tau$  are small with  $\tau$ : **the assumption of small fast–slow projection.**

The QE approximation defines the functions  $x_M^*$  as solutions to the following **MaxEnt** optimization problem:

$$S(x) \rightarrow \max \text{ subject to } m(x) = M. \quad (2.3.4)$$

The reasoning behind this approximation is simple: during the fast initial layer motion entropy increases and  $M$  almost does not change. Therefore, it is natural to assume (and even to prove using smallness of  $\tau$  and  $\epsilon$  if the entropy gradient in fast directions is separated from zero) that  $x_M^*$  in (2.3.3) is close to the solution to the MaxEnt optimization problem (2.3.4). Further,  $x_M^*$  denotes a solution to the MaxEnt problem.

Some additional conditions on  $m$  and  $S$  are needed for the regularity of the dependence of  $x_M^*$  on  $M$ . It is more convenient to discuss these conditions separately for more specific systems. In general settings, let us just assume that for

given  $S$  and  $m$  the dependence  $m(x)$  is differentiable.

A solution to (2.3.4),  $x_M^*$ , is the *QE state*, the correspondent value of the entropy

$$S^*(M) = S(x_M^*) \quad (2.3.5)$$

is the *QE entropy* and the equation

$$\frac{dM}{dt} = (Dm)|_{x_M^*} F(x_M^*) \quad (2.3.6)$$

represents the *QE dynamics*.

We use notation  $E_M$  for the space of slow variables.

**Remark.** The strong form of the slaving assumption, ‘everything becomes a function of the slow variables’, is too strong for practical needs. In practice, we need just to have a good dependence on  $M$  for the time derivative  $dM/dt$ . Moreover, the short-time fluctuations of  $dM/dt$  do not affect the dependence  $M(t)$  too much, and only the average values

$$\langle \dot{M} \rangle_\theta(t) = \frac{1}{\theta} \int_t^{t+\theta} \frac{dM}{dt}$$

for sufficiently small time scale  $\theta$  are important.

Let  $Q$  be the concentration vectors satisfying the atom balance constraints define by the equation (2.2.11). In the defined  $Q$  space, we choose such points which minimize the Lyapunov function  $G$  of the system that we are dealing with. Such a manifold is called Quasi Equilibrium Manifold, which allows to make a partition of spaces into  $L$  and  $L^\perp$  in order to decompose the system into fast and slow motions i.e fast-towards the QEM and slow along the QEM. Let us assume that we have  $n$ -chemical species and  $l$  atom balance constraints then we are left with  $n - l$  degrees of freedom. If  $q < (n - l)$  is the dimension of the QEM, then the variables of reduced description are  $\xi_1 \dots \xi_q$ , so that:

$$(m_1, c) = \xi_1, \dots, (m_q, c) = \xi_q, \quad (2.3.7)$$

where  $m_i$  is an  $n$ -dimensional vector. The solution of the variation problem  $G \rightarrow \min$ , under constraints (2.2.10) and (2.2.27), represents the QEM. We will discuss this approach in detail by considering an example in Section 2.8 along

with different parametric representations.

## 2.4 Quasi Equilibrium w.r.t Reactions and Chemical Species

Here we are discussing the idea for the construction of Quasi-Equilibrium with respect to reactions and species, for which first of all we have to decide the number of reactions to be equilibrated among all chemical reactions taken under consideration. For convenience, give the reactions an index number of  $s_1, \dots, s_k$ , and, by law of mass action, if these reaction reach an equilibrium, then the rates of forward and backward reactions become equal, so the quasi equilibrium manifold is define by the system of equations

$$W_{s_i}^+ = W_{s_i}^-, \quad i = 1, \dots, k. \quad (2.4.1)$$

Let  $L$  be the space generated by these reactions (usually fast) i.e.  $L = \text{lin}\{\gamma_{s_1}, \dots, \gamma_{s_k}\}$ . where  $\gamma_s$  are the stoichiometric vectors. In terms of conjugated variables say  $\mu$ , the quasi-equilibrium manifold forms a linear subspace  $L^\perp$  which is the orthogonal complement to the linear envelope of vectors  $L$ , i.e,

$$(L_{s_i}, \mu) = 0, \quad i = 1, \dots, k. \quad (2.4.2)$$

gives a  $\mu = \nabla G$ .

In the case of chemical species the idea is similar but without selecting a subset of reactions. Let  $A_{i_1}, \dots, A_{i_k}$  be the numbers of chemical species, assuming fast and to be a equilibrate. This means that the subspace  $L$  which is define by the balance equation

$$(b_i, c) = 0 \quad (2.4.3)$$

is a  $k$ -dimensional subspace, the space of concentrations with the coordinates  $c_{i_1}, \dots, c_{i_k}$ . The conjugate variables defined for the quasi-equilibrium manifold,  $L^\perp$  are given as,

$$\mu \in L^\perp, \quad \mu = \mu_1, \dots, \mu_n \quad (2.4.4)$$

The same idea of quasi-equilibrium manifold can also be defined by fictitious

reactions: Let  $g_1, \dots, g_q$  be a basis in  $L$ . Then 2.4.4 can be rewritten as follows:

$$(g_i, \mu) = 0, \quad i = 1, \dots, q. \quad (2.4.5)$$

Let us illustrate the above idea on an example of quasi equilibrium with respect to reactions in the case of oxidation of CO over Pt: It involve a four step chemical reaction discussed in detail in Chapter 5. The equilibrium conditions are

$$\begin{aligned} k_1^+ c_{O_2} c_{Pt}^2 &= k_1^- c_{PtO}^2 \\ k_2^+ c_{CO} c_{Pt} &= k_2^- c_{PtCO} \\ k_3^+ c_{CO} c_{PtO} &= k_3^- c_{CO_2} c_{Pt} \\ k_4^+ c_{PtO} c_{PtCO} &= k_4^- c_{CO_2} c_{Pt}^2 \end{aligned} \quad (2.4.6)$$

Similarly, the quasi-equilibrium with respect to species for the same reaction can be defined by assuming equilibrium over  $O_2, CO, CO_2, Pt, PtO, PtCO$  in a sub domain of reaction conditions.

Subspace  $L$  is defined by the balance constraints, oxygen balance, carbon balance and platinum balance.

$$\begin{aligned} 2c_{O_2} + c_{CO} + 2c_{CO_2} + c_{PtO} + c_{PtCO} &= 0, \\ c_{CO} + c_{CO_2} + c_{PtCO} &= 0, \\ c_{Pt} + c_{PtO} + c_{PtCO} &= 0. \end{aligned} \quad (2.4.7)$$

Subspace  $L$  is three-dimensional. Its basis,  $\{g_1, g_2, g_3\}$  in the coordinates  $c_{O_2}, c_{CO}, c_{CO_2}, c_{Pt}, c_{PtO}, c_{PtCO}$ , reads:

$$\begin{aligned} g_1 &= (1, 0, 0, 2, -2, 0), \\ g_2 &= (0, 1, 0, 1, 0, -1), \\ g_3 &= (0, 0, 1, 2, -1, -1). \end{aligned} \quad (2.4.8)$$

The corresponding above equation(2.4.8) will become

$$\begin{aligned}
 \mu_{O_2} + 2\mu_{Pt} &= 2\mu_{PtO}, \\
 \mu_{CO} + \mu_{Pt} &= \mu_{PtCO}, \\
 \mu_{CO_2} + 2\mu_{Pt} &= \mu_{PtO} + \mu_{PtCO}.
 \end{aligned}
 \tag{2.4.9}$$

Similarly the general construction of the quasi-equilibrium manifold in the space of construction can be defined by finding a subspace  $L$  which satisfies the balance constraints, i.e

$$(b_i, L) \equiv 0. \tag{2.4.10}$$

Thus the orthogonal complement of  $L$  in the space with coordinates  $\mu = \nabla G$  defines the quasi equilibrium manifold  $\Omega_L$ .

## 2.5 Preservation of Entropy Production

The crucial property of the QE dynamics is the *preservation of entropy production*: if we use (2.3.6) for the calculation of  $dS^*(M)/dt$  at point  $M$ , then we obtain the same result as for entropy production  $dS(x)/dt$  at point  $x = x_M^*$  due to the initial system (2.3.1): symbolically, we can write

$$\frac{dS^*(M)}{dt} = \frac{dS(x)}{dt}, \tag{2.5.1}$$

where the left hand side is computed due to the QE approximation (2.3.6) and the right hand side corresponds to the initial system (2.3.1).

To prove this identity let us mention that

$$\frac{dS^*(M)}{dt} = (DS^*)|_M \frac{dM}{dt} = (DS^*)|_M \circ (Dm)|_{x_M^*} F(x_M^*), \tag{2.5.2}$$

where  $\circ$  stands for superposition. On the other hand,

$$dS(x)/dt = (DS)|_x F(x). \tag{2.5.3}$$

To finalize the proof, we need an identity

$$(DS^*)|_M \circ (Dm)|_{x_M^*} = (DS)|_{x_M^*}. \quad (2.5.4)$$

Let us use the Lagrange multipliers representation of the MaxEnt problem:

$$(DS)|_x = \Lambda_M \circ (Dm)_x, \quad m(x) = M. \quad (2.5.5)$$

This system of two equations has two unknowns: the vector of state  $x$  and the linear functional  $\Lambda_M$  on the space of slow variables (the Lagrange multiplier), which depends on  $M$  as on a parameter.

By differentiation of the second equation  $m(x) = M$ , we get an identity

$$(Dm)|_{x_M^*} \circ (Dx_M^*)|_M = \text{id}_{E_M}, \quad (2.5.6)$$

where  $\text{id}$  is a unit operator.

Lagrange multiplier  $\Lambda_M$  is the differential of the QE entropy:

$$(DS^*)|_M = \Lambda_M. \quad (2.5.7)$$

Indeed, due to the chain rule,  $(DS^*)|_M = (DS)_{x_M^*} \circ (Dx_M^*)|_M$ , due to (2.5.5),  $(DS)|_x = \Lambda_M(Dm)_x$  and, finally,

$$\begin{aligned} (DS^*)|_M &= (DS)_{x_M^*} \circ (Dx_M^*)|_M = \Lambda_M \circ (Dm)_x \circ (Dx_M^*)|_M \\ &= \Lambda_M \circ \text{id}_{E_M} = \Lambda_M. \end{aligned}$$

Now we can prove the identity (2.5.4):

$$(DS^*)|_M \circ (Dm)|_{x_M^*} = \Lambda_M \circ (Dm)|_{x_M^*} = (DS)|_{x_M^*}$$

(here we use the Lagrange multiplier form (2.5.5) again).

The preservation of the entropy production leads to the *preservation of the type of dynamics*: if for the initial system (2.3.1) entropy production is non-negative,  $dS/dt \geq 0$  then for the QE approximation (2.3.6) the production of the QE entropy is also non-negative,  $dS^*/dt \geq 0$ .

In addition, if for the initial system  $(dS/dt)|_x = 0$  if and only if  $F(x) = 0$  then the same property holds in the QE approximation.

## 2.6 The Classics and the Classical Confusion

### 2.6.1 The Asymptotic of Fast Reactions

It is difficult to find who introduced the QE approximation. It was impossible before the works of Boltzmann and Gibbs, and it became very well known after the works of Janes.

Chemical kinetics has been a source for model reduction ideas for decades. The ideas of QE appear there very natural: fast reactions go to their equilibrium and, after that, remain almost equilibrium all the time. The general formalization of this idea looks as follows. The kinetic equation has the form

$$\frac{dN}{dt} = K_{sl}(N) + \frac{1}{\epsilon}K_{fs}(N) \quad (2.6.1)$$

Here  $N$  is the vector of composition with components  $N_i > 0$ ,  $K_{sl}$  corresponds to the slow reactions,  $K_{fs}$  corresponds to fast reaction and  $\epsilon > 0$  is a small number. The system of fast reactions has the linear conservation laws  $b_l(N) = \sum_j b_{lj}N_j$ :  $b_l(K_{fs}(N)) \equiv 0$ .

The fast subsystem

$$\frac{dN}{dt} = K_{fs}(N)$$

tends to a stable positive equilibrium  $N^*$  for any positive initial state  $N(0)$  and this equilibrium is a function of the values of the linear conservation laws  $b_l(N(0))$ . In the plane  $b_l(N) = b_l(N(0))$  the equilibrium is asymptotically stable and exponentially attractive.

Vector  $b(N) = (b_l(N))$  is the vector of slow variables and the QE approximation is

$$\frac{db}{dt} = b(K_{sl}(N^*(b))). \quad (2.6.2)$$

In chemical kinetics, equilibria can be described by conditional entropy maximum (or conditional extremum of other thermodynamic potentials). Therefore,

we have the direct application of the formalism from Section 2.3.

The QE approximation, the asymptotic of fast reactions, is well known in chemical kinetics. Another very important approximation was invented in chemical kinetics as well. It is the Quasi Steady State (QSS) approximation. QSS was proposed in [6] and was elaborated into an important tool for analysis of chemical reaction mechanisms and kinetics [58, 13, 36]. The classical QSS is based on the *relative smallness of concentrations* of some of “active” reagents (radicals, substrate-enzyme complexes or active components on the catalyst surface) [1, 60]. In the enzyme kinetics, its invention was traditionally connected to the so-called Michaelis–Menten kinetics.

### 2.6.2 QSS and the Briggs–Haldane Asymptotic

Perhaps the first very clear explanation of the QSS was done by Briggs and Haldane in 1925 [7]. Briggs and Haldane consider the simplest enzyme reaction  $S + E \rightleftharpoons SE \rightarrow P + E$  and mention that the total concentration of enzyme ( $[E] + [SE]$ ) is ‘negligibly small’ compared with the concentration of substrate  $[S]$ . After that they conclude that  $[SE]$  is ‘negligible compared with’  $[\dot{S}]$  and  $[\dot{P}]$  and produce the now famous ‘Michaelis–Menten’ formula, which was unknown to Michaelis and Menten:  $k_1[E][S] = (k_1^- + k_2^+)[ES]$  or

$$[ES] = \frac{[E][S]}{K_M + [S]} \quad \text{and} \quad [\dot{P}] = k_2^+[ES] = \frac{k_2[E][S]}{K_M + [S]}, \quad (2.6.3)$$

where the ‘Michaelis–Menten constant’ is

$$K_M = \frac{k_1^- + k_2^+}{k_1^+}.$$

There is plenty of misleading comments in later publications about QSS. Two most important confusions are:

- Enzymes (or catalysts, or radicals) participate in *fast reactions* and, hence, relax faster than substrates or stable components. This is obviously wrong for many QSS systems: for example, in the Michaelis–Menten system *all* reactions include both enzyme and either substrate or product, there are no separate fast reactions for enzyme and slow reactions for substrate and

product.

- *Concentrations of intermediates are constant* because in QSS we equate their time derivatives to zero. In general case, this is also wrong: we equate the kinetic expressions for some time derivatives to zero, indeed, but this just exploits the fact that the time derivatives of intermediates concentrations are small together with their values, but not obligatory zero. If we accept QSS then these derivatives are not zero as well: to prove this we can just differentiate the Michaelis–Menten formula (2.6.3) and find that  $[ES]$  in QSS is almost constant when  $[S] \gg K_M$ , this is an additional condition, different from the Briggs–Haldane condition  $[E] + [AE] \ll [S]$  (for more details see [60, 41, 70] and a simple detailed case study [8]).

After a simple transformation of variables the QSS smallness of concentration transforms into a separation of time scales in a standard singular perturbation form (see, for example [70, 32]). Let us demonstrate this on the traditional Michaelis–Menten System:

$$\begin{aligned} \frac{d[S]}{dt} &= -k_1^+ [S][E] + k_1^- [SE]; \\ \frac{d[SE]}{dt} &= k_1^+ [S][E] - (k_1^- + k_2^+) [SE]; \\ [E] + [SE] &= e = \text{const}, [S] + [P] = s = \text{const}. \end{aligned} \tag{2.6.4}$$

The Briggs–Haldane condition is  $e \ll s$ . Let us use dimensionless variables  $x = [S]/s$ ,  $\zeta = [SE]/e$ :

$$\begin{aligned} \frac{s}{e} \frac{dx}{dt} &= -sk_1^+ x(1 - \zeta) + k_1^- \zeta; \\ \frac{d\zeta}{dt} &= sk_1^+ x(1 - \zeta) - (k_1^- + k_2^+) \zeta. \end{aligned} \tag{2.6.5}$$

To obtain the standard singularly perturbed system with the small parameter at the derivative, we need to change the time scale. This means that when  $e \rightarrow 0$  the reaction goes proportionally slower and to study this limit properly we have

to adjust the time scale:  $d\tau = \frac{e}{s} dt$ :

$$\begin{aligned}\frac{dx}{d\tau} &= -sk_1^+ x(1 - \tilde{\zeta}) + k_1^- \tilde{\zeta}; \\ \frac{e}{s} \frac{d\tilde{\zeta}}{d\tau} &= sk_1^+ x(1 - \tilde{\zeta}) - (k_1^- + k_2^+) \tilde{\zeta}.\end{aligned}\tag{2.6.6}$$

For small  $e/s$ , the second equation is a fast subsystem. According to this fast equation, for a given constant  $x$ , the variable  $\tilde{\zeta}$  relaxes to

$$\tilde{\zeta}_{\text{QSS}} = \frac{sx}{K_M + sx}$$

exponentially, as  $\exp(-(sk_1^+ x + k_1^- + k_2^+)t)$ . Therefore, the classical singular perturbation theory based on the Tikhonov theorem [63, 66] can be applied to the system in the form (2.6.6) and the QSS approximation is applicable even on an infinite time interval [37]. This transformation of variables and introduction of slow time is a standard procedure for rigorous proof of QSS validity in catalysis [70], enzyme kinetics [24] and other areas of kinetics and chemical engineering [1].

It is worth to mention that the smallness of parameter  $e/s$  can be easily controlled in experiments, whereas the time derivatives, transformation rates and many other quantities just appear as a result of kinetics and cannot be controlled directly.

### 2.6.3 The Michaelis and Menten Asymptotic

QSS is not QE but the classical work of Michaelis and Menten [47] was done on the intersection of QSS and QE. After the brilliantly clear work of Briggs and Haldane, the name ‘Michaelis–Menten’ was attached to the Briggs and Haldane equation and the original work of Michaelis and Menten was considered as an important particular case of this approach, an approximation with additional and not necessary assumptions of QE. From our point of view, the Michaelis–Menten work includes more and may give rise to an important general class of kinetic models.

Michaelis and Menten studied ‘fermentative splitting of cane sugar’. They introduced three ‘compounds’: sucrose–ferment combination, fructose–ferment

combination and glucose–ferment combination. The fundamental assumption of their work was ‘that the rate of breakdown at any moment is proportional to the concentration of the sucrose–invertase compound’.

They started from the assumption that at any moment according to the mass action law

$$[S_i][E] = K_i[S_iE] \quad (2.6.7)$$

where  $[S_i]$  is the concentration of the  $i$ th sugar (here,  $i = 0$  for sucrose, 1 for fructose and 2 for glucose),  $[E]$  is the concentration of free invertase and  $K_i$  is the  $i$ th equilibrium constant.

For simplification, they use the assumption that the concentration of any sugar in question in *free state* is practically equal to that of the total sugar in question.

Finally, they obtain

$$[S_0E] = \frac{e[S_0]}{K_0(1 + q[P]) + [S_0]}, \quad (2.6.8)$$

where  $e = [E] + \sum_i[S_iE]$ ,  $[P] = [S_1] = [S_2]$  and  $q = \frac{1}{K_1^+} + \frac{1}{K_2^+}$ .

Of course, this formula may be considered as a particular case of the Briggs–Haldane formula (2.6.3) if we take  $k_1^- \gg k_2^+$  in (2.6.3) (i.e. the equilibration  $S + E \rightleftharpoons SE$  is much faster than the reaction  $SE \rightarrow P + E$ ) and assume that  $q = 0$  in (2.6.8) (i.e. fructose–ferment combination and glucose–ferment combination are practically absent).

This is the truth but may be not the complete truth. The Michaelis–Menten approach with many compounds which are present in small amounts and satisfy the QE assumption (2.6.7) is a seed of the general kinetic theory for perfect and non-perfect mixtures.

In the next section we discuss the invariant grid for the system based on a numerical technique.

## 2.7 Method of Invariant Grids and Numerical Algorithms

Method of Invariant Grids (MIG) is a model reduction numerical technique, commonly used in a combustion system based on a slow invariant manifold



The invariant grids tabulated here are used to integrate the reduced system. The above grid differentiation formulas establish the tangent space  $T_y$ , and the null space of the thermodynamic projector  $P_y$  at each node. The equation (2.2.1) also represents a motion in the defect of invariance direction  $(1 - P)J(F(y))$  in its grid version. Newton method with incomplete linearization has the same form as for continuous manifolds. The method based on invariant grid (suggested recently) has a great importance for the construction of relatively low dimension manifolds.

## 2.8 Simple example

In this section we consider a simple example provided by the catalytic reaction under a constant volume and pressure [22] with three components  $\tilde{A}_1, \tilde{A}_3, \tilde{A}_4$  and one catalyst  $\tilde{A}_2$ . Gives a two-step reaction:



The function (2.2.16) define a global potential at here, while (2.2.16) is the kinetic equation for the four-component vector of concentrations  $c = (c_1, c_2, c_3, c_4)^T$ , can be written as (2.2.6):

$$\dot{c} = J(c) = \gamma_1 W_1 + \gamma_2 W_2\tag{2.8.2}$$

where 1,2 represent the first and second step of (2.8.1). Stoichiometric vectors are given according to (2.2.5) and rates of reactions are defined by the law of mass action (2.2.7).

$$\begin{aligned}\gamma_1 &= (-1, -1, 1, 0), & W_1 &= W_1^+ - W_1^- = k_1^+ c_1 c_2 - k_1^- c_3, \\ \gamma_2 &= (0, 1, -1, 1), & W_2 &= W_2^+ - W_2^- = k_2^+ c_3 - k_2^- c_2 c_4.\end{aligned}\tag{2.8.3}$$

A  $2 \times 4$  Matrix  $Dc$  is obtained through the conservation law from the system (2.2.11)

$$Dc = Const. \Rightarrow \begin{bmatrix} 1 & 0 & 1 & 1 \\ 0 & 1 & 1 & 0 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = \begin{bmatrix} Const_1 \\ Const_2 \end{bmatrix}$$

$$\begin{bmatrix} \dot{c}_1 \\ \dot{c}_2 \\ \dot{c}_3 \\ \dot{c}_4 \end{bmatrix} = \begin{bmatrix} j_1 \\ j_2 \\ j_3 \\ j_4 \end{bmatrix} = \begin{bmatrix} k_1^- c_3 - k_1^+ c_1 c_2 \\ k_1^- c_3 - k_1^+ c_1 c_2 + k_2^+ c_3 - k_2^- c_2 c_4 \\ k_1^+ c_1 c_2 - k_1^- c_3 + k_2^- c_2 c_4 - k_2^+ c_3 \\ k_2^+ c_3 - k_2^- c_2 c_4 \end{bmatrix}, \quad (2.8.4)$$

and the Jacobian of the above matrix takes the form:

$$L = \left[ \frac{\partial j_i}{\partial c_j} \right] \Rightarrow \begin{bmatrix} -k_1^- c_2 & -k_1^+ c_1 & k_1^- & 0 \\ k_1^+ c_2 & -k_1^+ c_1 - k_2^+ c_4 & k_1^- + k_2^+ & -k_2^- c_2 \\ k_1^+ c_2 & k_1^+ c_1 + k_2^+ c_4 & -k_1^- - k_2^+ & k_2^- c_2 \\ 0 & -k_2^- c_4 & k_2^+ & -k_2^- c_2 \end{bmatrix} \quad (2.8.5)$$

$$\nabla G = \begin{bmatrix} \ln c_1 - \ln c_1^{eq} \\ \ln c_2 - \ln c_2^{eq} \\ \ln c_3 - \ln c_3^{eq} \\ \ln c_4 - \ln c_4^{eq} \end{bmatrix}, H = \begin{bmatrix} 1/c_1 & 0 & 0 & 0 \\ 0 & 1/c_2 & 0 & 0 \\ 0 & 0 & 1/c_3 & 0 \\ 0 & 0 & 0 & 1/c_4 \end{bmatrix}. \quad (2.8.6)$$

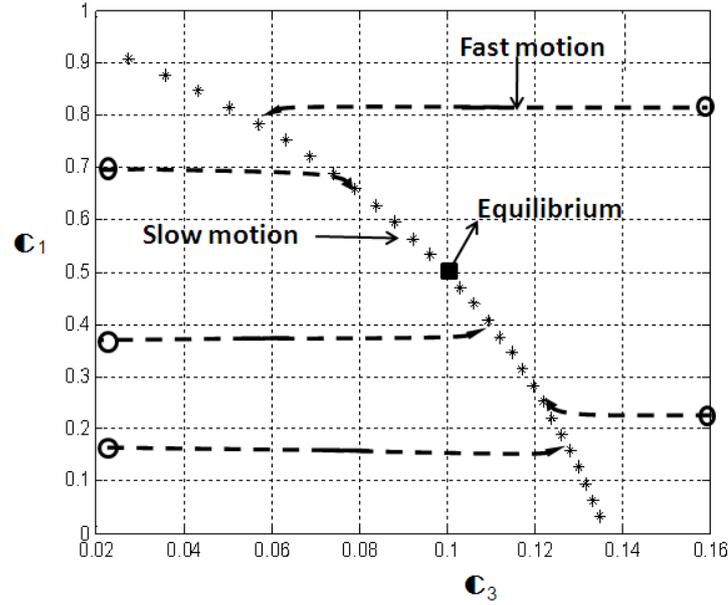
Now, to find invariant manifold from the shown in Figure 2.4, which will be our initial manifold, and by considering this initial manifold we apply method of invariant grid procedure (as discuss above). For a first approximation we take  $q = 1$  so that the four-dimensional vector  $m$  which gives us the reduced description variable  $\zeta$  will take the form  $m = (1, 0, 0, 0)$ , and the QEM must respect the following conditions:

$$G = \sum_{i=1}^4 c_i [\ln(c_i/c_i^{eq}) - 1] \rightarrow \min$$

$$(m, c) = \zeta$$

$$Dc = (const_1, const_2)^T. \quad (2.8.7)$$

Normally the above equation can be minimized by the Lagrange multipliers



**Figure 2.4:** Solution trajectories starting from different initial conditions (circles) approaching towards the equilibrium point (square) in the  $c_1 - c_3$  plane.

method, but the method fails if the number of constraints and variables increase. Due to this reason we need a special procedure to handle the situation. In that case the algorithm defined in [22], which is easy to implement in order to get the discrete structure of the QEM in any dimension is applied and can be further examined by the QEM geometrical construction. Here the following parameters are defined for the case of the two step chemical reaction

$$\begin{aligned}
 k_1^+ &= 1, \quad k_1^- = 0.5, \quad k_2^+ = 0.4, \quad k_2^- = 1, \\
 c_1^{eq} &= 0.5, \quad c_2^{eq} = 0.1, \quad c_3^{eq} = 0.1, \quad c_4^{eq} = 0.4, \\
 const_1 &= 1, \quad const_2 = 0.2.
 \end{aligned} \tag{2.8.8}$$

### 2.8.1 QEM Algorithm using Matlab

Let us implement the MIG method, as discussed above in detail in a Matlab program, where each steps is described for the proper understanding of the method and how it works. Figure 2.5 shows refinement from the initial manifold. The macroscopic parameter  $\zeta$  in this example is the concentration of the component  $\tilde{A}(\zeta = c_1)$ . Let  $\Omega$  be the solution of the system (2.8.7), and let  $\phi$

be the relation between  $c_3$  and  $c_1$  on the QE-manifold, so that  $c_3 = \phi(\xi)$ . The system (2.8.7) takes the following explicit form:

$$\begin{aligned} c_1 &= \xi, & c_2 &= \text{const}_2 - \phi(\xi) \\ c_3 &= \phi(\xi), & c_4 &= \text{const}_1 - \xi - \phi(\xi) \\ \frac{\partial G(\phi, \xi)}{\partial \phi} &= 0, & \frac{\partial^2 G(\phi, \xi)}{\partial \phi^2} &> 0. \end{aligned} \quad (2.8.9)$$

The solution of the system (2.8.9) delivers a quadratic expression for  $\phi(\xi)$ :

$$\phi(\xi) = \psi(\xi) - \sqrt{\psi^2(\xi) - \text{const}_2(\text{const}_1 - \xi)},$$

where

$$\psi(\xi) = (\text{const}_2(\text{const}_1 - c_1^{eq}) + c_3^{eq}(c_1^{eq} + c_3^{eq} - \xi)) / (2c_3^{eq})$$

The resulting manifold is quite far away from the invariant one so it needs to be corrected through MIG procedure and can be refined after two iterations only. Let us write the thermodynamic projector (2.2.24) for the case (2.8.4). Here the tangent subspace  $T_y$  is a line spanned by the vector  $e_y$ . If  $f$  is a vector parallel to  $T_y$  and  $z = (z_1, z_2, z_3, z_4)$  a generic four-dimensional vector which must be projected onto it, we can write:

$$\begin{aligned} e_y &= \omega f, \omega = 1/DG(f), \\ Pz &= DG(z)e_y = (\nabla G, z)e_y, \end{aligned} \quad (2.8.10)$$

so that the null space of  $P$  has the following equation:

$$(\nabla G, z) = g_1 z_1 + g_2 z_2 + g_3 z_3 + g_4 z_4 = 0, \quad (2.8.11)$$

where  $\nabla G = (g_1, g_2, g_3, g_4)$ . The dimension of  $S = (\ker P \cap \ker D)$  is 1; let  $b_1$  be a vector which spans  $S$ . When a set of concentration points is available (initial approximation of SIM), in each point, the Newton method must provide a correction ( $c = c_0 + \delta c : \delta c = \delta_1 b_1$ ). Here, Eq. (2.2.27) takes the simple form:

$$\delta_1 = -\frac{((1-P)J, b_1)}{((1-P)Lb_1, b_1)}. \quad (2.8.12)$$

## QEM ALGORITHM USING MATLAB

For 30 grid points we define the concentration spaces  $c_i$  in vectorial form as

$$A = [c_1, c_2, c_3, c_4]^T, \quad \text{where } T \text{ represent a transpose}$$

for Thermodynamic scalar product we use

$$f = F/A, \quad G_1 = G/A, \quad S_1 = S/A, \quad J_1 = J/A$$

$G(i, j) = \log[A(i, j) - A(i, j - 1)]$	<i>Gradient</i>
$F(i, j) = e^G / \ e^G\ $	<i>Tangent at each point</i>
$K(i, j) = F(i, j) / (G, f)$	$(, )$ <i>Euclidean scalar product</i>
$P(i, j) = G_1(i, j) \times K(i, j)$	<i>Thermodynamic Projector</i>
$L(i, j) = \frac{\partial J(c)}{\partial c_i}$	<i>Jacobian Matrix of kinetics J</i>
$S_1 = \text{null}(P \cap D)$	<i>Spanning set <math>b = S</math></i>

Now the step size is defined as

$$\text{delta}_1 = \frac{(Z, S_1)}{(ZLb, S_1)}, \quad Z = (1 - P), \text{ with Euclidean scalar product.}$$

Thus,

$$A_1 = A + \text{delta}_1. \quad \text{first refinement.}$$

Similarly, for the second refinement we proceed in the same manner but separately (optional) to get

$$A_2 = A_1 + \text{delta}_2. \quad \text{second refinement.}$$

The solution trajectories are shown in Figure 2.5. Our computations fully support the observation of [22] and prove that their computational experiments are reproducible.

Now in the next section we apply the same procedure by changing its parameter to see the line segment in the  $c_1 - c_3$  plane.

## QEM at different parameters

**1st Observation:** Let us change the parameters and consider the same system (2.8.7) for which,

$$k_1^+ = 4, \quad k_1^- = 2, \quad k_2^+ = 0.2, \quad k_2^- = 0.5,$$

$$c_1^{eq} = 0.5, \quad c_2^{eq} = 0.1, \quad c_3^{eq} = 0.1, \quad c_4^{eq} = 0.4,$$

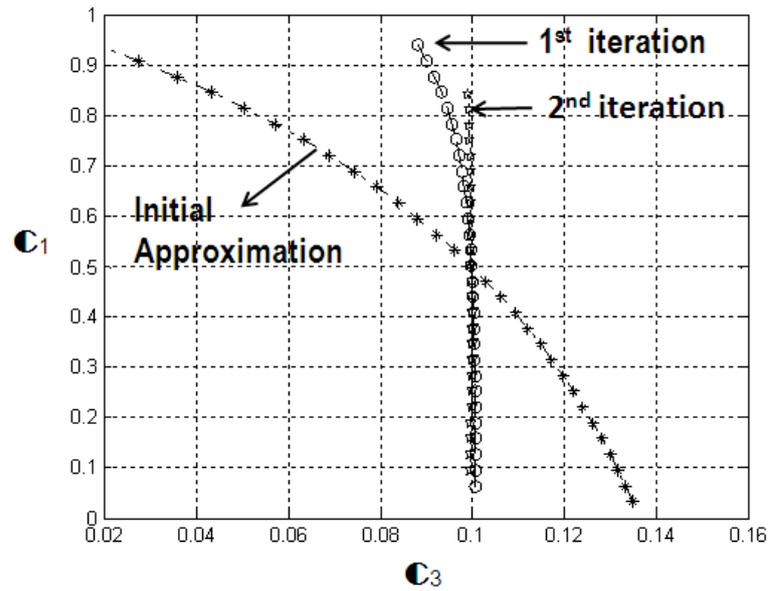


Figure 2.5: Grid refinement at each point by two iterations applied on Quasi Equilibrium Manifold composed of 30 grid-nodes.

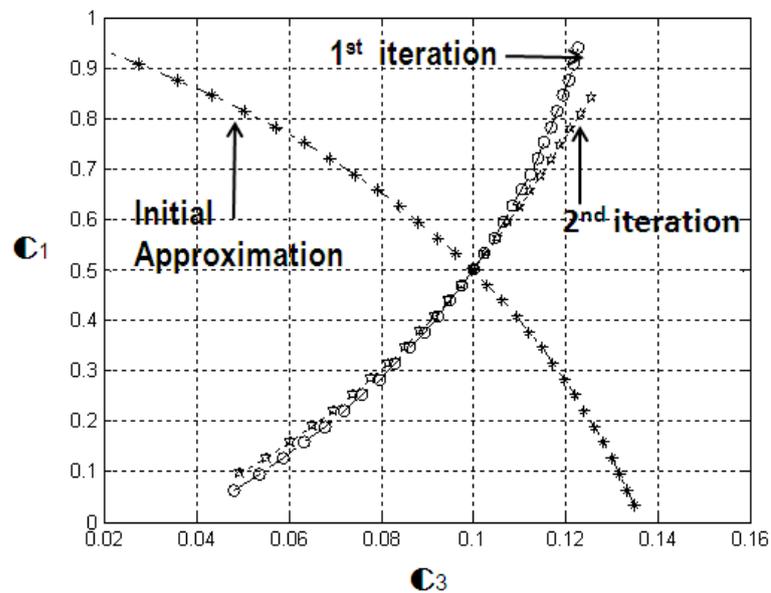
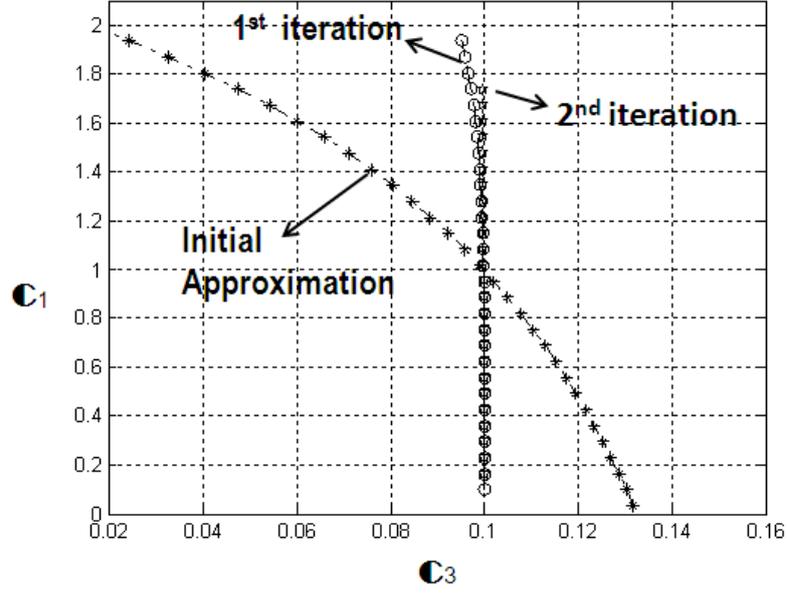


Figure 2.6: 1st Observation: Newton method with incomplete linearization: Two iterations starting from the QEM approximation for the refinement of each initial grid point.



**Figure 2.7:** 2nd Observation: Newton method with incomplete linearization: Two iterations starting from the QEM approximation for the refinement of each initial grid point.

$$const_1 = 1, \quad const_2 = 0.2 \quad (2.8.13)$$

If  $\Omega$  is the solution trajectories obtained by defining the relation between  $c_1$  and  $c_3$ . Equation 2.8.9 gives the initially approximated manifold and then by the refinement through MIG we get the slow invariant manifold shown in Figure 2.6.

**2nd Observation:** Similarly for the next calculations we use the following set of parameters.

$$\begin{aligned} k_1^+ &= 1, \quad k_1^- = 1, \quad k_2^+ = 1, \quad k_2^- = 1, \\ c_1^{eq} &= 1, \quad c_2^{eq} = 0.1, \quad c_3^{eq} = 0.1, \quad c_4^{eq} = 1, \\ const_1 &= 2.1, \quad const_2 = 0.2. \end{aligned} \quad (2.8.14)$$

Now again by obtaining the invariant manifold from the parameters defined by (2.8.14) which gives initial manifold and need to be refined due to its variation from the invariant one. Apply invariant grid procedure to find the SIM projection onto the  $c_1$  and  $c_3$  plane simply results in the line segment  $c_3 = c^{eq} = 0.1$ . So we expect that methods of reduced description provide the manifold in which we obtain the reduction of two dimensional kinetic system in order to

## QEM ALGORITHM USING MATLAB

into a one dimensional description. Using different initial conditions and parameters we calculated the QEM approximation after refining through an iterative process, which shows the efficiency of the Newton method.

# Chemical Reaction Stoichiometry and Mass Action Law

In any chemical reaction the mass of reactants will equal the mass of the products, this is what the law of conservation of mass, of energy, etc says. The rules of stoichiometric govern nearly all calculation related to chemical equation. Which are widely used in chemical engineering and metallurgy, we are going to discuss in this chapter.

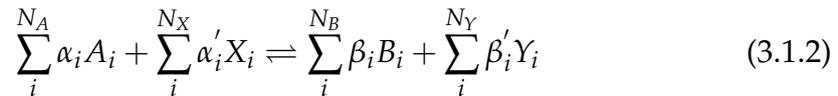
## 3.1 The idea of elementary reaction and stoichiometric equations

Vant't Hoff define, if a reaction involves one molecule (reaction:  $A \rightarrow B$ ) it will be classified as the 1st order or monomolecular and in the case when two molecules take part (reaction:  $A + B \rightarrow B$ , reaction :  $2A \rightarrow B$ ) the reaction is of the second order (bimolecular). Similarly with three molecules (reaction:  $3A \rightarrow B$ , reaction :  $2A + B \rightarrow C$ ) the reaction is of the third order (three-molecular) whereas more than three is considered to be improbable. In the case of an elementary reaction its rate depends on concentrations specified in some simple way whereas in case of more than one reaction or a sum of elementary reactions as in the case of complex reactions, its steps consist of two elementary reactions direct and inverse. A complex chemical system involves a number of steps of

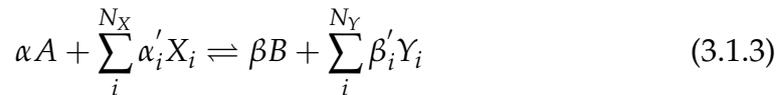
elementary reactions such as oxidation of hydrogen described



involve over thirty elementary reactions, as hydrogen oxidation takes place through intermediate species such as O,H,OH. Although they are low in concentration, they are of essential important for the reaction. In the gas phase catalyst reaction, the reactant on the one hand are gases and surface substances on the other side later on the surface of solid catalysts. A catalyst reaction is represented as



where  $A_i, B_i$  are initial substances and products,  $\alpha_i, \beta_i$  are their stoichiometric coefficients  $X_i, Y_i$  are the surface substances and  $\alpha'_i, \beta'_i$  are their stoichiometric coefficients. For simplicity  $\alpha, \beta = 1$  or  $0$ , which means that the catalytic reaction involves the participation of one molecule  $CH_4 + Z \rightleftharpoons 2CH_2 + H_2$  of gas or no molecules, such as  $ZCHOH \rightleftharpoons ZCO + H_2$ . Thus we are left with



$\alpha_i, \beta_i$  are usually 1,2,3 and  $\sum \alpha'_i, \sum \beta'_i \leq 3$ . Because of these number of elementary steps, the same substance can participate a number of times as an initial substance and as a reaction product. Just as an example



where  $S$  is any other substrate. Such types of steps are called autocatalytic and Non autocatalytic implies that at any value of  $S$  and  $i$  at least one of the values  $\alpha_{si}$  or  $\beta_{si}$  is zero. The stoichiometric coefficients will be considered only for mono, bi, and tri molecular reactions. The coefficient  $\alpha_{si}, \beta_{si}$  thus have values of 0,1,2,3, such that

$$\sum_{i=1}^n \alpha_{si}, \sum_{i=1}^n \beta_{si} \leq 3. \quad (3.1.5)$$

### 3.2 Stoichiometric Conservation Laws

Reaction rate in the case of an elementary reaction is defined as the number of elementary acts in the chemical conversion per unit reaction volume or per unit surface area for unit time. A chemical reaction can be written in general as



where  $\alpha_i, \beta_i$  are the stoichiometric coefficients which are always  $\leq 3$ .  $A_i, B_i$  are initial substances and products.  $N_A$  and  $N_B$  are the number of initial substances and reaction products respectively. The law of conservation is independent of what reactions take place between the species  $A_i$  because there exists a number of linear laws of conservation satisfy the equation

$$\frac{db_j}{dt} = \frac{d}{dt} \sum_{i=1}^n a_{ij} N_i = 0, \quad b_j = \text{constant}, \quad (3.2.2)$$

or in a matrix form it can be written as

$$\frac{db}{dt} = C \frac{dN}{dt} = 0, \quad b = CN = \text{constant} \quad (3.2.3)$$

but their vectors are not always linearly independent. The simplest example [55] is the reaction of butane isomerization. Let  $A_1$  be butene-1,  $A_2$  be iso butene-2 and  $A_3$  be *cis trans* butene-2. They consist of two elements carbon and hydrogen, and all  $A_i$  have the same composition,  $C_4H_8$ , The molecular matrix is of the form

$$A = \begin{bmatrix} 4 & 8 \\ 4 & 8 \\ 4 & 8 \end{bmatrix}. \quad (3.2.4)$$

and the laws of conservation

$$b_C = 4(N_1 + N_2 + N_3) = \text{Constant},$$

$$b_H = 8(N_1 + N_2 + N_3) = \text{Constant},$$

are linearly dependent such that  $2b_C = b_H$

## STOICHIOMETRIC CONSERVATION LAWS

Now, in order to solve a set of linear equations defined by the chemical reaction (3.1.2). It is better to apply matrix techniques of linear algebra and obtain a set of linearly independent vectors to get its basis. In a matrix form  $AX = B$ , and if  $B$  is zero, then the system is homogenous. The rank of the stoichiometric matrix give us the key substance (linearly independent vector of the matrix). In the case of oxidation of carbon monoxide over platinum the rank is three, given by  $(O, C, Z)$ . This means that in the  $O_2, CO, CO_2, Z, ZO, ZCO$  mixture there are three key substances. The chemical composition of the substance in a chemical reaction can be calculated from the molecular matrix  $A$  whose elements  $a_{ij}$  are atomic number of  $j$ th element entering into  $i$ th reactant molecule, so in a matrix form

$$A = \left\{ \begin{array}{ccc|c} \overbrace{O \ C \ Z} & & & \\ \hline 2 & 0 & 0 & O_2 \\ 1 & 1 & 0 & CO \\ 2 & 1 & 0 & CO_2 \\ 0 & 0 & 1 & Z \\ 1 & 0 & 1 & ZO \\ 1 & 1 & 1 & ZCO \end{array} \right\},$$

where the rows represent the substances and columns are the elements  $O, C, Z$ . The molecular masses of the substances are determined by the equation

$$M = AM_A, \quad (3.2.5)$$

where  $M$  represent the molecular masses and  $M_A$  is column vector of atomic masses. Stoichiometric vectors  $\gamma_i = \beta_i - \alpha_i$  are obtained from the stoichiometric matrix whose elements are the stoichiometric coefficients of the reacting substances. In the same example ( $CO$  oxidation over  $Pt$ ) it takes the form

$$\Gamma = \begin{bmatrix} -1 & 0 & 0 & -2 & 2 & 0 \\ 0 & -1 & 0 & -1 & 0 & 1 \\ 0 & -1 & 1 & 1 & -1 & 0 \\ 0 & 0 & 1 & 2 & -1 & -1 \end{bmatrix} \quad (3.2.6)$$

Here rows correspond to reactions and columns represent the reacting sub-

stances. It is necessary that the reaction steps must satisfy the mass conservation law for atoms of the each type. This requirement can be written in the form

$$\Gamma A = 0, \quad (3.2.7)$$

which mean that if we have chosen the right stoichiometric matrix equations then (3.2.7) must hold and we obtain

$$\Gamma A M_A = \Gamma M = 0. \quad (3.2.8)$$

which can be easily seen through the above equations.

### 3.3 Perfect system and mass action law for a catalytic reaction

From the stoichiometric equation of chemical reactions (3.2.1) the rate of a chemical reaction can be defined as a difference between the rates of direct and reverse reactions i.e,

$$w = w_i^+ - w_i^-. \quad (3.3.1)$$

In the case of equilibrium  $w = 0$ , which means that

$$w_i^+ = w_i^-. \quad (3.3.2)$$

The Law of Mass Action gives the dependence of the rate on the concentration of the reactants

$$\begin{aligned} w_i^+ &= k_i^+ c_{A_1}^{\alpha_1} c_{A_2}^{\alpha_2} \dots = k_i^+ \prod_{i=1}^{N_A} c_{A_i'}^{\alpha_i} \\ w_i^- &= k_i^- c_{B_1}^{\beta_1} c_{B_2}^{\beta_2} \dots = k_i^- \prod_{i=1}^{N_B} c_{B_i'}^{\beta_i} \end{aligned} \quad (3.3.3)$$

- where  $c_{A_i}, c_{B_i}$  are the concentration of initial and final(product) substances.
- $k_i^+, k_i^-$  are the rate coefficients for the direct and reverse reactions.
- and there ratio  $k_i^+ / k_i^- = k_{eq}$  represent equilibrium constants.

$k_i$  fit the Arrhenius relationship and decreases exponentially with increase temperature

$$\begin{aligned}k^+ &= k_0^+ \exp(-E^+ / RT), \\k^- &= k_0^- \exp(-E^- / RT),\end{aligned}\tag{3.3.4}$$

where  $k_0^+, k_0^-$  are the pre-exponential factors,  $E^+, E^-$  are the activation energy for the direct and reverse reaction,  $R, T$  are universal gas constants and absolute temperature. Homogenous catalytic reaction satisfies the relationship

$$w = w_i^+ - w_i^- = \frac{-1}{\alpha_i V} \frac{dN_{A_i}}{dt} = \frac{-1}{\beta_i V} \frac{dN_{B_i}}{dt}\tag{3.3.5}$$

where  $N_{A_i}, N_{B_i}$  are concentrations of substances in the system,  $V$  is the volume of the system. Similarly, for heterogenous catalyst reaction

$$w = w_i^+ - w_i^- = \frac{-1}{\alpha_i S_{cat}} \frac{dN_{A_i}}{dt} = \frac{-1}{\beta_i S_{cat}} \frac{dN_{B_i}}{dt}\tag{3.3.6}$$

$S_{cat}$  is the surface area of a catalyst for conversion. For those steps in which there is no change in the number of moles, equation above will take a form

$$w = w_i^+ - w_i^- = \frac{-1}{\alpha_i} \frac{dc_{A_i}}{dt} = \frac{-1}{\beta_i} \frac{dc_{B_i}}{dt}.\tag{3.3.7}$$

### 3.4 Principle of Detailed Balance

In order to understand the dynamical property of the chemical kinetics system, it is necessary to formulate the basic property of a closed system expressed by the principle of detailed balance (PDB) rest point for a closed system is a point of detailed balance where the rate of every step is equal to zero:

$$\begin{aligned}w_s^+ &= w_s^-, \\w_s &= w_s^+ - w_s^- = 0,\end{aligned}\tag{3.4.1}$$

which implies  $\dot{c} = \dot{N} = 0$ .

Onsager in 1930 gave an idea of substituting and extending the principle of de-

tailed balance to a wide range of chemical processes, where in the presence of an external magnetic field it is possible that equilibrium is not detailed. Then De Groot and Mazur made further modifications in this principle. A closed system, on the one hand means that there is no in flow out flow of substance, but also it is about equilibrium of the environment, which may be of several types: isothermal with respect to heat, isobaric or isochoric with respect to pressure and volume. Sometimes it is not easy to decide whether the system is in equilibrium or in a steady state.

Actually the state of the system is not literally steady or stationary, but the concentrations of one or more species are approximately constant compared to the other species changing much more rapidly. The rate of change of the concentration of one or more intermediates may be so close to zero that the steady state approximation is useful in treating the kinetics of the reaction system.

In the case of chemical kinetics, the kinetic equation is derived in terms of the law of mass/surface action, and it can be proved through above equation that in such a system a positive equilibrium point is unique and stable. In the non steady case the behavior of the closed system near this positive point of equilibrium is very simple, in that the positive point is a stable node. This means that the PDB imposes limitation on the equilibrium constants i.e the ratio of direct to reverse reaction rate constants which are

$$w_s^+ = w_s^-, \quad k_s^+(T) \prod_{i=1}^n c_i^{*\alpha_i} = k_s^-(T) \prod_{i=1}^n c_i^{*\beta_i}, \quad (3.4.2)$$

where  $c_i^*$  is an equilibrium concentration of  $A_i$ . Then after some transformation and taking the logarithm we obtain

$$\sum_{i=1}^n (\beta_{s_i} - \alpha_{s_i}) \ln c_i^* = \ln \left( \frac{k_s^+}{k_s^-} \right) = \ln k_s \quad (3.4.3)$$

where  $k_s$  is the equilibrium rate constant for the  $s$ -th step. In order to obtain explicit form for the condition on  $k_s$  it is necessary to find all solutions for the set of equations

$$\sum_s y_s \gamma_{si} = 0, \quad i = 1, 2, \dots, n. \quad (3.4.4)$$

where  $y$  is a row vector through which a complete set of solutions will be obtained. Consider an example a system of 3-isomers (the isomerization of

butenes)



$$\Gamma = \begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ 1 & 0 & -1 \end{bmatrix}, \tag{3.4.6}$$

so that  $y\Gamma = 0$  gives

$$\begin{aligned} -y_1 + y_3 &= 0, \\ y_1 - y_2 &= 0, \\ y_2 - y_3 &= 0, \end{aligned}$$

where above system is satisfied by the  $y_1 = y_2 = y_3$  constant coefficient say  $y = (1, 1, 1)$  the respective condition of equilibrium constant is  $y \ln k = 0$ , or

$$\begin{aligned} \ln k_1 + \ln k_2 + \ln k_3 &= 0, \\ k_1 k_2 k_3 &= 1. \end{aligned} \tag{3.4.7}$$

### 3.5 Thermodynamic Lyapunov Functions: Entropy, Free Energy, Free Entropy

Lyapunov considered analytical solutions of equations of invariance near a fixed point [55]. He obtain the solutions in a form of the Taylor series expansion and proved the convergence of the power series near the non-resonant fixed point (the Lyapunov auxiliary theorem). For the construction of a slow invariant manifold Gorban & Karlin proposed an idea in 1992 and for the realization for generic dissipative system is discussed in 1994, famous in kinetic theory based on the Boltzmann kinetic equation.

In case of isochoric and isothermal conditions a Lypunov function is related to

the Helmholtz energy given by

$$G = \sum c_i [\ln(\frac{c_i}{c_i^*}) - 1].$$

where  $c^*$  represents the steady state. There gradient and second derivative take a simple form

$$\nabla G = \left. \frac{\partial G}{\partial c_i} \right|_{V,T} = \ln\left(\frac{c_i}{c_i^*}\right), \quad H(i,j) = \left. \frac{\partial^2 G}{\partial c_i \partial c_j} \right|_{V,T} = \delta_{ij} \frac{1}{c_i}.$$

where  $\delta_{ij}$  denotes the Kronecher delta.

In the case of isobaric, isoenthalpic, and isolated system it is difficult to find gradient and Hessian matrix explicitly because of its dependence on non-linear relations, for detail see [23].

The entropy of the system does not depend on kinetic constants [54]. It is the same for different details of kinetics and depends only on the equilibrium data. In the Boltzmann equation there exists only one universal Lyapunov functional [57]. It is the entropy (we do not distinguish functionals which are connected by multiplication on a constant or adding a constant). For the Fokker Plank Equation there exists a big family of universal Lyapunov functionals. For all four classical conditions the thermodynamic Lyapunov functions  $G_\bullet$  for kinetic equations are known [56]:

$$\begin{aligned} U, V = const, \quad G_{U,V} &= -S/k_B; \\ V, T = const, \quad G_{V,T} &= F/k_B T = U/k_B T - S/k_B, \\ H, P = const, \quad G_{H,P} &= -S/k_B; \\ P, T = const, \quad G_{P,T} &= G/T = H/k_B T - S/k_B. \end{aligned} \quad (3.5.1)$$

where  $F = U - TS$  is the free energy (Helmholtz free energy),  $G = H - TS$  is the free enthalpy (Gibbs free energy). In order to get the dimensionless coordinates the thermodynamics Lyapunov function must be normalized. The function decrease while there derivatives  $\partial G_\bullet(const, N)/\partial N_i$  are the same functions of  $c$

and  $T$  for all classical conditions can be represented as:

$$\begin{aligned}\check{\mu}_i(c, T) &= \frac{\partial G_{\bullet}(const, N)}{\partial N_i} \\ &= \frac{\mu_i^{chem}(c, T)}{k_B T}\end{aligned}$$

where  $\mu_i^{chem}(c, T)$  is the chemical potential of  $A_i$ .

## CHAPTER 4

# Kinetic Model of Chemical Reaction

Chemical kinetics deals with the rates of chemical reactions and factors which influence the rates and the explanation of the rates in terms of the reaction mechanisms of chemical processes. On the other hand by knowing pressure, temperature, medium, concentration, etc, of a reaction, one can measure the rate of change of reactants or products with respect to time. In equilibrium, the energy relations between the products and the reactants are calculated based on thermodynamics without the involvement of intermediates. Berzelius(1836) observed that there exist such substances which increase the rate of a reaction by loosening the bonds holding the atoms of the reacting molecules are now call catalyst where as it is also shown in a number of experiments in which it slow down the reaction so we can say that it can alter the rate of reaction while keeping itself unchanged.

While in this slow and fast reactions the reaction stoichiometry (element measure) allows us to determine the amount of substance that is consumed or produced by a reaction. It was Richter (German chemist) who discovered that it is possible to quantify the substance produced or consumed by a chemical reactions, and normally its measurement can be taken in two parts: the first part is how much of a reactant is consumed in a chemical reaction and the second is its product formation.

## 4.1 General Kinetics with Fast Intermediates Present in Small Amount

### 4.1.1 Stoichiometry of Complexes

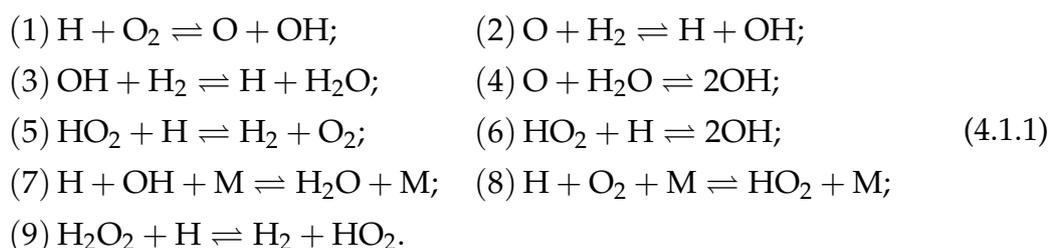
In this Section, we return to the very general reaction network.

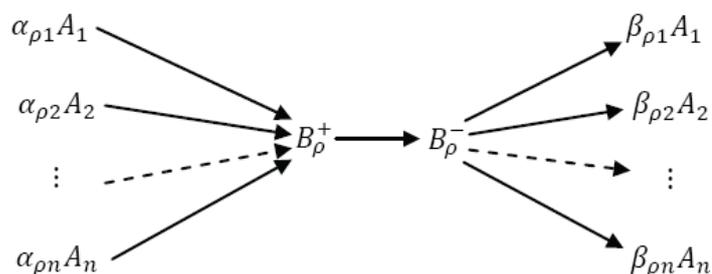
Let us call all the formal sums that participate in the stoichiometric equations (2.2.4), the *complexes*. The set of complexes for a given reaction mechanism (2.2.4) is  $\Theta_1, \dots, \Theta_q$ . The number of complexes  $q \leq 2m$  (reaction number) and it is possible that  $q < 2m$  because some complexes may coincide for different reactions.

A complex  $\Theta_i$  is a formal sum  $\Theta_i = \sum_{j=1}^n v_{ij} A_j = (v_i, A)$ , where  $v_i$  is a vector with coordinates  $v_{ij}$ .

Each elementary reaction (2.2.4) may be represented in the form  $\Theta_\rho^- \rightarrow \Theta_\rho^+$ , where  $\Theta_\rho^\pm$  are the complexes which correspond to the right and the left sides (2.2.4). The whole mechanism is naturally represented as a digraph of transformation of complexes: vertices are complexes and edges are reaction.

Let us consider simple example: 18 elementary reactions (9 pairs of mutually reverse reactions) from the hydrogen combustion mechanism (see, for example, [49]).



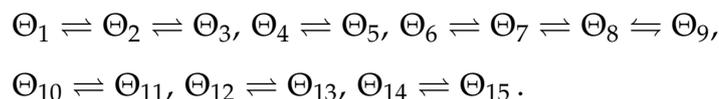


**Figure 4.1:** A  $2n$ -tail scheme of an extended elementary reaction (4.1.3)

There are 15 different complexes here:

$$\begin{aligned} \Theta_1 &= H + O_2, \quad \Theta_2 = O + OH, \quad \Theta_3 = O + H_2, \quad \Theta_4 = OH + H_2, \\ \Theta_5 &= H + H_2O, \quad \Theta_6 = O + H_2O, \quad \Theta_7 = 2OH, \quad \Theta_8 = HO_2 + H, \\ \Theta_9 &= H_2 + O_2, \quad \Theta_{10} = H + OH + M, \quad \Theta_{11} = H_2O + M, \\ \Theta_{12} &= H + O_2 + M, \quad \Theta_{13} = HO_2 + M, \quad \Theta_{14} = H_2O_2 + H, \\ \Theta_{15} &= H_2 + HO_2. \end{aligned}$$

The reaction set (4.1.1) can be represented as



We can see that this digraph of transformation of complexes has a very simple structure: there is four isolated pairs of complexes, one connected group of three complexes and one connected group of four complexes.

### 4.1.2 Stoichiometry of Compounds

For each complex  $\Theta_j$  we introduce an additional component  $B_j$ , an intermediate compound and  $B_\rho^\pm$  are those compounds  $B_j$  ( $1 \leq j \leq q$ ), which correspond to the right and left sides of (2.2.4).

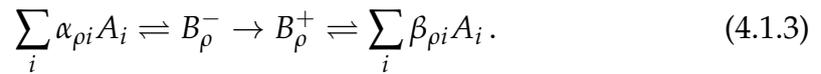
We call these components "compounds" following the English translation of the original Michaelis–Menten paper [47] and keep "complexes" for the formal

linear combinations  $\Theta_j$ .

An extended reaction mechanism includes two type of reactions: equilibration between a complex and its compound ( $q$  reactions, one for each complex)



and transformation of compounds  $B_\rho^- \rightarrow B_\rho^+$  ( $m$  reactions, one for each elementary reaction from (2.2.4)). So, instead of the reaction (2.2.4) we can write



Of course, if the input or output complexes coincide for two reactions then the correspondent equilibration reactions also coincide. The extended list of components includes  $n + q$  components:  $n$  initial species  $A_i$  and  $q$  compounds  $B_j$ . The correspondent composition vector  $N^\oplus$  is a direct sum of two vectors, the composition vector for initial species,  $N$ , with coordinates  $N_i$  ( $i = 1, \dots, n$ ) and the composition vector for compounds,  $Y$ , with coordinates  $Y_j$  ( $j = 1, \dots, q$ ):  $N^\oplus = N \oplus Y$ .

The space of composition vectors  $E$  is a direct sum of  $n$ -dimensional  $E_A$  and  $q$ -dimensional  $E_B$ :  $E = E_A \oplus E_B$ .

For concentrations of  $A_i$  we use the notation  $c_i$  and for concentrations of  $B_j$  we use  $\zeta_j$ .

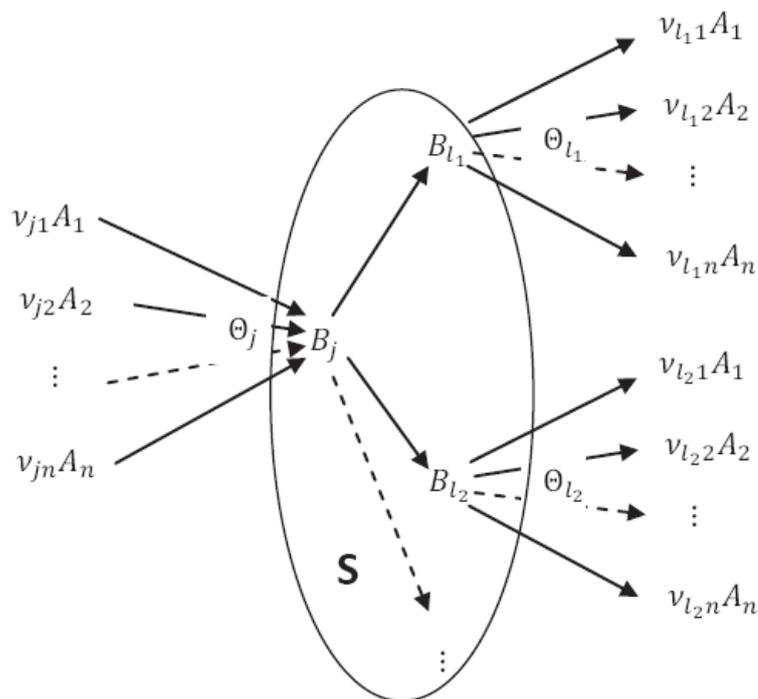
The stoichiometric vectors for reactions  $\Theta_j \rightleftharpoons B_j$  (4.1.2) are direct sums:  $g^j = -v_j \oplus e_j$ , where  $e_j$  is the  $j$ th standard basis vector of the space  $R^q = E_B$ , the coordinates of  $e_j$  are  $e_{jl} = \delta_{jl}$ :

$$g^j = (-v_{j1}, -v_{j2}, \dots, -v_{jn}, \underbrace{0, \dots, 0}_l, 1, 0, \dots, 0) \quad (4.1.4)$$

The stoichiometric vectors of equilibration reactions (4.1.2) are linearly independent because there exists exactly one vector for each  $l$ .

The stoichiometric vectors  $\gamma^{jl}$  of reactions  $B_j \rightarrow B_l$  belong entirely to  $E_B$ . They have  $j$ th coordinate  $-1$ ,  $l$ th coordinate  $+1$  and other coordinates are zeros.

To exclude some degenerated cases a hypothesis of *weak reversibility* is accepted.



**Figure 4.2:** A multichannel view of the complex transformation. The hidden reactions between compounds are included in the oval  $S$ .

Let us consider a digraph with vertices  $\Theta_i$  and arrow reactions from (2.2.4). The system is weakly reversible if for any two vertices  $\Theta_i, \Theta_j$  existence of an oriented path from  $\Theta_i$  to  $\Theta_j$  implies existence of oriented path from  $\Theta_j$  to  $\Theta_i$ .

Of course, this weak reversibility property is equivalent to weak reversibility of the reaction network between compounds  $B_j$ .

### 4.1.3 Energy, Entropy and Equilibria of Compounds

In this section, we define the free energy of the system. The basic hypothesis is that the amount of compounds  $B_j$  is much smaller than amount of initial components  $A_i$ . Following this hypothesis, we neglect the energy of compound interactions (which is quadratic in their concentrations), take the energy of their interaction with  $A_i$  in the linear approximation, and use the perfect entropy for  $B_i$ . These standard assumptions for a small admixtures give for the free energy:

$$F = Vf(c, T) + VRT \sum_{j=1}^q \zeta_j \left( \frac{u_j(c, T)}{RT} + \ln \zeta_j - 1 \right) \quad (4.1.5)$$

Let us introduce a *standard equilibrium* concentration for  $B_j$ . Due to the Boltzmann distribution ( $\exp(-u/RT)$ ) and formula (4.1.5)

$$\zeta_j^*(c, T) = \frac{1}{Z} \exp\left(-\frac{u_j(c, T)}{RT}\right), \quad (4.1.6)$$

where  $1/Z$  is the normalization factor. Let us select here the normalization  $Z = 1$  and write:

$$F = Vf(c, T) + VRT \sum_{j=1}^q \zeta_j \left( \ln \left( \frac{\zeta_j}{\zeta_j^*(c, T)} \right) - 1 \right). \quad (4.1.7)$$

We assume that the standard equilibrium concentrations  $\zeta_j^*(c, T)$  are much smaller than the concentrations of  $A_i$ . It is always possible because functions  $u_j$  are defined up to an additive constant.

The formula for free energy is necessary to define the fast equilibria (4.1.2). Such an equilibrium is the minimizer of the free energy on the straight line parameterized by  $a$ :  $c_i = c_i^0 - av_{ji}$ ,  $\zeta_j = a$ .

If we neglect the products  $\zeta_j \partial \zeta_j^*(c, T) / \partial c_i$  as the second order small quantities then the minimizers have the very simple form:

$$\vartheta_j = \sum_i v_{ji} \frac{\mu_i(c, T)}{RT}, \quad (4.1.8)$$

or

$$\zeta_j = \zeta_j^*(c, T) \exp\left(\frac{\sum_i v_{ji} \mu_i(c, T)}{RT}\right), \quad (4.1.9)$$

where

$$\mu_i = \frac{\partial f(c, T)}{\partial c_i}$$

is the chemical potential of  $A_i$  and

$$\vartheta_j = \ln \left( \frac{\zeta_j}{\zeta_j^*} \right)$$

( $RT\vartheta_j = \frac{1}{V} \frac{\partial F}{\partial \zeta_j}$  is the chemical potential of  $B_j$ ).

The thermodynamic equilibrium of the system of reactions  $B_j \rightarrow B_l$  that corresponds to the reactions (4.1.3) is the free energy minimizer under given values

of the conservation laws.

For the systems with fixed volume, the *stoichiometric conservation laws* of the monomolecular system of reactions are sums of the concentrations of  $B_j$  which belong to various connected components of the reaction graph. Under the hypothesis of weak reversibility there is no other conservation law.

Let the graph of reactions  $B_j \rightarrow B_l$  have  $d$  connected components  $C_s$  and let  $V_s$  be the set of indexes of those  $B_j$  which belong to  $C_s$ :  $B_j \in C_s$  if and only if  $j \in V_s$ . For each  $C_s$  there exists a stoichiometric conservation law

$$\beta_s = \sum_{j \in V_s} \zeta_j. \quad (4.1.10)$$

For any set of positive values of  $\beta_s$  ( $s = 1, \dots, d$ ) and given  $c, T$  there exists a unique conditional maximizer  $\zeta_j^{\text{eq}}$  of the free energy (4.1.7): for the compound  $B_j$  from the  $s$ th connected component ( $j \in V_s$ ) this equilibrium concentration is

$$\zeta_j^{\text{eq}} = \beta_s \frac{\zeta_j^*(c, T)}{\sum_{l \in V_s} \zeta_l^*(c, T)} \quad (4.1.11)$$

Inverse, positive values of concentrations  $\zeta_j$  are the equilibrium concentrations (4.1.11) for some values of  $\beta_s$  if and only if for any  $s = 1, \dots, d$

$$\vartheta_j = \vartheta_l \text{ if } j, l \in V_s \quad (4.1.12)$$

( $\vartheta_j = \ln(\zeta_j/\zeta_j^*)$ ). This system of equations together with the equilibrium conditions (4.1.9) constitute the equilibrium of the systems. All the equilibria form a linear subspace in the space with coordinates  $\mu_i/RT$  ( $i = 1, \dots, n$ ) and  $\vartheta_j$  ( $j = 1, \dots, q$ ).

Our expression for the free energy (4.1.7) does not assume anything special about free energy of the mixture of  $A_i$ . The density of this free energy  $f(c, T)$  may be arbitrary (later, we will add the standard assumption about convexity of  $f(c, T)$  as a function of  $c$ ). For the compounds  $B_i$ , we assume that this is a very small addition to the mixture of  $A_i$ , neglect all quadratic terms in concentrations of  $B_i$  and use the entropy of the perfect systems ( $p \ln p$ ) for this small admixture.

This approach results in the explicit expressions for the fast equilibria (4.1.9)

and expression of the equilibrium compound concentrations through the values of the stoichiometric conservation laws (4.1.11).

#### 4.1.4 Markov Kinetics of Compounds

For the kinetics of compounds transformations  $B_j \rightarrow B_l$  the same hypothesis of the smallness of concentrations leads to the only reasonable assumption: the linear (monomolecular) kinetics with the rate constant  $\kappa_{lj} > 0$ . This "constant" is a function of  $c, T$ :  $\kappa_{lj}(c, T)$ . The order of indexes at  $\kappa$  is inverse to the order of them in reaction:  $\kappa_{lj} = \kappa_{l \leftarrow j}$ .

The Master Equation for the concentration of  $B_j$  gives:

$$\frac{d\zeta_j}{dt} = \sum_{l, l \neq j} (\kappa_{jl}\zeta_l - \kappa_{lj}\zeta_j) . \quad (4.1.13)$$

The crucial question arises: when does this kinetics respect thermodynamics? This means: when does the free energy decrease due to the system (4.1.13)?

The necessary and sufficient condition for matching the kinetics and thermodynamics is: the standard equilibrium  $\zeta^*$  (4.1.6) should be an equilibrium for (4.1.13), that is, for every  $j = 1, \dots, q$

$$\sum_{l, l \neq j} \kappa_{jl}\zeta_l^* = \sum_{l, l \neq j} \kappa_{lj}\zeta_j^* . \quad (4.1.14)$$

This condition is necessary because the standard equilibrium is the free energy minimizer for given  $c, T$  and  $\sum_j \zeta_j = \sum_j \zeta_j^*$ . The sum  $\sum_j \zeta_j$  conserves due to (4.1.13). Therefore, if we assume that  $F$  decreases monotonically due to (4.1.13) then the point of conditional minimum of  $F$  on the plane  $\sum_j \zeta_j = const$  (under given  $c, T$ ) should be an equilibrium point for this kinetic system.

To prove the sufficiency of this condition, let us calculate the time derivative  $dF/dt$  due to (4.1.13). For calculation of this derivative, another equivalent form of (4.1.13) is convenient. Let us use the equilibrium condition (4.1.14) and write

$$\sum_{l, l \neq j} \kappa_{lj}\zeta_j = \left( \sum_{l, l \neq j} \kappa_{lj}\zeta_j^* \right) \frac{\zeta_j}{\zeta_j^*} = \sum_{l, l \neq j} \kappa_{jl}\zeta_l^* \frac{\zeta_j}{\zeta_j^*} .$$

Therefore, under condition (4.1.14) the Master Equation (4.1.13) has the equivalent form:

$$\frac{d\zeta_j}{dt} = \sum_{l, l \neq j} \kappa_{jl} \zeta_l^* \left( \frac{\zeta_l}{\zeta_l^*} - \frac{\zeta_j}{\zeta_j^*} \right). \quad (4.1.15)$$

In this form, it is obvious that  $\zeta_j^*$  is equilibrium for the kinetic equation.

To demonstrate negativity of  $dF/dt$ , we will present a bit more general expression. Let  $h(x)$  be a smooth convex function on the positive real axis. A Csiszár–Morimoto function  $H_h(\zeta)$  is (see the review [31]):

$$H_h(\zeta) = \sum_l \zeta_l^* h \left( \frac{\zeta_l}{\zeta_l^*} \right).$$

The time derivative of  $H_h(\zeta)$  due to (4.1.13) under condition (4.1.14) is:

$$\begin{aligned} & \frac{dH_h(\zeta)}{dt} \\ &= \sum_{l, j, j \neq l} h' \left( \frac{\zeta_j}{\zeta_j^*} \right) \kappa_{jl} \zeta_l^* \left( \frac{\zeta_l}{\zeta_l^*} - \frac{\zeta_j}{\zeta_j^*} \right) \\ &= \sum_{l, j, j \neq l} \kappa_{jl} \zeta_l^* \left[ h \left( \frac{\zeta_j}{\zeta_j^*} \right) - h \left( \frac{\zeta_l}{\zeta_l^*} \right) + h' \left( \frac{\zeta_j}{\zeta_j^*} \right) \left( \frac{\zeta_l}{\zeta_l^*} - \frac{\zeta_j}{\zeta_j^*} \right) \right] \leq 0. \end{aligned} \quad (4.1.16)$$

To prove this formula for  $dH/dt$  it is necessary to mention that for any  $q$  numbers  $h_i$ ,  $\sum_{i, j, j \neq i} \kappa_{ij} \zeta_j^* (h_j - h_i) = 0$ . The last inequality in (4.1.16) holds because of the convexity of  $h(x)$ :  $h'(x)(y - x) \leq h(y) - h(x)$  (Jensen's inequality).

For the free energy (4.1.7) we should take the Csiszár–Morimoto function  $H_h(\zeta)$  with  $h(x) = x(\ln x - 1)$ .

So, the condition (4.1.14) is necessary and sufficient for accordance between the Markov kinetics of compounds (4.1.13) and the thermodynamics of them.

**Remark:** In the condition (4.1.14) any of equilibrium states  $\zeta^{\text{eq}}$  (4.1.11) can be used. Those conditions are equivalent. To prove this equivalence let us calculate the difference between two "free energies": due to (4.1.11)

$$\begin{aligned} & \sum_j \zeta_j \left( \ln \left( \frac{\zeta_j}{\zeta_j^*} \right) - 1 \right) - \sum_j \zeta_j \left( \ln \left( \frac{\zeta_j}{\zeta_j^{\text{eq}}} \right) - 1 \right) \\ &= \sum_j \zeta_j \ln \left( \frac{\zeta_j^{\text{eq}}}{\zeta_j^*} \right) = \sum_s \beta_s(\zeta) \ln \left( \frac{\beta_s(\zeta^{\text{eq}})}{\beta_s(\zeta^*)} \right), \end{aligned} \quad (4.1.17)$$

where  $\beta_s(\zeta) = \sum_{j \in V_s} \zeta_j$  (4.1.10) and  $V_s$  corresponds to the connected components of the graph of compounds transformations. The result is constant in time for the Master Equation, hence, these functionals are equivalent: they both either are the Lyapunov functions for (4.1.13) or are not, simultaneously.

#### 4.1.5 Thermodynamics and Kinetics of the Extended System

In this section, we consider the complete extended system, which consists of species  $A_i$  ( $i = 1, \dots, n$ ) and compounds  $B_j$  ( $j = 1, \dots, q$ ) and includes reaction of equilibration (4.1.2) and transformations of compounds  $B_j \rightarrow B_l$  which correspond to the reactions (4.1.3).

Thermodynamic properties of the system are summarized in the free energy function (4.1.7). For kinetics of compounds we accept the Markov model (4.1.13) with the equilibrium condition (4.1.14), which guarantees matching between thermodynamics and kinetics.

For the equilibration reactions (4.1.2) we select a very general form of the kinetic law. The only requirement is: this reaction should go to its equilibrium, which is described as the conditional minimizer of free energy  $F$  (4.1.9). For each reaction  $\Theta_j \rightleftharpoons B_j$  (where the complex is a formal combination:  $\Theta_j = \sum_i v_{ji} A_i$ ) we introduce the reaction rate  $w_j$ . This rate should be positive if

$$\vartheta_j < \sum_i v_{ji} \frac{\mu_i(c, T)}{RT} \quad (4.1.18)$$

and negative if

$$\vartheta_j > \sum_i v_{ji} \frac{\mu_i(c, T)}{RT}. \quad (4.1.19)$$

The general way to satisfy these requirement is to select  $q$  continuous function of real variable  $w_j(x)$ , which are negative if  $x > 0$  and positive if  $x < 0$ . For the equilibration rates we take

$$w_j = w_j \left( \vartheta_j - \sum_i v_{ji} \frac{\mu_i(c, T)}{RT} \right). \quad (4.1.20)$$

If several dynamical systems defined by equations  $\dot{x} = J_1, \dots, \dot{x} = J_v$  on the

same space have the same Lyapunov function  $F$ , then for any conic combination  $J = \sum_k a_k J_k$  ( $a_k \geq 0$ ,  $\sum_k a_k > 0$ ) the dynamical system  $\dot{x} = J$  also has the Lyapunov function  $F$ .

The free energy (4.1.7) decreases monotonically due to any reaction  $\Theta_j \rightleftharpoons B_j$  with reaction rate  $w_j$  (4.1.20) and also due to the Markov kinetics (4.1.13) with the equilibrium condition (4.1.14). Therefore, the free energy decreases monotonically due to the following kinetic system:

$$\begin{aligned} \frac{dc_i}{dt} &= - \sum_{j=1}^q \nu_{ji} w_j; \\ \frac{d\zeta_j}{dt} &= w_j + \sum_{l, l \neq j} (\kappa_{jl} \zeta_l - \kappa_{lj} \zeta_j), \end{aligned} \tag{4.1.21}$$

where the coefficients  $\kappa_{jl}$  satisfy the matching condition (4.1.14).

This general system (4.1.21) describes kinetics of extended system and satisfies all the basic conditions (thermodynamics and smallness of compound concentrations). In the next Sections we will study the QE approximations to this system and exclude the unknown functions  $w_j$  from it.

#### 4.1.6 QE Elimination of Compounds and the Complex Balance Condition

In this section, we use the QE formalism developed for chemical kinetics in Section 2.2.1 for simplification of the compound kinetics.

First of all, let us describe  $L^\perp$ , where the space  $L$  is the subspace in the extended concentration space spanned by the stoichiometric vectors of fast equilibration reactions (4.1.2). The stoichiometric vector for the equilibration reactions have a very special structure (4.1.4). Dimension of the space  $L$  is equal to the number of complexes:  $\dim L = q$ . Therefore, dimension of  $L^\perp$  is equal to the number of components  $A_i$ :  $\dim L^\perp = n$ . For each  $A_i$  we will find a vector  $b_i \in L^\perp$  that has the following first  $n$  coordinates:  $b_{ik} = \delta_{ik}$  for  $k = 1, \dots, n$ . The condition

$(b_i, g_j) = 0$  gives immediately:  $b_{i,n+j} = v_{ji}$ . Finally,

$$b_i = \underbrace{(0, \dots, 0, 1, 0, \dots, 0)}_i, v_{1i}, v_{2i}, \dots, v_{qi} \quad (4.1.22)$$

The correspondent slow variables are

$$b_i(c, \zeta) = c_i + \sum_j \zeta_j v_{ji}. \quad (4.1.23)$$

In the QE approximation all  $w_j = 0$  and the kinetic equations (4.1.21) give in this approximation

$$\frac{db_i}{dt} = \sum_{lj, l \neq j} (\kappa_{jl} \zeta_l - \kappa_{lj} \zeta_j) v_{ji}. \quad (4.1.24)$$

In these equations, we have to use the dependence  $\zeta(b)$ . Here we use the QSS Michaelis and Menten assumption: the compounds are present in small amounts,

$$c_i \gg \zeta_j.$$

In this case, we can take  $b_i$  instead of  $c_i$  (i.e. take  $\mu(b, T)$  instead of  $\mu(c, T)$ ) in the formulas for equilibria (4.1.9):

$$\zeta_j = \zeta_j^*(b, T) \exp\left(\frac{\sum_i v_{ji} \mu_i(b, T)}{RT}\right). \quad (4.1.25)$$

In the final form of the QE kinetic equation there remain two "offprints" of the compound kinetics: two sets of functions  $\zeta_j^*(b, T) \geq 0$  and  $\kappa_{jl}(b, T) \geq 0$ . These functions are connected by the identity (4.1.14). The final form of the equations is

$$\begin{aligned} \frac{db_i}{dt} = \sum_{lj, l \neq j} & \left( \kappa_{jl} \zeta_l^*(b, T) \exp\left(\frac{\sum_i v_{li} \mu_i(b, T)}{RT}\right) \right. \\ & \left. - \kappa_{lj} \zeta_j^*(b, T) \exp\left(\frac{\sum_i v_{ji} \mu_i(b, T)}{RT}\right) \right) v_{ji}. \end{aligned} \quad (4.1.26)$$

The identity (4.1.14),  $\sum_{l, l \neq j} \kappa_{jl} \zeta_l^* = \sum_{l, l \neq j} \kappa_{lj} \zeta_j^*$ , provides a sufficient condition for decreasing of free energy due to the kinetic equations (4.1.26). This is a direct consequence of the theorem about the preservation of entropy production in the

QE approximations (see Section 2.5). In addition, in the next Section we give the explicit formula for entropy production in (4.1.26) and direct proof of its positivity.

Let us stress that the functions  $\zeta_j^*(b, T)$  and  $\kappa_{jl}(b, T)$  participate in equations (4.1.26) and in identity (4.1.14) in the form of the product. Below we use for this product a special notation:

$$\varphi_{jl}(b, T) = \kappa_{jl}(b, T)\zeta_l^*(b, T), \quad (j \neq l). \quad (4.1.27)$$

We call this function  $\varphi_{jl}(b, T)$  the *kinetic factor*. The identity (4.1.14) for the kinetic factor is

$$\sum_{l, l \neq j} \varphi_{jl}(b, T) = \sum_{l, l \neq j} \varphi_{lj}(b, T) \quad \text{for all } j \neq l. \quad (4.1.28)$$

We call the *thermodynamic factor* (or the Boltzmann factor) the second multiplier in the reaction rates,

$$\Omega_l(b, T) = \exp\left(\frac{\sum_i \nu_{li}\mu_i(b, T)}{RT}\right). \quad (4.1.29)$$

In this notation, the kinetic equations (4.1.26) have a simple form

$$\frac{db_i}{dt} = \sum_{l, l \neq j} (\varphi_{jl}(b, T)\Omega_l(b, T) - \varphi_{lj}(b, T)\Omega_j(b, T))\nu_{ji}. \quad (4.1.30)$$

The general equations (4.1.30) have the form of "sum over complexes". Let us return to the more usual "sum over reactions" form. An elementary reaction corresponds to the pair of complexes  $\Theta_l, \Theta_j$  (4.1.3). It has the form  $\Theta_l \rightarrow \Theta_j$  and the reaction rate is  $r = \varphi_{jl}\Omega_l$ . In the right hand side in (4.1.30) this reaction appears two times: one time with sign '+' and the vector coefficient  $\nu_j$  and the second time with sign '-' and the vector coefficient  $\nu_l$ . The stoichiometric vector of this reaction is  $\gamma = \nu_j - \nu_l$ . Let us enumerate the elementary reactions by index  $\rho$ , which corresponds to the pair  $(j, l)$ . Finally, we transform (4.1.3) into

the sum over reactions form

$$\begin{aligned}\frac{db_i}{dt} &= \sum_{lj, l \neq j} \varphi_{jl}(b, T) \Omega_l(b, T) (v_{ji} - v_{li}) \\ &= \sum_{\rho} \varphi_{\rho}(b, T) \Omega_{\rho}(b, T) \gamma_{\rho i}.\end{aligned}\tag{4.1.31}$$

In the vector form it looks as follows:

$$\frac{db}{dt} = \sum_{\rho} \varphi_{\rho}(b, T) \Omega_{\rho}(b, T) \gamma_{\rho}.\tag{4.1.32}$$

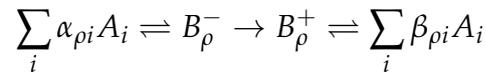
Stueckelberg [59] introduced fast intermediates with Markov kinetics for the Boltzmann equation, deduced the formula (4.1.28) for this case and demonstrated that it implies the  $H$ -theorems without hypothesis about microreversibility. He used the language of  $S$ -matrix and channels and called the conservation of probability “the unitarity of the  $S$ -matrix”.

Horn and Jackson [25] found independently the analogue of the Stueckelberg conditions (4.1.28) for the general mass action kinetics and called them the complex balance condition.

### 4.1.7 The Big Michaelis–Menten–Stueckelberg Theorem

Let us summarize the results of our analysis in one statement.

Let us consider the reaction mechanism illustrated by Figure. 4.2 (4.1.3):



under the following assumptions:

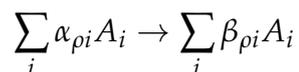
1. Concentrations of the compounds  $B_{\rho}$  are much smaller than the concentrations of the components  $A_i$  ( $\zeta_{\rho} < \varepsilon c_i$ ,  $\varepsilon \ll 1$ );
2. Concentrations of the compounds  $B_{\rho}$  are close to their quasiequilibrium values (4.1.25)

$$\zeta_j^{QE} = \zeta_j^*(b, T) \exp\left(\frac{\sum_i v_{ji} \mu_i(b, T)}{RT}\right)$$

$|\zeta_j - \zeta_j^{QE}| < \varepsilon \zeta_j^{QE}$ ,  $\varepsilon \ll 1$  (this may be due to fast reversible reactions in (4.1.3));

3. Kinetics of transitions between compounds is linear (Markov) kinetics.

Under these assumptions, kinetics of components  $A_i$  may be described with accuracy  $O(1)$  by the reaction mechanism



with the reaction rates

$$r_\rho = \varphi_\rho \exp \frac{(\alpha_\rho, \mu)}{RT}$$

where the kinetic factors  $\varphi_\rho$  satisfy the condition (4.1.28):

$$\sum_{\rho, \alpha_\rho = \mathbf{v}} \varphi_\rho \equiv \sum_{\rho, \beta_\rho = \mathbf{v}} \varphi_\rho$$

for any vector  $\mathbf{v}$  from the set of vectors  $\{\alpha_\rho, \beta_\rho\}$ . This statement includes the generalized mass action law for  $r_\rho$  and the balance identity for kinetic factors that is sufficient for the entropy growth as it is shown in the next Section 4.2.

## 4.2 General Kinetics and Thermodynamics

### 4.2.1 General Formalism

To produce the general kinetic law and the complex balance conditions, we use “construction staging”: the intermediate complexes with fast equilibria, the Markov kinetics and other important and interesting physical and chemical hypothesis.

In this section, we delete these construction staging and start from the forms (4.1.29), (4.1.32) as the basic laws. We use also the complex balance conditions (4.1.28) as a hint for the general conditions which guarantee accordance between kinetics and thermodynamics.

Let us consider a domain  $U$  in  $n$ -dimensional real vector space  $E$  with coordinates  $N_1, \dots, N_n$ . For each  $N_i$  a symbol (component)  $A_i$  is given. A dimension-

less entropy (or *free entropy*, for example, Massieu, Planck, or Massieu–Planck potential which correspond to the selected conditions [14])  $S(N)$  is defined in  $U$ . ‘Dimensionless’ means that we use  $S/R$  instead of physical  $S$ . This choice of units corresponds to the informational entropy ( $p \ln p$  instead of  $k_B p \ln p$ ).

The dual variables, potentials, are defined as the partial derivatives of  $S$ :

$$\check{\mu}_i = -\frac{\partial S}{\partial N_i} \quad (4.2.1)$$

**Warning:** this definition differs from the chemical potentials (5.2.1) by the factor  $1/RT$ : for constant volume the Massieu–Planck potential is  $-F/T$  and we, in addition, divide it on  $R$ . On the other hand, we keep the same sign as for the chemical potentials, and this differs from the standard Legendre transform for  $S$ . (It is the Legendre transform for a function  $-S$ ).

The reaction mechanism is defined by the stoichiometric equations (2.2.4)

$$\sum_i \alpha_{\rho i} A_i \rightarrow \sum_i \beta_{\rho i} A_i$$

( $\rho = 1, \dots, m$ ). In general, there is no need to assume that the stoichiometric coefficients  $\alpha_{\rho i}, \beta_{\rho i}$  are integers.

The assumption that they are nonnegative,  $\alpha_{\rho i} \geq 0, \beta_{\rho i} \geq 0$ , may be needed to prove that the kinetic equations preserve positivity of  $N_i$ . If  $N_i$  is the number of particles then it is a natural assumption but we can use other extensive variables instead, for example, we included energy in the list of variables to describe the non-isothermal processes [9]. In this case, the coefficient  $\alpha_U$  for the energy component  $A_U$  in an exothermic reaction is negative.

So, for variables that are positive (bounded from below) by their physical sense, we will use the inequalities  $\alpha_{\rho i} \geq 0, \beta_{\rho i} \geq 0$ , when necessary, but in general, for arbitrary extensive variables, we do not assume positivity of stoichiometric coefficients. As it is usually, the stoichiometric vector of reaction is  $\gamma_\rho = \beta_\rho - \alpha_\rho$  (the “gain minus loss” vector).

For each reaction, a *nonnegative* quantity, reaction rate  $r_\rho$  is defined. We assume that this quantity has the following structure:

$$r_\rho = \varphi_\rho \exp(\alpha_\rho, \check{\mu}). \quad (4.2.2)$$

where  $(\alpha_\rho, \check{\mu}) = \sum_i \alpha_{\rho i} \check{\mu}_i$ .

In the standard formalism of chemical kinetics the reaction rates are intensive variables and in kinetic equations for  $N$  an additional factor appears, the volume. For heterogeneous systems, there may be several ‘volumes’ (including interphase surfaces).

Each reaction has its own ‘volume’, an extensive variable  $V_\rho$  (some of them usually coincide), and we can write

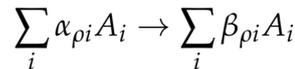
$$\frac{dN}{dt} = \sum_\rho V_\rho \gamma_\rho \varphi_\rho \exp(\alpha_\rho, \check{\mu}). \quad (4.2.3)$$

In these notations, both the kinetic and the Boltzmann factors are intensive (and local) characteristics of the system.

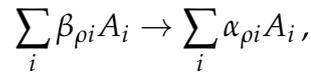
Let us, for simplicity of notations, consider a system with one volume,  $V$  and write

$$\frac{dN}{dt} = V \sum_\rho \gamma_\rho \varphi_\rho \exp(\alpha_\rho, \check{\mu}). \quad (4.2.4)$$

Below we use the form (4.2.4). All our results will hold also for the multi-volume systems (4.2.3) under one important assumption: the elementary reaction



goes in the same volume as the reverse reaction



or symbolically,

$$V_\rho^+ = V_\rho^-. \quad (4.2.5)$$

If this condition (4.2.5) holds then the detailed balance conditions and the complex balance conditions will hold separately in all volumes  $V_\rho$ .

An important particular case of (4.2.4) gives us the Mass Action Law. Let us take the perfect free entropy

$$S = - \sum_i N_i \left( \ln \left( \frac{c_i}{c_i^*} \right) - 1 \right), \quad (4.2.6)$$

where  $c_i = N_i/V \geq 0$  are concentrations and  $c_i^* > 0$  are the standard equilibrium concentrations. Under isochoric conditions,  $V = \text{const}$ , there is no difference between the choice of the main variables,  $N$  or  $c$ .

For the perfect function (4.2.6),

$$\check{\mu}_i = \ln \left( \frac{c_i}{c_i^*} \right), \quad \exp(\alpha_\rho, \check{\mu}) = \prod_i \left( \frac{c_i}{c_i^*} \right)^{\alpha_{\rho i}} \quad (4.2.7)$$

and for the reaction rate function (4.2.2) we get

$$r_\rho = \varphi_\rho \prod_i \left( \frac{c_i}{c_i^*} \right)^{\alpha_{\rho i}}. \quad (4.2.8)$$

The standard assumption for the Mass Action Law in physics and chemistry is that  $\varphi$  and  $c^*$  are functions of temperature:  $\varphi_\rho = \varphi_\rho(T)$  and  $c_i^* = c_i^*(T)$ . To return to the kinetic constants notation (2.2.7) we should write:

$$\frac{\varphi_\rho}{\prod_i c_i^{*\alpha_{\rho i}}} = k_\rho$$

Equation (4.2.4) is the general form of the kinetic equation we would like to study. In many senses, this form is too general before we impose restrictions on the values of the kinetic factors. For physical and chemical systems, thermodynamics is a source of restrictions:

1. The energy of the Universe is constant.
2. The entropy of the Universe tends to a maximum.

(R. Clausius, 1865 [15].)

The first sentence should be extended: the kinetic equations should respect several conservation laws: energy, amount of atoms of each kind (if there is no nuclear reactions in the system) conservation of total probability and, sometimes, some other conservation laws. All of them have the form of conservation of values of some linear functionals:  $l(N) = \text{const}$ . If the input and output flows are added to the system then

$$\frac{dl(N)}{dt} = Vv^{\text{in}}l^{\text{in}} - v^{\text{out}}l(N),$$

where  $v^{\text{in,out}}$  are the input and output fluxes per unit volume,  $l^{\text{in}}$  are the input densities (concentration). The standard requirement is that every reaction respects all these conservation laws. The formal expression of this requirement is:

$$l(\gamma_\rho) = 0 \text{ for all } \rho. \quad (4.2.9)$$

There is a special term for these conservation laws: the *stoichiometric conservation laws*. All the main conservation laws are assumed to be the stoichiometric ones.

Analysis of the stoichiometric conservation laws is a simple linear algebra task: we have to find the linear functionals that annulate all the stoichiometric vectors  $\gamma_\rho$ . In contrast, entropy is not a linear function of  $N$  and analysis of entropy production is not so simple.

In the next Subsection we discuss various conditions which guarantee the positivity of entropy production in kinetic equations (4.2.4).

## 4.2.2 Accordance Between Kinetics and Thermodynamics

### General Entropy Production Formula

Let us calculate  $dS/dt$  due to equations (4.2.4):

$$\frac{dS}{dt} = -V \sum_{\rho} (\gamma_{\rho}, \check{\mu}) \varphi_{\rho} \exp(\alpha_{\rho}, \check{\mu}). \quad (4.2.10)$$

An auxiliary function  $\theta(\lambda)$  of one variable  $\lambda \in [0, 1]$  is convenient for analysis of  $dS/dt$ :

$$\theta(\lambda) = \sum_{\rho} \varphi_{\rho} \exp[(\check{\mu}, (\lambda\alpha_{\rho} + (1 - \lambda)\beta_{\rho}))]. \quad (4.2.11)$$

With this function, the entropy production (4.2.10) has a very simple form:

$$\frac{dS}{dt} = V \left. \frac{d\theta(\lambda)}{d\lambda} \right|_{\lambda=1} \quad (4.2.12)$$

The auxiliary function  $\theta(\lambda)$  allows the following interpretation. Let us intro-

duce the deformed stoichiometric mechanism with the stoichiometric vectors

$$\alpha_\rho(\lambda) = \lambda\alpha_\rho + (1 - \lambda)\beta_\rho, \beta_\rho(\lambda) = \lambda\beta_\rho + (1 - \lambda)\alpha_\rho.$$

For  $\lambda = 1$ , this is the initial mechanism, for  $\lambda = 0$  this is an inverted mechanism with interchange of  $\alpha$  and  $\beta$ , for  $\lambda = 1/2$  this is a trivial mechanism (the left and right hand sides of the stoichiometric equations coincide).

For the deformed mechanism, let us take the same kinetic factors and calculate the Boltzmann factors with  $\alpha_\rho(\lambda)$ :

$$r_\rho(\lambda) = \varphi_\rho \exp(\alpha_\rho(\lambda), \check{\mu}).$$

In this notation, the auxiliary function  $\theta(\lambda)$  is a sum of reaction rates for the deformed reaction mechanism:

$$\theta(\lambda) = \sum_\rho r_\rho(\lambda).$$

In particular,  $\theta(1) = \sum_\rho r_\rho$ , this is just the sum of reaction rates.

Function  $\theta(\lambda)$  is convex. Indeed,

$$\frac{d^2\theta(\lambda)}{d\lambda^2} = \sum_\rho \varphi_\rho (\gamma_\rho, \check{\mu})^2 \exp[(\check{\mu}, (\lambda\alpha_\rho + (1 - \lambda)\beta_\rho))] \geq 0.$$

This convexity gives the following *necessary and sufficient condition for positivity of entropy production*:

$$\frac{dS}{dt} > 0 \text{ if and only if } \theta(\lambda) < \theta(1) \text{ for some } \lambda < 1.$$

In several next subsections we study various important particular sufficient conditions for positivity of entropy production.

### Detailed Balance

The most celebrated condition which gives the positivity of entropy production is the principle of detailed balance. Boltzmann used this principle to prove his

famous  $H$ -theorem [10].

Let us join elementary reactions in pairs:

$$\sum_i \alpha_{\rho i} A_i \rightleftharpoons \sum_i \beta_{\rho i} A_i. \quad (4.2.13)$$

After this joining, the total amount of stoichiometric equations decreases. If there is no reverse reaction then we can add it formally, with zero kinetic factor. The reaction rates and kinetic factors for direct and inverse reactions we will distinguish by the upper plus or minus:

$$r_\rho^+ = \varphi_\rho^+ \exp(\alpha_\rho, \check{\mu}), \quad r_\rho^- = \varphi_\rho^- \exp(\beta_\rho, \check{\mu}), \quad r_\rho = r_\rho^+ - r_\rho^-.$$

$$\frac{dN}{dt} = V \sum_\rho \gamma_\rho r_\rho. \quad (4.2.14)$$

In this notation, the principle of detailed balance is very simple: the thermodynamic equilibrium in the direction  $\gamma_\rho$ , given by the standard condition  $(\gamma_\rho, \check{\mu}) = 0$ , is equilibrium for the correspondent pair of mutually reverse reactions from (4.2.13). For kinetic factors this transforms into the simple and beautiful condition:

$$\varphi_\rho^+ \exp(\alpha_\rho, \check{\mu}) = \varphi_\rho^- \exp(\beta_\rho, \check{\mu}) \Leftrightarrow (\gamma_\rho, \check{\mu}) = 0,$$

therefore

$$\varphi_\rho^+ = \varphi_\rho^-. \quad (4.2.15)$$

For the systems with detailed balance we can take  $\varphi_\rho = \varphi_\rho^+ = \varphi_\rho^-$  and write for the reaction rate:

$$r_\rho = \varphi_\rho (\exp(\alpha_\rho, \check{\mu}) - \exp(\beta_\rho, \check{\mu})).$$

M. Feinberg called this kinetic law the ‘‘Marselin–De Donder’’ kinetics [48]. This representation of the reaction rates gives for the auxiliary function  $\theta(\lambda)$ :

$$\begin{aligned} \theta(\lambda) = \sum_\rho \varphi_\rho & (\exp[(\check{\mu}, (\lambda\alpha_\rho + (1-\lambda)\beta_\rho))] \\ & + \exp[(\check{\mu}, (\lambda\beta_\rho + (1-\lambda)\alpha_\rho))]). \end{aligned} \quad (4.2.16)$$

Each term in this sum is symmetric with respect to change  $\lambda \mapsto (1-\lambda)$ . There-

fore,  $\theta(1) = \theta(0)$  and, because of convexity of  $\theta(\lambda)$ ,  $\theta'(1) \geq 0$ . This means positivity of entropy production.

The principle of detailed balance is a sufficient but not a necessary condition of the positivity of entropy production. This was clearly explained, for example, by L. Onsager [44]. Interrelations between positivity of entropy production, Onsager reciprocal relations and detailed balance were analyzed in detail by N.G. van Kampen [52].

### Complex Balance

The principle of detailed balance gives us  $\theta(1) = \theta(0)$  and this equality holds for each pair of mutually reverse reactions.

Let us start now from the equality  $\theta(1) = \theta(0)$ . We return to the initial stoichiometric equations (2.2.4) without joining of direct and reverse reactions. The equality reads

$$\sum_{\rho} \varphi_{\rho} \exp(\check{\mu}, \alpha_{\rho}) = \sum_{\rho} \varphi_{\rho} \exp(\check{\mu}, \beta_{\rho}). \quad (4.2.17)$$

Exponential functions  $\exp(\check{\mu}, y)$  form linearly independent family in the space of functions of  $\check{\mu}$  for any finite set of pairwise different vectors  $y$ . Therefore, the following approach is natural: let us equalize in (4.2.17) the terms with the same Boltzmann-type factor  $\exp(\check{\mu}, y)$ . Here we have to return to the complex-based representation of reactions (see Section 4.1.1).

Let us consider the family of vectors  $\{\alpha_{\rho}, \beta_{\rho}\}$  ( $\rho = 1, \dots, m$ ). Usually, some of these vectors coincide. Assume that there are  $q$  different vectors among them. Let  $y_1, \dots, y_q$  be these vectors. For each  $j = 1, \dots, q$  we take

$$R_j^+ = \{\rho \mid \alpha_{\rho} = y_j\}, \quad R_j^- = \{\rho \mid \beta_{\rho} = y_j\}.$$

We can rewrite the equality (4.2.17) in the form

$$\sum_{j=1}^q \exp(\check{\mu}, y_j) \left[ \sum_{\rho \in R_j^+} \varphi_{\rho} - \sum_{\rho \in R_j^-} \varphi_{\rho} \right] = 0. \quad (4.2.18)$$

The Boltzmann factors  $\exp(\check{\mu}, y_j)$  form the linearly independent set. Therefore

the natural way to meet these condition is: for any  $j = 1, \dots, q$

$$\sum_{\rho \in R_j^+} \varphi_\rho - \sum_{\rho \in R_j^-} \varphi_\rho = 0. \quad (4.2.19)$$

This is the general *complex balance condition*. This condition is sufficient for entropy growth, because it provides the equality  $\theta(1) = \theta(0)$ .

If we assume that  $\varphi_\rho$  are constants or, for chemical kinetics, depend only on temperature, then the conditions (4.2.19) give the general solution to equation (4.2.18).

Is the complex balance condition more general than the detailed balance? Yes, and this is obvious: for the Master equation (4.1.13) the complex balance condition is trivially valid for all admissible constants. The first order kinetics always satisfies the complex balance conditions. On the contrary, the class of the Master equations with detailed balance is rather special. The class of all Master equations has dimension  $n^2 - n$  (constants for all transitions  $A_i \rightarrow A_j$  are independent). For the time-reversible Markov chains (the Master equations with detailed balance) there is only  $n(n+1)/2 - 1$  independent constants:  $n - 1$  for equilibrium state and  $n(n-1)/2$  for transitions  $A_i \rightarrow A_j$  ( $i > j$ ), because for reverse transitions the constant can be calculated through the detailed balance.

Is the complex balance condition necessary for entropy growth? In general, for nonlinear reaction systems, it is not. In the next Section we will give a more general condition and demonstrate that there are systems that violate the complex balance condition, but satisfy this more general inequality.

### G-Inequality

Gorban [30] proposed the following inequality for analysis of accordance between thermodynamics and kinetics:  $\theta(1) \geq \theta(0)$ . This means that for any values of  $\check{\mu}$

$$\sum_{\rho} \varphi_{\rho} \exp(\check{\mu}, \alpha_{\rho}) \geq \sum_{\rho} \varphi_{\rho} \exp(\check{\mu}, \beta_{\rho}). \quad (4.2.20)$$

In the form of sum over complexes (similarly to (4.2.18)) it has the form

$$\sum_{j=1}^q \exp(\check{\mu}, y_j) \left[ \sum_{\rho \in R_j^+} \varphi_\rho - \sum_{\rho \in R_j^-} \varphi_\rho \right] \geq 0. \quad (4.2.21)$$

Let us call these inequalities, (4.2.20), (4.2.21), the G-inequalities.

Here, two remarks are needed. First, functions  $\exp(\check{\mu}, y_j)$  are linearly independent but this does not allow us to transform inequalities (4.2.21) similarly to (4.2.19) even for constant kinetic factors: inequality between linear combinations of independent functions may exist and the "simplified system",

$$\sum_{\rho \in R_j^+} \varphi_\rho - \sum_{\rho \in R_j^-} \varphi_\rho \geq 0 \text{ for all } j,$$

is not equivalent to the G-inequality.

Second, this simplified inequality is equivalent to the complex balance condition (with equality instead of  $\geq$ ). Indeed, for any  $\rho = 1, \dots, m$  there exist exactly one  $j_1$  and one  $j_2 \neq j_1$  with properties:  $\rho \in R_{j_1}^+, \rho \in R_{j_2}^-$ . Therefore, for any reaction mechanism with reaction rates (4.2.2) the identity holds:

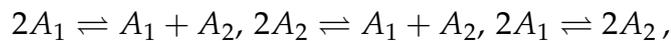
$$\sum_{\rho} \left[ \sum_{\rho \in R_{j_1}^+} \varphi_\rho - \sum_{\rho \in R_{j_2}^-} \varphi_\rho \right] = 0.$$

If all terms in this sum are non-negative then all of them are zeros.

Nevertheless, if at least one of the vectors  $y_j$  is a convex combination of others,

$$\sum_{k, k \neq j} \lambda_k y_k = y_j \text{ for some } \lambda_k \geq 0, \sum_{k, k \neq j} \lambda_k = 1,$$

then the G-inequality has more solutions than the condition of complex balance. Let us take a very simple example with two components,  $A_1$  and  $A_2$ , three reactions and three complexes:



$$y_1 = (2, 0), y_2 = (0, 2), y_3 = (1, 1),$$

$$R_1^+ = \{1, 3\}, R_2^+ = \{2, -3\}, R_3^+ = \{-1, -2\},$$

$$R_1^- = \{-1, -3\}, R_2^- = \{-2, 3\}, R_3^- = \{1, 2\}$$

The complex balance condition for this system is:

$$\begin{aligned} (\varphi_1 - \varphi_{-1}) + (\varphi_3 - \varphi_{-3}) &= 0; \\ (\varphi_2 - \varphi_{-2}) - (\varphi_3 - \varphi_{-3}) &= 0. \end{aligned} \tag{4.2.22}$$

The G-inequality for this system is

$$\begin{aligned} (\varphi_1 + \varphi_3 - \varphi_{-1} - \varphi_{-3})a^2 + (\varphi_2 + \varphi_{-3} - \varphi_{-2} - \varphi_3)b^2 \\ + (\varphi_{-1} + \varphi_{-2} - \varphi_1 - \varphi_2)ab \geq 0 \text{ for all } a, b > 0 \end{aligned} \tag{4.2.23}$$

(here,  $a, b$  stand for  $\exp(\check{\mu}_1), \exp(\check{\mu}_2)$ ). Let us use for the coefficients at  $a^2$  and  $b^2$  notations  $\psi_a$  and  $\psi_b$ . Coefficient at  $ab$  in (4.2.23) is  $-(\psi_a + \psi_b)$ , linear combinations  $\psi_a$  and  $\psi_b$  are linearly independent and we get the following task: to find all pairs  $\psi_a, \psi_b$  which satisfy the inequality

$$\psi_a a^2 + \psi_b b^2 \geq (\psi_a + \psi_b)ab \text{ for all } a, b > 0.$$

Asymptotics  $a \rightarrow 0$  and  $b \rightarrow 0$  give  $\psi_a, \psi_b \geq 0$ .

Let us use homogeneity of functions in (4.2.23), exclude one normalization factor from  $a, b$  and one factor from  $\psi_a, \psi_b$  and reduce the number of variables:  $b = 1 - a, \psi_a = 1 - \psi_b$ : we have to find all such  $\psi_b \in [0, 1]$  that for all  $a \in ]0, 1[$

$$a^2(1 - \psi_b) + (1 - a)^2\psi_b - a(1 - a) \geq 0$$

The minimizer of this quadratic function of  $a$  is  $a_{\min} = \frac{1}{4} + \frac{1}{2}\psi_b, a_{\min} \in ]0, 1[$  for all  $\psi_b \in [0, 1]$ . The minimal value is  $-2(\frac{1}{2}\psi_b - \frac{1}{4})^2$ . It is nonnegative if and only if  $\psi_b = \frac{1}{2}$ . When we return to the nonnormalized variables  $\psi_a, \psi_b$  then we get the general solution of the G-inequality for this example:  $\psi_a = \psi_b \geq 0$ . For the kinetic factors this means:

$$\begin{aligned} (\varphi_1 - \varphi_{-1}) + 2(\varphi_3 - \varphi_{-3}) - (\varphi_2 - \varphi_{-2}) &= 0; \\ (\varphi_1 - \varphi_{-1}) + (\varphi_3 - \varphi_{-3}) &\geq 0; \\ (\varphi_2 - \varphi_{-2}) - (\varphi_3 - \varphi_{-3}) &\geq 0. \end{aligned} \tag{4.2.24}$$

These conditions are wider (weaker) than the complex balance conditions for this example (4.2.22).

In the Stueckelberg language [59], the microscopic reasons for the  $G$ -inequality instead of the complex balance (4.1.28) can be explained as follows: some channels of the scattering are unknown (hidden), hence, instead of unitarity of  $S$ -matrix (conservation of the microscopic probability) we have an inequality (the microscopic probability does not increase).

We can use other values of  $\lambda_0 \in [0, 1[$  in inequality  $\theta(1) \geq \theta(\lambda_0)$  and produce constructive sufficient conditions of accordance between thermodynamics and kinetics. For example, condition  $\theta(1) \geq \theta(1/2)$  is weaker than  $\theta(1) \geq \theta(0)$  because of convexity  $\theta(\lambda)$ .

One can ask a reasonable question: why we do not use directly positivity of entropy production ( $\theta'(1) \geq 0$ ) instead of this variety of sufficient conditions. Of course, this is possible, but inequalities like  $\theta(1) \geq \theta(0)$  or equations like  $\theta(1) = \theta(0)$  include linear combinations of exponents of linear functions and often can be transformed in algebraic equations or inequalities like in the example above. Inequality  $\theta'(1) \geq 0$  includes transcendent functions like  $f \exp f$  (where  $f$  is a linear function) which make its study more difficult.

## 4.3 Linear Deformation of Entropy

### 4.3.1 Kinetics Does not Respect Thermodynamics? Deformation of Entropy May Help

Kinetic equations in the general form (4.2.4) are very general, indeed. They can be used for the approximation of any dynamical system in  $U$  [3]. In previous sections we discussed a question: with the entropy is given, how to construct the system in the form (4.2.4) with positivity of the entropy production? The reverse question is also important: the system in the form (4.2.4) is given. Could we find such a new entropy that this system guarantees positivity of this (new) entropy production?

Existence of such an entropy is very useful for analysis of stability of the system. For example, let us take an arbitrary Mass Action Law system (4.2.8). This is a

rather general system with the polynomial right hand side. Is it stable or not? May there occur bifurcations of steady states, oscillations and other interesting effects of the dynamics, or does it monotonically approach equilibrium?

With the positivity of entropy productions these questions are much simpler, and dynamics is monotonic, could not return to the vicinity of the starting point and all the non-wandering points are steady states.

For the global analysis of an arbitrary system of differential equations it is desirable either to construction a general Lyapunov function or to prove that it does not exists. For the Lyapunov functions of the general form this task may be quite difficult. Therefore, various finite-dimensional spaces of trial functions are often in use. For example, quadratic polynomials of several variables provide a very popular class of trial Lyapunov function.

In this Section, we discuss the  $n$ -parametric families of Lyapunov functions which are produced by the addition of linear function to the entropy:

$$S(N) \mapsto S_{\Delta\check{\mu}}(N) = S(N) - \sum_i \Delta\check{\mu}_i N_i \quad (4.3.1)$$

The change in potentials  $\check{\mu}$  is simply the addition of  $\Delta\check{\mu}$ :  $\check{\mu}_i \mapsto \check{\mu}_i + \Delta\check{\mu}_i$ .

Let us take a general kinetic equation (4.2.4). We do not like to change the reaction rates. The Boltzmann factor  $\Omega_\rho = \exp(\check{\mu}, \alpha_\rho)$  transforms due to the change of the entropy:  $\Omega_\rho \mapsto \Omega_\rho \exp(\Delta\check{\mu}, \alpha_\rho)$ . Therefore, the transformation of the kinetic factors should be  $\varphi_\rho \mapsto \varphi_\rho \exp(-\Delta\check{\mu}, \alpha_\rho)$  in order to keep the product  $r_\rho = \Omega_\rho \varphi_\rho$  constant.

For the new entropy,  $S = S_{\Delta\check{\mu}}$ , with the new potential and kinetic factors the entropy production is given by (4.3.2):

$$\begin{aligned} \frac{dS}{dt} &= - \sum_\rho (\gamma_\rho, \check{\mu}) \varphi_\rho \exp(\alpha_\rho, \check{\mu}) \\ &= - \sum_\rho (\gamma_\rho, \check{\mu}^{\text{old}} + \Delta\check{\mu}) \varphi_\rho^{\text{old}} \exp(\alpha_\rho, \check{\mu}^{\text{old}}) \\ &= \frac{dS^{\text{old}}}{dt} - \sum_\rho (\gamma_\rho, \Delta\check{\mu}) \varphi_\rho^{\text{old}} \exp(\alpha_\rho, \check{\mu}^{\text{old}}), \end{aligned} \quad (4.3.2)$$

where the superscript "old" corresponds to the non-deformed quantities.

### 4.3.2 How to Restore Detailed Balance by Entropy Deformation?

It may be very useful to find such a vector  $\Delta\check{\mu}$  that in new variables  $\varphi_\rho^+ = \varphi_\rho^-$ . For the analysis of the detailed balance condition, we group reactions in pairs of mutually inverse reactions (4.2.13). Let us consider an equation of the general form (4.2.14) with  $r_\rho = r_\rho^+ - r_\rho^-$ ,  $\varphi_\rho^\pm > 0$ .

The problem is: to find such a vector  $\Delta\check{\mu}$  that

$$\varphi_\rho^+ \exp(-\Delta\check{\mu}, \alpha_\rho) = \varphi_\rho^- \exp(-\Delta\check{\mu}, \beta_\rho), \quad (4.3.3)$$

or, in the equivalent form of the linear equation

$$(-\Delta\check{\mu}, \gamma_\rho) = \ln \left( \frac{\varphi_\rho^+}{\varphi_\rho^-} \right) \quad (4.3.4)$$

The necessary and sufficient conditions for the existence of such  $\Delta\check{\mu}$  are known from linear algebra: for every set of numbers  $a_\rho$  ( $\rho = 1, \dots, m$ )

$$\sum_\rho a_\rho \gamma_\rho = 0 \Rightarrow \sum_\rho a_\rho \ln \left( \frac{\varphi_\rho^+}{\varphi_\rho^-} \right) = 0 \quad (4.3.5)$$

To check these conditions, it is sufficient to find a basis of solutions of the uniform systems of linear equations

$$\sum_\rho a_\rho \gamma_{\rho i} = 0 \quad (i = 1, \dots, m)$$

(that is, to find a basis of  $\text{coim}\Gamma$ ,  $\Gamma = (\gamma_{\rho i})$ ) and then check for these basis vectors the condition  $\sum_\rho a_\rho \ln \left( \frac{\varphi_\rho^+}{\varphi_\rho^-} \right) = 0$  to prove or disprove that the vector with coordinates  $\ln \left( \frac{\varphi_\rho^+}{\varphi_\rho^-} \right)$  belongs to  $\text{im}\Gamma$ .

For some of the reaction mechanisms it is possible to restore the detailed balance condition for the general kinetic equation unconditionally. For these reactions, for any set of positive kinetic factors, there exists such a vector  $\Delta\check{\mu}$  that the detailed balance condition (4.3.4) is valid for the deformed entropy. According to (4.3.5) this means that there is no nonzero solution  $a_\rho$  for the equation

$\sum_{\rho} a_{\rho} \gamma_{\rho} = 0$ . In other words, vectors  $\gamma_{\rho}$  are independent.

### 4.3.3 How to Restore Complex Balance by Entropy Deformation?

The complex balance conditions (4.2.19) are, in general, weaker than the detailed balance but they are still sufficient for the entropy growth.

Let us consider an equation of the general form (4.2.14). We need to find such a vector  $\Delta\check{\mu}$  that in new variables with the new entropy and kinetic factors the complex balance conditions  $\sum_{\rho \in R_j^+} \varphi_{\rho}^{\text{new}} - \sum_{\rho \in R_j^-} \varphi_{\rho}^{\text{new}} = 0$  hold.

For our purpose, it is convenient to return to the presentation of reactions as transitions between complexes. The complexes,  $\Theta_1, \dots, \Theta_q$  are the linear combinations,  $\Theta_j = (y_j, A)$ .

Each elementary reaction (2.2.4) with the reaction number  $\rho$  may be represented in the form  $\Theta_j \rightarrow \Theta_l$ , where  $\Theta_j = \sum y_j A_j$ ,  $\rho \in R_j^+$  ( $\alpha_{\rho} = y_j$ ) and  $\rho \in R_j^-$  ( $\beta_{\rho} = y_l$ ). For this reaction, let us use the notation  $\varphi_{\rho} = \varphi_{lj}$ . We used this notation in the analysis of kinetics of compounds (Section 4.1.6). The complex balance conditions are

$$\sum_{j, j \neq l} (\varphi_{lj} - \varphi_{jl}) = 0. \quad (4.3.6)$$

To obtain these conditions after the entropy deformation, we have to find such  $\Delta\check{\mu}$  that

$$\sum_{j, j \neq l} (\varphi_{lj} \exp(-\Delta\check{\mu}, y_j) - \varphi_{jl} \exp(-\Delta\check{\mu}, y_l)) = 0. \quad (4.3.7)$$

This is exactly the equation for equilibrium of a Markov chain with transition coefficients  $\varphi_{lj}$ . Vector  $(-\Delta\check{\mu}, y_j)$  should be an equilibrium state for this chain (without normalization to the unit sum of coordinates).

For this finite Markov chain a graph representation is useful: vertices are complexes and oriented edges are reactions. To provide existence of a positive equilibrium we assume *weak reversibility* of the chain: if there exists an oriented path from  $\Theta_j$  to  $\Theta_l$  then there exists an oriented path from  $\Theta_l$  to  $\Theta_j$ .

Let us demonstrate how to transform this problem of entropy deformation into a linear algebra problem. First of all, let us find any positive equilibrium of the

chain,  $\zeta_j^* > 0$ :

$$\sum_{j,j \neq l} (\varphi_{lj} \zeta_j^* - \varphi_{jl} \zeta_l^*) = 0. \quad (4.3.8)$$

This is a system of linear equations. If we have already an arbitrary equilibrium of the chain then other equilibria allow a very simple description. We already found this description for kinetics of compounds (4.1.11)

Let us consider the Master equation for the Markov chain with coefficients  $\varphi_{lj}$ :

$$\frac{d\zeta}{dt} = \sum_{j,j \neq l} (\varphi_{lj} \zeta_j - \varphi_{jl} \zeta_l) = 0. \quad (4.3.9)$$

Let the graph of complex transformations  $\Theta_j \rightarrow \Theta_l$  have  $d$  connected components  $C_s$  and let  $V_s$  be the set of indexes of those  $\Theta_j$  which belong to  $C_s$ :  $\Theta_j \in C_s$  if and only if  $j \in V_s$ . For each  $C_s$  there exists a conservation law for the Master equation (4.3.9)

$$\zeta_s = \sum_{j \in V_s} \zeta_j = \text{const}. \quad (4.3.10)$$

For any set of positive values of  $\zeta_s$  ( $s = 1, \dots, q$ ) there exists a unique equilibrium vector  $\zeta^{\text{eq}}$  for (4.3.9) with this values  $\zeta_s$ :

$$\zeta_j^{\text{eq}} = \zeta_s \frac{\zeta_j^*(c, T)}{\sum_{l \in V_s} \zeta_l^*(c, T)}. \quad (4.3.11)$$

The set of equilibria is a linear space with the natural coordinates  $\zeta_s$  ( $s = 1, \dots, d$ ). We are interested in the positive ortant of this space,  $\zeta_s > 0$ . For positive  $\zeta_s$ , logarithms of  $\zeta^{\text{eq}}$  form a  $d$ -dimensional linear manifold in  $R^q$ :

$$\ln \zeta_j^{\text{eq}} = \ln \zeta_s + \ln \left( \frac{\zeta_j^*(c, T)}{\sum_{l \in V_s} \zeta_l^*(c, T)} \right). \quad (4.3.12)$$

The natural coordinates on this manifold are  $\ln \zeta_s$ .

Let us notice that the vector  $\zeta^\circ$  with coordinates

$$\zeta_j^\circ = \left( \frac{\zeta_j^*(c, T)}{\sum_{l \in V_s} \zeta_l^*(c, T)} \right) \text{ for } j \in V_s$$

is also an equilibrium for (4.3.9). The equations for  $\Delta\check{\mu}$  are

$$(-\Delta\check{\mu}, y_j) - \ln \check{\zeta}_s = \ln \zeta_j^\circ \text{ for } j \in V_s. \quad (4.3.13)$$

This is a system of linear equations with respect to  $n + d$  variables  $\Delta\check{\mu}_i$  ( $i = 1, \dots, n$ ) and  $\ln \check{\zeta}_s$  ( $s = 1, \dots, d$ ). Let the coefficient matrix of this system be denoted by  $\mathbf{M}$ .

Analysis of solutions and solvability of such equations is one of the standard linear algebra tasks. If this system has a solution then the complex balance in the original system can be restored by the linear deformation of the entropy. If this system is solvable for any right hand side, then for this reaction mechanism we always can find the entropy, which provides the complex balance condition.

Unconditional solvability of (4.3.13) means that the right hand side matrix of this system has rank  $q$ . Let us express this rank through two important characteristics: it is  $\text{rank}\{\gamma_1, \dots, \gamma_m\} + d$ , where  $d$  is the number of connected components in the graph of transformation of complexes.

To prove this formula, let us write down the matrix  $\mathbf{M}$  of the system (4.3.13). First, we change the enumeration of complexes. We group the complexes from the same connected component together and arrange these groups in the order of the connected component number. After this change of enumeration,  $\{1, \dots, |V_1|\} = V_1$ ,  $\{|V_1| + 1, \dots, |V_1| + |V_2|\} = V_2$ , ...,  $\{|V_1| + |V_2| + \dots + |V_{d-1}| + 1, \dots, |V_1| + |V_2| + \dots + |V_d|\} = V_d$ .

Let  $y_j$  be here the row-vector. The matrix is

$$\mathbf{M} = \begin{bmatrix} y_1 & 1 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ y_{|V_1|} & 1 & 0 & \dots & 0 \\ y_{|V_1|+1} & 0 & 1 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ y_{|V_1|+\dots+|V_d|} & 0 & 0 & \dots & 1 \end{bmatrix} \quad (4.3.14)$$

$\mathbf{M}$  consists of  $d$  blocks  $\mathbf{M}_s$ , which correspond to connected components  $C_s$  of

the graph of transformation of complexes:

$$\mathbf{M}_s = \begin{bmatrix} y_{|V_1|+\dots+|V_{s-1}|+1} & 0 & \dots & 1 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ y_{|V_1|+\dots+|V_s|} & 0 & \dots & 1 & \dots \end{bmatrix} \quad (4.3.15)$$

The first  $n$  columns in this matrix are filled by the vectors  $y_j$  of complexes, which belong to the component  $C_s$ , then follow  $s - 1$  columns of zeros, after that, there is one column of units, and then again zeros. Here, in (4.3.14), (4.3.15) we multiplied the last  $d$  columns by  $-1$ . This operation does not change the rank of the matrix.

Other elementary operations that do not change the rank, are: we can add to any row (column) a linear combination of other rows (columns).

We will use these operations to simplify blocks (4.3.15) but first we have to recall several properties of spanning trees [11]. Let us consider a connected, undirected graph  $G$  with the set of vertices  $\mathcal{V}$  and the set of edges  $\mathcal{E} \subset \mathcal{V} \times \mathcal{V}$ . A spanning tree of  $G$  is a selection of edges of  $G$  that form a tree spanning every vertex. For a connected graph with  $V$  vertices, any spanning tree has  $V - 1$  edges. Let for each vertex  $\Theta_j$  of  $G$  a  $n$ -dimensional vector  $y_j$  is given. Then for every edge  $(\Theta_j, \Theta_l) \in \mathcal{E}$  a vector  $\gamma_{jl} = y_j - y_l$  is defined. We identify vectors  $\gamma$  and  $-\gamma$  and the order of  $j, l$  is not important. Let us use  $\Gamma_G$  for this set of  $\gamma_{jl}$ :

$$\Gamma_G = \{y_j - y_l \mid (\Theta_j, \Theta_l) \in \mathcal{E}\}.$$

For any spanning tree  $T$  of graph  $G$  we have the following property:

$$\text{span}\Gamma_G = \text{span}\Gamma_T, \quad (4.3.16)$$

in particular,  $\text{rank}\Gamma_G = \text{rank}\Gamma_T$ .

For the digraphs of reactions between complexes, we create undirected graphs just by neglecting the directions of edges. We keep for them the same notations as for original digraphs. Let us select any spanning tree  $T_s$  for the connected component  $C_s$  in the graph of transformation of complexes. In  $T_s$  we select arbitrarily a root complex. After that, any other complex  $\Theta_j$  in  $C_s$  has a unique parent. This is the vertex connected to it on the path to the root. For the root

complex of  $C_s$  we use special notation  $\Theta_s^\circ$ .

Now, we transform the block (4.3.15) without change of rank: for each non-root complex we subtract from the correspondent row the row, which correspond to its unique parent. After these transformations (and, maybe, some permutations of rows), the block  $\mathbf{M}_s$  get the following form:

$$\begin{bmatrix} \gamma_1^s & 0 & \dots & 0 & \dots \\ \gamma_2^s & 0 & \dots & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \gamma_{|V_1|-1}^s & 0 & \dots & 0 & \dots \\ y_s^\circ & 0 & \dots & 1 & \dots \end{bmatrix}. \quad (4.3.17)$$

Here,  $\{\gamma_1^s, \gamma_2^s, \dots, \gamma_{|V_1|-1}^s\}$  is  $\Gamma_{T_s}$  for the spanning tree  $T_s$  and  $y_s^\circ$  is the coefficient vector for the root complex  $\Theta_s^\circ$ .

From the obtained structure of blocks we immediately find that the rank of the rows with  $\gamma$  is  $\text{rank}\{\gamma_1, \dots, \gamma_m\} + d$  due to (4.3.16). Additional  $d$  rows with  $y_s^\circ$  are independent due to their last coordinates and add  $d$  to rank. Finally,

$$\text{rank}\mathbf{M} = \text{rank}\{\gamma_1, \dots, \gamma_m\} + d \quad (4.3.18)$$

Obviously,  $\text{rank}\mathbf{M} \leq q$ . If  $\text{rank}\mathbf{M} = q$  then it is always possible to restore the positivity of the entropy production by the linear deformation of the entropy.

Feinberg [50] called the difference  $q - \text{rank}\mathbf{M}$  the *deficiency* of the reaction network. For example, for the ‘Michaelis–Menten’ reaction mechanism  $E + S \rightleftharpoons ES \rightleftharpoons P + S$   $\text{rank}\{\gamma_1, \gamma_2\} = 2$ ,  $d = 1$ ,  $q = 3$ ,  $\text{rank}\mathbf{M} = 3$  and deficiency is 0.

For the adsorption (the Langmuir–Hinshelwood) mechanism of CO oxidation (5.2.17)  $\text{rank}\{\gamma_1, \gamma_2, \gamma_3\} = 3$ ,  $d = 3$ ,  $q = 6$ ,  $\text{rank}\mathbf{M} = 6$  and deficiency is 0. To apply the results about the entropy deformation to this reaction mechanism, it is necessary to introduce an inverse reaction to the third elementary reaction in (5.2.17),  $\text{PtO} + \text{PtCO} \rightarrow \text{CO}_2 + 2\text{Pt}$  with an arbitrarily small but positive constant in order to make the mechanism weakly reversible.

Let us consider the Langmuir–Hinshelwood mechanism for reduced list of components. Let us assume that the gas concentrations are constant because of control or time separation or just as a model ‘fast system’ and just include

them in the reaction rate constants for intermediates. Then the mechanism is  $2\text{Pt} \rightleftharpoons 2\text{PtO}$ ,  $\text{Pt} \rightleftharpoons \text{PtCO}$ ,  $\text{PtO} + \text{PtCO} \rightarrow 2\text{Pt}$ . For this system,  $\text{rank}\{\gamma_1, \gamma_2, \gamma_3\} = 2$ ,  $d = 2$ ,  $q = 5$ ,  $\text{rank}\mathbf{M} = 4$  and deficiency is 1. Bifurcations in this system are known [70].

For the fragment of the reaction mechanism of the hydrogen combustion (4.1.1),  $\text{rank}\{\gamma_1, \dots, \gamma_m\} = 6$ ,  $d = 6$ ,  $q = 15$ ,  $\text{rank}\mathbf{M} = 12$  and deficiency is 3.

#### 4.3.4 Existence of Points of Detailed and Complex Balance

Our formulation of the conditions of detailed and complex balance is not standard: we formulate them as the identities (4.2.15) (4.2.17). These identities have a global nature and describe the properties of reaction rates for all states.

The usual approach to the principle of detailed balance is based on equilibria. The standard formulation is: *in all equilibria every process is balanced with its reverse process*. Without special forms of kinetic law this principle cannot have any consequences for global dynamics. Nevertheless, if we fix the kinetic law then the consequences may be very important. For example, if kinetics of elementary reactions follow the Mass Action law then existence of a positive equilibrium with detailed balance implies existence of the Lyapunov function in the form of the perfect free entropy:

$$Y = - \sum_i c_i \left( \ln \left( \frac{c_i}{c_i^*} \right) - 1 \right),$$

where  $c_i^*$  is that positive equilibrium with detailed balance (see, for example, [70]).

In this Section we demonstrate that for the general kinetic law (4.2.2), which gives the expression of reaction rates through the entropy gradient, if the kinetic factors are constant (or a function of temperature) then the existence of the points of detailed (or complex) balance means that the linear deformation of the entropy exists which restores the global detailed (or complex) balance conditions (4.2.15) (or (4.2.17)).

The condition that the kinetic factors are constant means that for a given set of values  $\{\varphi_\rho\}$  a state with any admissible values of  $\check{\mu}$  is physically possible

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(admissible). This condition allows us to vary the potentials  $\check{\mu}$  independently of  $\{\varphi_\rho\}$ .

Let us assume that for the general kinetic system with the elementary reaction rates given by (4.2.2) a point of detailed balance exists. This means that for some value of  $\check{\mu} = \check{\mu}^*$  (the detailed balance point in the Legendre transform) and for all  $\rho$   $r_\rho^+ = r_\rho^-$ :

$$\varphi_\rho^+ \exp(\alpha_\rho, \check{\mu}^*) = \varphi_\rho^- \exp(\alpha_\rho, \check{\mu}^*).$$

This formula is exactly the condition (4.3.3) of existence of  $\Delta\check{\mu}$  which allow us to deform the entropy for restoring the detailed balance in the global form (4.2.15).

If we assume that the point of complex balance exists then there exists such a value of  $\check{\mu} = \check{\mu}^*$  (a point of complex balance in the Legendre transform) that

$$\sum_{j,j \neq l} (\varphi_{lj} \exp(\check{\mu}^*, y_j) - \varphi_{jl} \exp(\check{\mu}^*, y_l)) = 0.$$

This is exactly the deformation condition (4.3.7) with  $\Delta\check{\mu} = -\check{\mu}^*$ .

To prove these statements we used an additional condition about the possibility to vary  $\check{\mu}$  under given  $\{\varphi_\rho\}$ .

So, we demonstrated that for the general kinetic law (4.2.2) the existence of a point of detailed balance is equivalent to the existence of such linear deformation of the entropy that the global condition (4.2.15) holds. Analogously, the existence of a point of complex balance is equivalent to the global condition of complex balance after some linear deformation of the entropy.

### 4.3.5 Why the Detailed Balance is More Popular than the Complex Balance?

The complex balance conditions are mathematically nice and more general than the principle of detailed balance. They are linked by Stueckelberg to the Markov models ("S-matrix models") of microscopic kinetics. Many systems satisfy these conditions (after linear deformation of the entropy) just because of the algebraic structure of the reaction mechanism (see Section 4.3.3). Nevertheless, it is used much less than the classical detailed balance. Why?

## WHY THE DETAILED BALANCE IS MORE POPULAR THAN THE COMPLEX BALANCE?

The answer is simple: because the principle of detailed balance is valid for most of physical and chemical systems. Onsager revealed the physical reason for detailed balance [44]. This is *microreversibility*: the microscopic laws of motion are invertible in time: if we observe the microscopic dynamics of particles in the backward movie then we cannot find the difference from the real world. This difference occurs in the macroscopic world.

In microphysics and the  $S$ -matrix theory this microreversibility property has the name " $T$ -invariance".

Let us demonstrate how  $T$ -invariance in micro-world implies detailed balance in macro-world.

Following Gibbs, we accept the ensemble-based point of view on the macroscopic states: they are probability distributions in the space of detailed microscopic states.

First of all, we assume that under given values of conservation laws equilibrium state exists and is unique.

Second assumption is that the rates of elementary processes are microscopically observable quantities. This means that somebody (a "demon"), who observes all the events in the microscopical world can count the rates of elementary reactions.

$T$ -invariance and uniqueness of equilibrium give together: equilibrium is  $T$ -invariant: if we change all the microscopic time derivatives (velocities)  $v$  to  $-v$  then nothing will change.

$T$ -transformation changes all reactions to the reverse reactions, just by reversion of arrows, but the number of the events remain the same: any reaction transforms into its reverse reaction but does not change the reaction rate. This can be formulated also as follows:  $T$ -transformation maps all  $r_\rho^+$  into the correspondent  $r_\rho^-$ .

Hence, because of the  $T$ -invariance, the equilibrium rate of each reaction is equal to the equilibrium rate of the reverse reaction.

How may the assumptions be violated? Existence of several equilibria in thermodynamics is quite unexpected for homogeneous systems but requires more attention for the systems with phase separation. Nevertheless, if we assume

## WHY THE DETAILED BALANCE IS MORE POPULAR THAN THE COMPLEX BALANCE?

that a multi-phase system consists of several homogeneous phases, and each of these phases is in uniform equilibrium, then we return to the previous assumption (with some white spots for non-uniform interfaces).

$T$ -invariance may be violated if the microscopic description is not reversible in time. Magnetic field and the Coriolis force are the classical examples for violation of the microscopic reversibility. In a linear approximation near equilibrium the corresponding modification of the Onsager relations gives the Onsager–Casimir relations [16]. Despite several attempts for nonlinear formulation of the Onsager–Casimir relations (see [33]) the principle of detailed balance seems still to be the best nonlinear version of the Onsager relations, and the conditions of the complex balance seem to give the proper relations between kinetic coefficients in the absence of the microscopic reversibility for nonlinear systems. It is important to mention here that all these relations are used together with the general kinetic law (4.2.2).

Observability of the rates of elementary reactions deserves a special study. Two approaches to the reaction rate are possible. If we accept that the general kinetic law (4.2.2) is valid then we can find the kinetic factors by observation of  $dc/dt$  in several points because the Boltzmann factors are linearly independent. In this sense, they are observable but one can claim the approximation point of view and state that the general kinetic law (4.2.2) without additional conditions on kinetic factors is very general and allows to approximate any dynamical system. From this point of view, kinetic coefficients are just some numbers in the approximation algorithm and are not observable. This means that there is no such a microscopic thing as the rate of elementary reaction, and the set of reactions serves just for the approximation of the right hand side of the kinetic equation. We cannot fully disprove this point of view but can just say that in some cases the collision-based approach with physically distinguished elementary reactions is based on the solid experimental and theoretical background. If the elementary reactions physically exist then the detailed balance for  $T$ -invariant systems is proved.

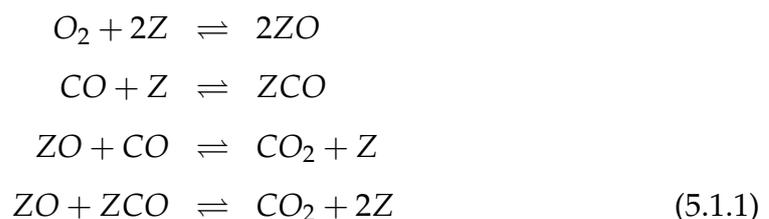
# Quasi Equilibrium and Quasi-Steady State Approximation

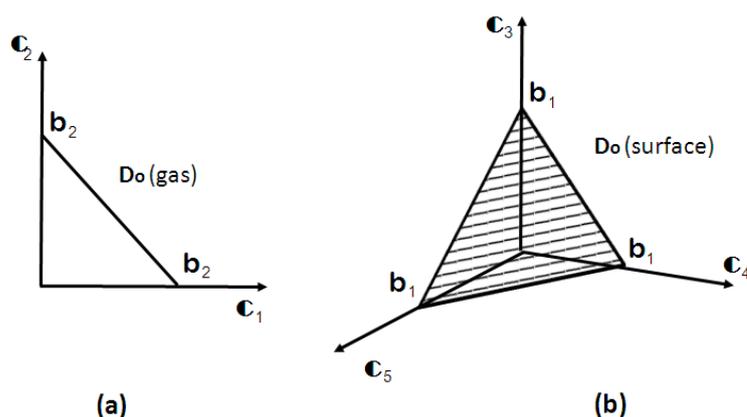
Here we discuss in detail our case study of the oxidation of carbon monoxide over platinum, the main mechanism along with its complexity and applying the Quasi equilibrium (QE) and Quasi Steady State Approximation (QSSA) to it. We measure its role and in the case of stiffness, how to get rid of it.

## 5.1 Oxidation of Carbon monoxide over Platinum

During the last decade the CO over Pt was commonly used for testing the latest physical methods in order to study the structure and composition of catalysts e.g low Energy Electron Diffraction (LEES), Auger Electron Spectroscopy (AES), X-ray Photon Spectroscopy (XPS), molecular beam techniques etc. Here we consider again a four step complex chemical reaction of CO oxidation over Pt. For details see [35].

Although for its description, various steps are used from the mechanisms we take the following ones for case study





**Figure 5.1:** Balance Polyhedra for catalytic isomerization [35] (a) For gas (b) for surface compounds

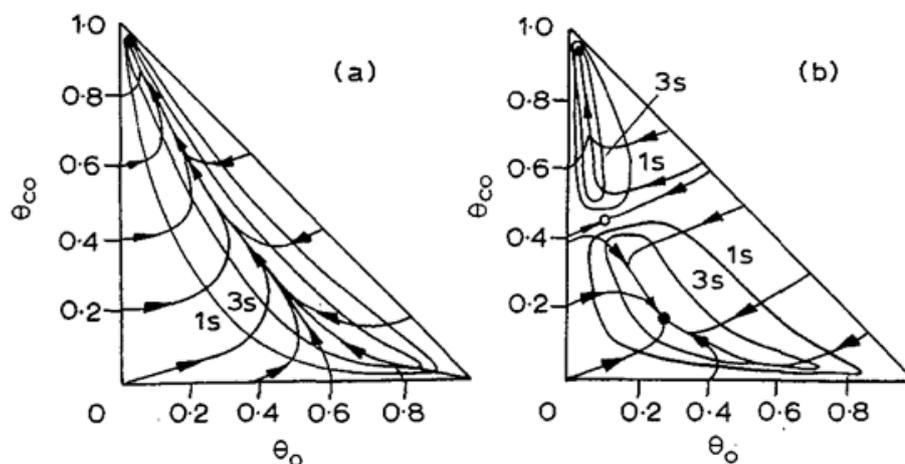
in the above equation  $ZO$ ,  $ZCO$ ,  $Z$  are adsorbed oxygen. The above mechanism involve two different routes:

1. Impact: steps 1 to 4 Eley- Rideal (E-R).
2. Adsorption: steps 1 to 3 Langmuir-Hinshelwood (L-H).

(1) CO oxidation follows the adsorption mechanism (this viewpoint was reported in the pioneering studies of Palmer, Smith and Malakhov) whose kinetic characteristics (reaction rate constants) depend significantly on the surface composition, (2) alongside the adsorption mechanism, there is a contribution from the interaction of adsorbed oxygen with CO in the pre-adsorption state ("precursor state"). Here we discuss in detail the various steps of this mechanism as proceeding from the experimental data.

### Adsorption-Desorption of $O_2$

A molecular form of reactive oxygen at high pressure is obtained by the oxygen adsorption over platinum metal. As a result, well ordered structure is often formed on metal surfaces, which diffuse into catalyst bulk under high temperature and pressure. Due to this dissolved oxygen in a subsurface layer changes the reaction rate constants. Often, under certain conditions oxygen adsorption



**Figure 5.2:** Reaction Phase Patterns  $P_{O_2} = 2.3 \times 10^{-7}$  and  $P_{CO} = 2.2 \times 10^{-7}$  Torr [35]. (a) Unique steady state,  $T = 450K$ . (b) Three steady states  $T = 490K$

can lead to surface reconstruction. Thus sticking coefficient of oxygen depends on the surface composition.

### Adsorption-Desorption of CO

CO is a monomolecular, its activation energy is particularly zero as is the case of oxygen. But oxygen doesn't inhibit CO adsorption. The sticking coefficient is weakly dependent on the surface concentration of CO.

### The $CO_2$ formation step

After the modification in the previous results in 1970 it was shown through a number of experimental results that if oxygen is preadsorbed over platinum surface at ( $T > 263k$ ) it reacts with CO immediately in a gas phase as a result  $CO_2$  formed independent of temperature which agree with the impact mechanism. On the other side there is a formation of  $CO_2$  by the interaction of CO and  $O_2$  which implies the adsorption mechanism.

The two route mechanism was proposed by Winterbottom, where as Campbell applied L-H mechanism to describe titration of adsorbed oxygen by carbon monoxide gases and assumed that

- Formation energy of  $\text{CO}_2$  depends on oxygen surface coverage.
- CO production is inhibited by oxygen at  $T > 529\text{k}$ .
- The parameter of  $\text{CO}_2$  formation changes sharply with reaction temperature.

Through numerical computation for the adsorption mechanism we define two time scales:

- Fast scale for the initial segment.
- Slow scale characterizes motion to the steady state.

This separation of time scale is due to sharp difference in parameters, i.e, temperature as shown in Figure 5.2, where a unique steady state will be obtained if  $T = 450\text{K}$  and three steady states in case of  $T = 490\text{K}$ . Slow reaction is distinctly observed: if the trajectory approaches the unstable steady state the system rapidly enters its neighborhood (after one sec) and then relatively slowly (during 100 sec) moves towards its stable steady state.

## 5.2 Formalism of QE Approximation for Chemical Kinetics

In this Section, we describe the general formalism of the QE for chemical kinetics following [32].

The general construction of the quasi-equilibrium manifold gives the following procedure. First, let us consider the chemical reactions in a constant volume under the isothermal conditions. The free energy  $F(N, T) = Vf(c, T)$  should decrease due to reactions. In the space of concentrations, one defines a subspace of fast motions  $L$ . It should be spanned by the stoichiometric vectors of *fast reactions*.

Slow coordinates are linear functions that annulate  $L$ . These functions form a subspace in the space of linear functions on the concentration space. Dimension

of this space is  $s = n - \dim L$ . It is necessary to choose any basis in this subspace. We can use for this purpose a basis  $b_j$  in  $L^\perp$ , an orthogonal complement to  $L$  and define the basic functionals as  $b_j(N) = (b_j, N)$ .

The description of the QE manifold is very simple in the Legendre transform. The chemical potentials are partial derivatives

$$\mu_i = \frac{\partial F(N, T)}{\partial N_i} = \frac{\partial f(c, T)}{\partial c_i}. \quad (5.2.1)$$

Let us use  $\mu_i$  as new coordinates. In these new coordinates (the “conjugated coordinates”), the QE manifold is just an orthogonal complement to  $L$ . This subspace,  $L^\perp$ , is defined by equations

$$\sum_i \mu_i \gamma_i = 0 \text{ for any } \gamma \in L. \quad (5.2.2)$$

It is sufficient to take in (5.2.2) not all  $\gamma \in L$  but only elements from a basis in  $L$ . In this case, we get the system of  $n - \dim L$  linear equations of the form (5.2.2) and their solution does not cause any difficulty. For the actual computations, one requires the inversion from  $\mu$  to  $c$ .

It is worth to mention that the problems of the selection of the slow variables and of the description of the QE manifold in the conjugated variables can be considered as the same problem of description of the orthogonal complement,  $L^\perp$ .

To finalize the construction of the QE approximation, we should find for any given values of slow variables (and of conservation laws)  $b_i$  the correspondent point on the QE manifold. This means that we have to solve the system of equations:

$$b(N) = b; \quad (\mu(c, T), \gamma_\rho) = 0, \quad (5.2.3)$$

where  $b$  is the vector of slow variables,  $\mu$  is the vector of chemical potentials and vectors  $\gamma_\rho$  form a basis in  $L$ . After that, we have the QE dependence  $c_{QE}(b)$  and for any admissible value of  $b$  can find all the reaction rates and calculate  $\dot{b}$ .

Unfortunately, the system (5.2.3) can be solved analytically only in some special cases. In general case, we have to solve it numerically. For this purpose, it may be convenient to keep the optimization statement of the problem:  $S \rightarrow \max$

subject to given  $b$ . There exists plenty of methods of convex optimization for solution of this problem.

For the first example, let us return to the simplest enzyme reaction  $E + S \rightleftharpoons ES \rightarrow P + S$ , the traditional Michaelis–Menten System (2.6.4) (it is simpler than the system studied by Michaelis and Menten [47]). Let us assume that the reaction  $E + S \rightleftharpoons ES$  is fast. This means that both  $k_1^+$  and  $k_1^-$  include large parameters:  $k_1^+ = \frac{1}{\epsilon}\kappa_1$ ,  $k_1^- = \frac{1}{\epsilon}\kappa_{-1}$ . For small  $\epsilon$ , we will apply the QE approximation. Only three components participate in the fast reaction,  $A_1 = S$ ,  $A_2 = E$ ,  $A_3 = ES$ . For analysis of the QE manifold we do not need to involve other components.

The stoichiometric vector of the fast reaction is  $\gamma = (-1, -1, 1)$ . The space  $L$  is one-dimensional and its basis is this vector  $\gamma$ . The space  $L^\perp$  is two-dimensional and one of the convenient bases is  $b_1 = (1, 0, 1)$ ,  $b_2 = (0, 1, 1)$ . The correspondent slow variables are  $b_1(N) = N_1 + N_3$ ,  $b_2(N) = N_2 + N_3$ . The first slow variable is the sum of the free substrate and the substrate captured in the enzyme–substrate complex. The second of them is the conserved quantity, the total amount of enzyme.

The equation for the QE manifold is (2.6.7):  $k_1 c_1 c_2 = k_1^- c_3$  or  $\frac{c_1 c_2}{c_1^* c_2^*} = \frac{c_3}{c_3^*}$  because  $k_1 c_1^* c_2^* = k_1^- c_3^*$ , where  $c_i^* = c_i^*(T) > 0$  are the so-called standard equilibrium values and for perfect systems  $\mu_i = RT \ln(c_i/c_i^*)$ ,  $F = RTV \sum_i c_i (\ln(c_i/c_i^*) - 1)$ .

Let us fix the slow variables and find  $c_{1,2,3}$ . Equations (5.2.3) turn into

$$c_1 + c_3 = b_1, \quad c_2 + c_3 = b_2, \quad k_1 c_1 c_2 = k_1^- c_3.$$

Here we change dynamic variables from  $N$  to  $c$  because this is a homogeneous system with constant volume.

If we use  $c_1 = b_1 - c_3$  and  $c_2 = b_2 - c_3$  then we obtain a quadratic equation for  $c_3$ :

$$k_1 c_3^2 - (k_1 b_1 + k_1 b_2 + k_1^-) c_3 + k_1 b_1 b_2 = 0. \quad (5.2.4)$$

Therefore,

$$c_3(b_1, b_2) = \frac{1}{2} \left( b_1 + b_2 + \frac{k_1^-}{k_1} \right) - \frac{1}{2} \sqrt{\left( b_1 + b_2 + \frac{k_1^-}{k_1} \right)^2 - 4b_1 b_2}.$$

The sign ‘-’ is selected to provide positivity of all  $c_i$ . This choice provides also the proper asymptotic:  $c_3 \rightarrow 0$  if any of  $b_i \rightarrow 0$ . For other  $c_{1,2}$  we should use  $c_1 = b_1 - c_3$  and  $c_2 = b_2 - c_3$ .

The time derivatives of concentrations are:

$$\begin{aligned}
 \dot{c}_1 &= -k_1 c_1 c_2 + k_1^- c_3 + v_{\text{in}} c_1^{\text{in}} - v_{\text{out}} c_1, \\
 \dot{c}_2 &= -k_1 c_1 c_2 + (k_1^- + k_2) c_3 + v_{\text{in}} c_2^{\text{in}} - v_{\text{out}} c_2, \\
 \dot{c}_3 &= k_1 c_1 c_2 - (k_1^- + k_2) c_3 + v_{\text{in}} c_3^{\text{in}} - v_{\text{out}} c_3, \\
 \dot{c}_4 &= k_2 c_3 + v_{\text{in}} c_4^{\text{in}} - v_{\text{out}} c_4,
 \end{aligned} \tag{5.2.5}$$

where we added external flux with input and output velocities (per unite volume)  $v_{\text{in}}$  and  $v_{\text{out}}$  and input concentrations  $c^{\text{in}}$ . This is done to stress that the QE approximation holds also for a system with fluxes if the fast equilibrium subsystem is fast enough.

The slow system is

$$\begin{aligned}
 \dot{b}_1 &= \dot{c}_1 + \dot{c}_3 = -k_2 c_3 + v_{\text{in}} b_1^{\text{in}} - v_{\text{out}} b_1, \\
 \dot{b}_2 &= \dot{c}_2 + \dot{c}_3 = v_{\text{in}} b_2^{\text{in}} - v_{\text{out}} b_2, \\
 \dot{c}_4 &= k_2 c_3 + v_{\text{in}} c_4^{\text{in}} - v_{\text{out}} c_4,
 \end{aligned} \tag{5.2.6}$$

where  $b_1^{\text{in}} = c_1^{\text{in}} + c_3^{\text{in}}$ ,  $b_2^{\text{in}} = c_2^{\text{in}} + c_3^{\text{in}}$ .

Now, we should use the expression for  $c_3(b_1, b_2)$ :

$$\begin{aligned}
 \dot{b}_1 &= -k_2 \frac{1}{2} \left[ \left( b_1 + b_2 + \frac{k_1^-}{k_1} \right) - \frac{1}{2} \sqrt{\left( b_1 + b_2 + \frac{k_1^-}{k_1} \right)^2 - 4b_1 b_2} \right] \\
 &\quad + v_{\text{in}} b_1^{\text{in}} - v_{\text{out}} b_1, \\
 \dot{c}_4 &= k_2 \frac{1}{2} \left[ \left( b_1 + b_2 + \frac{k_1^-}{k_1} \right) - \frac{1}{2} \sqrt{\left( b_1 + b_2 + \frac{k_1^-}{k_1} \right)^2 - 4b_1 b_2} \right] \\
 &\quad + v_{\text{in}} c_4^{\text{in}} - v_{\text{out}} c_4, \\
 \dot{b}_2 &= v_{\text{in}} b_2^{\text{in}} - v_{\text{out}} b_2.
 \end{aligned} \tag{5.2.7}$$

It is obvious here that in the reduced system (5.2.7) there exists one reaction from the lumped component with concentration  $b_1$  (the total amount of sub-

strate in free state and in the substrate–enzyme complex) into the component (product) with concentration  $c_4$  the rate of this reaction is  $k_2c(b_1b_2)$ . The lumped component with concentration  $b_2$  (the total amount of the enzyme in free state and in the substrate–enzyme complex) affects the reaction rate but does not change in the reaction.

Let us use for simplification of this system the assumption of the substrate excess (we follow the logic of the original Michaelis and Menten paper [47]):

$$[S] \gg [SE], \text{ i.e. } b_1 \gg c_3. \quad (5.2.8)$$

Under this assumption, the quadratic equation (5.2.4) transforms into

$$\left(1 + \frac{b_2}{b_1} + \frac{k_1^-}{k_1 b_1}\right) c_3 = b_2 + o\left(\frac{c_3}{b_1}\right) \quad (5.2.9)$$

and in this approximation

$$c_3 = \frac{b_2 b_1}{b_1 + b_2 + \frac{k_1^-}{k_1}} \quad (5.2.10)$$

(compare to (2.6.8) and (2.6.3): this equation includes an additional term  $b_2$  in denominator because we did not assume formally anything about the smallness of  $b_2$  in (5.2.8)).

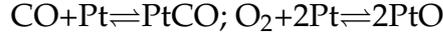
After this simplification, the QE slow equations (5.2.6) take the form

$$\begin{aligned} \dot{b}_1 &= -\frac{k_2 b_2 b_1}{b_1 + b_2 + \frac{k_1^-}{k_1}} + v_{\text{in}} b_1^{\text{in}} - v_{\text{out}} b_1, \\ \dot{b}_2 &= v_{\text{in}} b_2^{\text{in}} - v_{\text{out}} b_2, \\ \dot{c}_4 &= \frac{k_2 b_2 b_1}{b_1 + b_2 + \frac{k_1^-}{k_1}} + v_{\text{in}} c_4^{\text{in}} - v_{\text{out}} c_4. \end{aligned} \quad (5.2.11)$$

This is the typical form in the reduced equations for catalytic reactions: nominator in the reaction rate corresponds to the “brutto reaction”  $S + E \rightarrow P + E$  [70].

For the second example, let us assume equilibrium with respect to adsorption

in the CO on Pt oxidation:



(for detailed discussion of the modeling of CO on Pt oxidation, this “Mona Liza” of catalysis, we address readers to [70]). The list of components involved in these 2 reactions is:  $A_1 = \text{CO}$ ,  $A_2 = \text{O}_2$ ,  $A_3 = \text{Pt}$ ,  $A_4 = \text{PtO}$ ,  $A_5 = \text{PtCO}$  ( $\text{CO}_2$  does not participate in the adsorption and may be excluded at this point).

Subspace  $L$  is two-dimensional, It is spanned by the stoichiometric vectors,  $\gamma_1 = (-1, 0, -1, 0, 1)$ ,  $\gamma_2 = (0, -1, -2, 2, 0)$ .

The orthogonal complement to  $L$  is a three-dimensional subspace spanned by vectors  $(0, 2, 0, 1, 0)$ ,  $(1, 0, 0, 0, 1)$ ,  $(0, 0, 1, 1, 1)$ . This basis is not orthonormal but convenient because of integer coordinates.

The correspondent slow variables are

$$\begin{aligned} b_1 &= 2N_2 + N_4 = 2N_{\text{O}_2} + N_{\text{PtO}}; \\ b_2 &= N_1 + N_5 = N_{\text{CO}} + N_{\text{PtCO}}; \\ b_3 &= N_3 + N_4 + N_5 = N_{\text{Pt}} + N_{\text{PtO}} + N_{\text{PtCO}}. \end{aligned} \quad (5.2.12)$$

For heterogeneous systems, caution is needed in transition between  $N$  and  $c$  variables because there are two “volumes” and we cannot put in (5.2.12)  $c_i$  instead of  $N_i$ :  $N_{\text{gas}} = V_{\text{gas}}c_{\text{gas}}$  but  $N_{\text{surf}} = V_{\text{surf}}c_{\text{surf}}$ , where  $V_{\text{gas}}$  is the volume of gas,  $V_{\text{surf}}$  is the area of surface.

There is a law of conservation of the catalyst:  $N_{\text{Pt}} + N_{\text{PtO}} + N_{\text{PtCO}} = b_3 = \text{const}$ . Therefore, we have two non-trivial dynamical slow variables,  $b_1$  and  $b_2$ . They have a very clear sense:  $b_1$  is the amount of atoms of oxygen accumulated in  $\text{O}_2$  and  $\text{PtO}$  and  $b_2$  is the amount of atoms of carbon accumulated in  $\text{CO}$  and  $\text{PtCO}$ .

The free energy for the perfect heterogeneous system has the form

$$F = V_{\text{gas}}RT \sum_{A_i \text{ gas}} c_i \left( \ln \left( \frac{c_i}{c_i^*} \right) - 1 \right) + V_{\text{surf}}RT \sum_{A_i \text{ surf}} c_i \left( \ln \left( \frac{c_i}{c_i^*} \right) - 1 \right), \quad (5.2.13)$$

where  $c_i$  are the correspondent concentrations and  $c_i^* = c_i^*(T) > 0$  are the so-called standard equilibrium values.

From this expression (5.2.13) we get the chemical potentials of the perfect mixture

$$\mu_i = RT \ln \left( \frac{c_i}{c_i^*} \right). \quad (5.2.14)$$

The QE manifold in the conjugated variables is given by equations:

$$-\mu_1 - \mu_3 + \mu_5 = 0; \quad -\mu_2 - 2\mu_3 + 2\mu_4 = 0.$$

It is trivial to resolve these equations with respect to  $\mu_{3,4}$ , for example:

$$\mu_4 = \frac{1}{2}\mu_2 + \mu_3; \quad \mu_5 = \mu_1 + \mu_3$$

or with the standard equilibria:

$$\frac{c_4}{c_4^*} = \frac{c_3}{c_3^*} \sqrt{\frac{c_2}{c_2^*}}, \quad \frac{c_5}{c_5^*} = \frac{c_1}{c_1^*} \frac{c_3}{c_3^*},$$

or in the kinetic form (we assume that the kinetic constants are in accordance with thermodynamics and all these forms are equivalent):

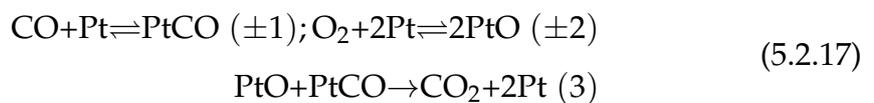
$$k_1 c_1 c_3 = k_1^- c_5, \quad k_2 c_2 c_3^2 = k_2^- c_4^2. \quad (5.2.15)$$

The next task is to solve the system of equations:

$$\begin{aligned} k_1 c_1 c_3 = k_1^- c_5, \quad k_2 c_2 c_3^2 = k_2^- c_4^2, \quad 2V_{\text{gas}} c_2 + V_{\text{surf}} c_4 = b_1, \\ V_{\text{gas}} c_1 + V_{\text{surf}} c_5 = b_2, \quad V_{\text{surf}} (c_3 + c_4 + c_5) = b_3. \end{aligned} \quad (5.2.16)$$

This is a system of five equations with respect to five unknown variables,  $c_{1,2,3,4,5}$ . We have to solve them and use the solution for calculation of reaction rates in the QE equations for the slow variables. Let us construct these equations first, and then return to (5.2.16).

We assume the adsorption (the Langmuir-Hinshelwood) mechanism of CO oxidation:



The kinetic equations for this system (including the flux in the gas phase) is

$$\begin{aligned}
 \text{CO} \quad \dot{N}_1 &= V_{\text{surf}}(-k_1 c_1 c_3 + k_1^- c_5) + V_{\text{gas}}(v_{\text{in}} c_1^{\text{in}} - v_{\text{out}} c_1), \\
 \text{O}_2 \quad \dot{N}_2 &= V_{\text{surf}}(-k_2 c_2 c_3^2 + k_2^- c_4^2) + V_{\text{gas}}(v_{\text{in}} c_2^{\text{in}} - v_{\text{out}} c_2), \\
 \text{Pt} \quad \dot{N}_3 &= V_{\text{surf}}(-k_1 c_1 c_3 + k_1^- c_5 - 2k_2 c_2 c_3^2 + 2k_2^- c_4^2 \\
 &\quad + 2k_3 c_4 c_5), \\
 \text{PtO} \quad \dot{N}_4 &= V_{\text{surf}}(2k_2 c_2 c_3^2 - 2k_2^- c_4^2 - k_3 c_4 c_5), \\
 \text{PtCO} \quad \dot{N}_5 &= V_{\text{surf}}(k_1 c_1 c_3 - k_1^- c_5 - k_3 c_4 c_5), \\
 \text{CO}_2 \quad \dot{N}_6 &= V_{\text{surf}}k_3 c_4 c_5 + V_{\text{gas}}(v_{\text{in}} c_6^{\text{in}} - v_{\text{out}} c_6).
 \end{aligned} \tag{5.2.18}$$

Here  $v_{\text{in}}$  and  $v_{\text{out}}$  are the fluxes rates (per unite volume).

For the slow variables this equation gives:

$$\begin{aligned}
 \dot{b}_1 &= 2\dot{N}_2 + \dot{N}_4 = -V_{\text{surf}}k_3 c_4 c_5 + 2V_{\text{gas}}(v_{\text{in}} c_2^{\text{in}} - v_{\text{out}} c_2) \\
 \dot{b}_2 &= \dot{N}_1 + \dot{N}_5 = -V_{\text{surf}}k_3 c_4 c_5 + V_{\text{gas}}(v_{\text{in}} c_1^{\text{in}} - v_{\text{out}} c_1); \\
 \dot{b}_3 &= \dot{N}_3 + \dot{N}_4 + \dot{N}_5 = 0 \\
 \dot{N}_6 &= V_{\text{surf}}k_3 c_4 c_5 + V_{\text{gas}}(v_{\text{in}} c_6^{\text{in}} - v_{\text{out}} c_6)
 \end{aligned} \tag{5.2.19}$$

This system looks quite simple. Only one reaction,



is visible. If we know expressions for  $c_{3,5}(b)$  then this reaction rate is also known. In addition, to work with the rates of fluxes, the expressions for  $c_{1,2}(b)$  are needed.

The system of equations (5.2.16) is explicitly solvable but the result is quite cumbersome. Therefore, let us consider its simplification without explicit analytic solution. We assume the following smallness:

$$b_1 \gg N_4 \quad b_2 \gg N_5 \tag{5.2.21}$$

Together with this smallness assumptions equations (5.2.16) give:

$$\begin{aligned}
 c_3 &= \frac{b_3}{V_{\text{surf}} \left( 1 + \frac{k_1}{k_1^-} \frac{b_2}{V_{\text{gas}}} + \sqrt{\frac{1}{2} \frac{k_2}{k_2^-} \frac{b_1}{V_{\text{gas}}}} \right)}, \\
 c_4 &= \sqrt{\frac{1}{2} \frac{k_2}{k_2^-} \frac{b_1}{V_{\text{gas}}}} \frac{b_3}{V_{\text{surf}} \left( 1 + \frac{k_1}{k_1^-} \frac{b_2}{V_{\text{gas}}} + \sqrt{\frac{1}{2} \frac{k_2}{k_2^-} \frac{b_1}{V_{\text{gas}}}} \right)}, \\
 c_5 &= \frac{k_1}{k_1^-} \frac{b_2}{V_{\text{gas}}} \frac{b_3}{V_{\text{surf}} \left( 1 + \frac{k_1}{k_1^-} \frac{b_2}{V_{\text{gas}}} + \sqrt{\frac{1}{2} \frac{k_2}{k_2^-} \frac{b_1}{V_{\text{gas}}}} \right)}.
 \end{aligned} \tag{5.2.22}$$

In this approximation, we have for the reaction (5.2.20) rate

$$r = k_3 c_4 c_5 = k_3 \frac{k_1}{k_1^-} \sqrt{\frac{1}{2} \frac{k_2}{k_2^-} \frac{b_1}{V_{\text{gas}}}} \frac{\sqrt{b_1 b_2}}{V_{\text{gas}}^{3/2}} \frac{b_3^2}{V_{\text{surf}}^2 \left( 1 + \frac{k_1}{k_1^-} \frac{b_2}{V_{\text{gas}}} + \sqrt{\frac{1}{2} \frac{k_2}{k_2^-} \frac{b_1}{V_{\text{gas}}}} \right)^2}.$$

This expression gives the closure for the slow QE equations (5.2.19).

We finalize here the illustration of the general QE procedure for chemical kinetics. As we can see, the simple analytic description of the QE approximation is available, when the fast reactions have no joint reagents. In general case, we need either a numerical solver for (5.2.3) or some additional hypotheses about smallness. Michaelis and Menten used, in addition to the QE approach, the hypothesis about smallness of the amount of intermediate complexes. This is the typical QSS hypothesis.

Of course, validity of all the simplification hypotheses is a crucial question. For example, for the CO oxidation, if we accept the hypothesis about the quasiequilibrium adsorption then we get a simple dynamics which monotonically tends to the steady state. The state of the surface is unambiguously presented as a continuous function of the gas composition. The pure QSS hypothesis results for the Langmuir-Hinshelwood reaction mechanism (5.2.17) without quasiequilibrium adsorption in bifurcations and the multiplicity of steady states [70]. The problem of validity of simplifications cannot be solved as a purely theoretical question without the knowledge of kinetic constants or some additional experimental data.

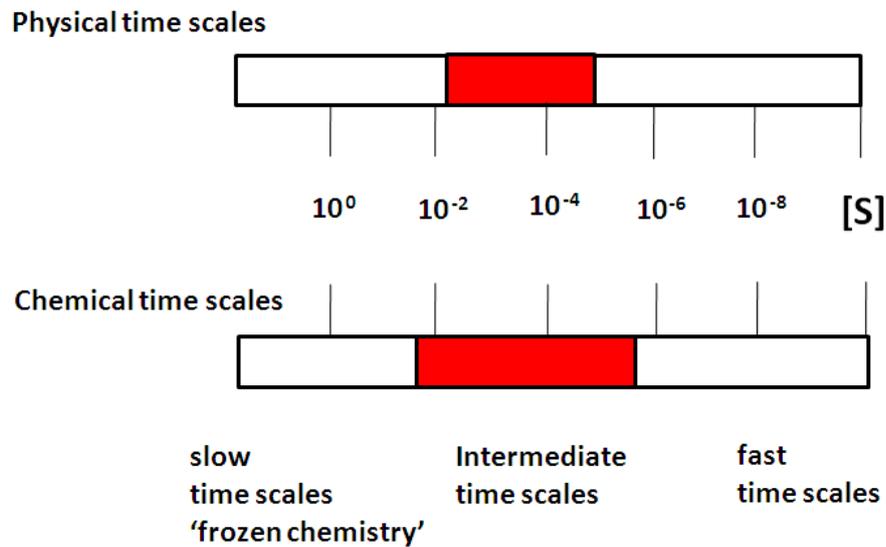


Figure 5.3: Transport Phenomena: Time scales of physical and chemical processes [40].

## 5.3 Transforming stiff to nonstiff

### Removing Stiffness

Although there is no specific definition for stiffness, it is an important aspect for the initial value problem of ordinary differential equations. One can say that the problem is stiff if the eigenvalue of the Jacobian matrix has a real part which is at all large and positive, and at least some component are very stable i.e one eigenvalue has a negative large part, that the problem is stiff in some interval and not in others parts or we can say that the solution is slowly varying with respect to negative part of the eigenvalues, which means that the solution is smooth and the norm of its derivative is much smaller than the norm of the derivative of exponential. The areas of chemical engineering, nonlinear mechanics, biochemistry and life sciences are sources of stiff problems. In mathematical modeling of chemically reacting gas flows tens of chemical reactions with quite different speeds are taken into account. Stiff systems are requiring the development of the special difference scheme, with increased requirements to the stability numerical results confirm the effectiveness, high accuracy and suitability for stiff systems of these schemes. This means that one can examine

the consequence of these two attributes (Accuracy, Tolerance) when solving stiff problem by conventional explicit methods. The chemical model often takes the form of non-linear ODE or PDE which most of the time are not possible to solve analytically. So people proceed through by considering these chemical model to mathematical model to be able to study the behavior of system including reactant, product, and there intermediate which are taking place from milliseconds to years and with the numerical help measures the behavior of each concentration variable in a very small or infinitesimal time interval. There is a major difference between physical and chemical time scale as shown in Figure 5.3.

With the help of model reduction the system becomes easier to handle but for this the necessary thing is to know the interrelation (correlation) between the different species and in the last few decades various model reduction methods have been developed. Among them the most common and largely used ones are Steady State Assumption and Quasi Equilibrium etc.

## 5.4 The Main Transformation of the Vector Field

QE approximation pretends to exclude the fast variables and reduce equations to the slow manifold. This approximation to the slow manifold is given by a system of nonlinear equations which, unfortunately, very often could not be explicitly resolved. In this Section, we demonstrate how the classical QE methods could be modified to remove the stiffness. For most of the realistic chemical kinetic systems the equations for the equilibrium surface could not be resolved analytically. Nevertheless, this equilibrium surface is a stable invariant manifold for a non-stiff system which we derive explicitly.

Let us return to the notation of Section (2.3): we consider a system in a domain  $U$  of a real vector space  $E$  given by differential equations (2.3.1)  $dx/dt = F(x)$ . We assume that for any  $x_0 \in U$  solution  $x(t; x_0)$  to initial problem  $x(0) = x_0$  for (2.3.1) exists for all  $t > 0$  and belongs to  $U$ . A dependence  $M = m(x)$  is given.

In general, the QE approximation results in the nonlinear equation for the QE manifold:  $\Phi(x, M) = 0$ . The slaving assumption means that the solution to (2.3.1) goes fast into a small vicinity of this manifold and then slowly moves in such a vicinity. To create the explicit reduced system we need to solve the

equation. Explicit form of this solution is usually unavailable, and we have to use numerical methods. For the QE approximation with convex entropy, the natural choice of this method is numerical conditional maximization of the entropy (2.3.4).

A natural question appears: why is this model a reduction of the original model, indeed, if we have to solve the multidimensional optimization problem at each calculation of the right hand side for  $dM/dt$ ? Among other problems, this approach restricts our ability to use implicit methods.

Here we propose to revise the problem statement. What is our main problem: to reduce dimension or to remove stiffness? Of course, it is desirable to solve both problems but if it is impossible then let us study the problem of stiffness removal.

The problem of stiffness removal is one of the classical problems in numerical methods [21]. It appears in various settings, from computational fluid dynamics [38] to chemical kinetics and combustion [64]. Here we propose a particular way of using the QE approximation for stiffness removal.

The QE approximation produces a differential–algebraic problem

$$\Phi(x, M) = 0, \quad \frac{dM}{dt} = (D_x m)F(x). \quad (5.4.1)$$

To use these equations, one has to solve first the algebraic equation, find  $x = x(M)$ , and then use it in the differential equation. There are many approaches to combine the numerical methods for the solution of the reduced differential equations with methods for the solution of the equations of the QE approximation.

The idea of using ODE methods for solving differential–algebraic systems directly was introduced by Gear in 1971 [17] and developed further in many works [18]. We also use this idea and return from the system (5.4.1) to the differential equations but with removing stiffness from the original system (2.3.1). The idea is very simple. Let us differentiate the algebraic part of the QE system (5.4.1):

$$(D_x \Phi)dx + (D_M \Phi)dM = 0.$$

According to this relation, let us take

$$(D_x\Phi)\frac{dx}{dt} = -(D_M\Phi)(D_xm)F(x), \quad M = m(x). \quad (5.4.2)$$

This is again the system of equations with two vector variables,  $x$  and  $M$  but instead of nonlinear equation for  $x$  and differential equation for  $M$  we get a linear equation for  $\dot{x}$  and explicit formula for  $M$ .

The first important property of (5.4.2) is that the QE manifold given by the equation  $\Phi(x, M) = 0$  is a (positively) invariant manifold for (5.4.2): if for initial conditions  $\Phi(x(0), m(x(0))) = 0$  then for  $t > 0$   $\Phi(x(t), m(x(t))) = 0$ . Indeed, the first equation in (5.4.2) can be read as a condition for the conservation in time of the quantity  $\Phi(x, m(x))$ . Therefore, the zero value is also preserved by the dynamics.

If the slow variables  $M$  are slow indeed then the operator  $(D_xm)$  from the right hand side of the differential equation in (5.4.2) should remove the fast dynamics and the system (5.4.2) becomes non-stiff.

For example, let us consider the system of fast reactions. Like in (2.6.1), we have a system

$$\begin{aligned} \frac{dN}{dt} &= K_{sl}(N) + \frac{1}{\epsilon} K_{fs}(N) \\ &= K_{sl}(N) + \frac{1}{\epsilon} \sum_{\rho} \gamma_{\rho}^f r_{\rho}. \end{aligned} \quad (5.4.3)$$

Under standard QE assumptions for chemical kinetics (including entropy growth + weak reversibility for MAL, for example), the fast system

$$\dot{N} = \frac{1}{\epsilon} \sum_{\rho} \gamma_{\rho}^f r_{\rho}$$

has a stable positive equilibrium, which is unique for any set of values of the linear conservation laws  $b_l(N) = \sum_i b_{lj} N_j$ :  $b_l(\gamma_{\rho}^f) \equiv 0$  for all  $l$  and  $\rho$ .

Let  $L = \text{span}\{\gamma_{\rho}^f\}$ , then vectors  $b_l$  correspond to a basis in  $L^{\perp}$ , and we should take  $M_l = (b_l, N)$ . The fast part of the vector field (5.4.3) vanishes in projection on the slow variables and the correspondent system (5.4.2) is not stiff.

Unfortunately, another problem may appear: the neutral stability instead of

stiffness. The new system (5.4.2) may drift tangentially to the QE manifold. To avoid this problem, we can add to this system the gradient flow of entropy increasing in fast directions. This flow is simple, non-stiff and guaranties stability of the QE manifold.

This stabilizing term is produced by orthogonal projection of  $\text{grad}S$  on  $\ker Dm$  (or, for chemical example, this is just an orthogonal projection of  $\text{grad}S$  on  $L = \text{span}\{\gamma_\rho^f\}$ ). Let  $P_\perp : E \rightarrow \ker Dm$  is this orthogonal projection. For a non-linear  $m$ , this projector depends on  $x$  as a parameter.

The stabilized non-stiff dynamics for the QE approximation is:

$$(D_x\Phi) \frac{dx}{dt} = -(D_M\Phi)(D_x m)F(x) + a(D_x\Phi)P_\perp \text{grad}S, \quad M = m(x). \quad (5.4.4)$$

where  $a > 0$  is the stabilization parameter.

The stabilization term  $aP_\perp \text{grad}S$  has zero input in  $\dot{M}$  (i.e. in the slow dynamics) and does not violate invariance of the QE manifold with respect to (5.4.2).

## 5.5 Example: Catalytic Oxidation

Let us return to the heterogeneous catalysis example, the CO oxidation on Pt [70]. The list of components is  $A_1 = \text{CO}$ ,  $A_2 = \text{O}_2$ ,  $A_3 = \text{Pt}$ ,  $A_4 = \text{PtO}$ ,  $A_5 = \text{PtCO}$ ,  $A_6 = \text{CO}_2$ . We assume a fast adsorption: the fast reactions are



with the stoichiometric vectors

$$\gamma_1 = (-1, 0, -1, 0, 1), \quad \gamma_2 = (0, -1, -2, 2, 0).$$

The subspace of fast motion is  $L = \text{span}\{\gamma_1, \gamma_2\}$ . The orthogonal complement to  $L$  is

$$L^\perp = \text{span}\{(0, 2, 0, 1, 0), (1, 0, 0, 0, 1), (0, 0, 1, 1, 1)\}.$$

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The orthonormal basis of  $L^\perp$  is obtained by the Gram-Schmidt procedure:

$$e_1 = \frac{1}{\sqrt{5}}(0, 2, 0, 1, 0), \quad e_2 = \frac{1}{\sqrt{2}}(1, 0, 0, 0, 1),$$

$$e_3 = \frac{1}{\sqrt{230}}(-5, -4, 10, 8, 5).$$

We omit here the component  $A_6$  because it does not participate in the fast reactions. In general,  $L^\perp$  has an additional basis vector  $(0, 0, 0, 0, 0, 1)$  and the sixth coordinate of the vectors in  $L$  is zero.

The orthogonal projector on  $L^\perp$  is  $P_\perp$ :

$$P_\perp x = e_1(e_1, x) + e_2(e_2, x) + e_3(e_3, x)$$

or in the matrix form,  $P_\perp$  is

$$\frac{1}{5} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 4 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} + \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \end{bmatrix} + \frac{1}{230} \begin{bmatrix} 25 & 20 & -50 & -40 & -25 \\ 20 & 16 & -40 & -32 & -20 \\ -50 & -40 & 100 & 80 & 50 \\ -40 & -32 & 80 & 64 & 40 \\ -25 & -20 & 50 & 40 & 25 \end{bmatrix} \quad (5.5.1)$$

The slow variables  $M$  are represented by a 3D vector

$$M = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} 2N_2 + N_4 \\ N_1 + N_5 \\ N_3 + N_4 + N_5 \end{bmatrix} = \begin{bmatrix} 2V_{\text{gas}}c_2 + V_{\text{surf}}c_4 \\ V_{\text{gas}}c_1 + V_{\text{surf}}c_5 \\ V_{\text{surf}}c_3 + V_{\text{surf}}c_4 + V_{\text{surf}}c_5 \end{bmatrix} \quad (5.5.2)$$

We assume the adsorption (the Langmuir-Hinshelwood) mechanism of CO oxidation (5.2.17). For our purposes, it is convenient to write the equations for

EXAMPLE: CATALYTIC OXIDATION

concentrations: instead of (5.2.18) we get

$$\begin{aligned}
 \text{CO} \quad \dot{c}_1 &= \frac{V_{\text{surf}}}{V_{\text{gas}}}(-k_1 c_1 c_3 + k_1^- c_5) + (v_{\text{in}} c_1^{\text{in}} - v_{\text{out}} c_1), \\
 \text{O}_2 \quad \dot{c}_2 &= \frac{V_{\text{surf}}}{V_{\text{gas}}}(-k_2 c_2 c_3^2 + k_2^- c_4^2) + (v_{\text{in}} c_2^{\text{in}} - v_{\text{out}} c_2), \\
 \text{Pt} \quad \dot{c}_3 &= -k_1 c_1 c_3 + k_1^- c_5 - 2k_2 c_2 c_3^2 + 2k_2^- c_4^2 + 2k_3 c_4 c_5, \\
 \text{PtO} \quad \dot{c}_4 &= 2k_2 c_2 c_3^2 - 2k_2^- c_4^2 - k_3 c_4 c_5, \\
 \text{PtCO} \quad \dot{c}_5 &= k_1 c_1 c_3 - k_1^- c_5 - k_3 c_4 c_5, \\
 \text{CO}_2 \quad \dot{c}_6 &= \frac{V_{\text{surf}}}{V_{\text{gas}}} k_3 c_4 c_5 + (v_{\text{in}} c_6^{\text{in}} - v_{\text{out}} c_6).
 \end{aligned} \tag{5.5.3}$$

Let us find the modified dynamical equation (5.4.2). For this purpose, we need  $\Phi(x, M)$ ,  $D_x \Phi(x, M)$ ,  $D_M \Phi(x, M)$  and  $m$  (where  $x = c$  and  $M = b$ ). The vector field  $F(x)$  is given by (5.5.3). The equation for the QE manifold ( $\Phi(x, M) = 0$ ) is (5.2.16):

$$\Phi(c, b) = \begin{bmatrix} k_1 c_1 c_3 - k_1^- c_5 \\ k_2 c_2 c_3^2 - k_2^- c_4^2 \\ 2V_{\text{gas}} c_2 + V_{\text{surf}} c_4 - b_1 \\ V_{\text{gas}} c_1 + V_{\text{surf}} c_5 - b_2 \\ V_{\text{surf}}(c_3 + c_4 + c_5) - b_3 \end{bmatrix} = 0. \tag{5.5.4}$$

For the differentials of  $\Phi$  this equation gives

$$D_c \Phi(c, b) = \left[ \frac{\partial \Phi_i(c, b)}{\partial c_j} \right] = \begin{bmatrix} k_1 c_3 & 0 & k_1 c_1 & 0 & -k_1^- \\ 0 & k_2 c_3^2 & 2k_2 c_2 c_3 & -2k_2^- c_4 & 0 \\ 0 & 2V_{\text{gas}} & 0 & V_{\text{surf}} & 0 \\ V_{\text{gas}} & 0 & 0 & 0 & V_{\text{surf}} \\ 0 & 0 & V_{\text{surf}} & V_{\text{surf}} & V_{\text{surf}} \end{bmatrix}; \tag{5.5.5}$$

$$D_b \Phi(c, b) = \left[ \frac{\partial \Phi_i(c, b)}{\partial b_j} \right] = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}. \tag{5.5.6}$$

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The matrix  $m$  is

$$m = \begin{bmatrix} 0 & 2V_{\text{gas}} & 0 & V_{\text{surf}} & 0 \\ V_{\text{gas}} & 0 & 0 & 0 & V_{\text{surf}} \\ 0 & 0 & V_{\text{surf}} & V_{\text{surf}} & V_{\text{surf}} \end{bmatrix} \quad (5.5.7)$$

For linear operators  $m$  the term  $D_M mF(x)$  in the right hand side of (5.4.2) is just  $mF(x)$ . For the vector field (5.5.3) and matrix (5.5.7) this term is

$$mF(c) = \begin{bmatrix} -V_{\text{surf}}k_3c_4c_5 + 2V_{\text{gas}}(v_{\text{in}}c_2^{\text{in}} - v_{\text{out}}c_2) \\ -V_{\text{surf}}k_3c_4c_5 + V_{\text{gas}}(v_{\text{in}}c_1^{\text{in}} - v_{\text{out}}c_1) \\ 0 \end{bmatrix} \quad (5.5.8)$$

Let us calculate  $(D_b\Phi(c, b))mF(c)$ :

$$(D_b\Phi(c, b))mF(c) = \begin{bmatrix} 0 \\ 0 \\ V_{\text{surf}}k_3c_4c_5 - 2V_{\text{gas}}(v_{\text{in}}c_2^{\text{in}} - v_{\text{out}}c_2) \\ V_{\text{surf}}k_3c_4c_5 - V_{\text{gas}}(v_{\text{in}}c_1^{\text{in}} - v_{\text{out}}c_1) \\ 0 \end{bmatrix} \quad (5.5.9)$$

Finally, the system (5.4.2) in our example is

$$\begin{bmatrix} k_1c_3 & 0 & k_1c_1 & 0 & -k_1^- \\ 0 & k_2c_3^2 & 2k_2c_2c_3 & -2k_2^-c_4 & 0 \\ 0 & 2V_{\text{gas}} & 0 & V_{\text{surf}} & 0 \\ V_{\text{gas}} & 0 & 0 & 0 & V_{\text{surf}} \\ 0 & 0 & V_{\text{surf}} & V_{\text{surf}} & V_{\text{surf}} \end{bmatrix} \begin{bmatrix} \dot{c}_1 \\ \dot{c}_2 \\ \dot{c}_3 \\ \dot{c}_4 \\ \dot{c}_5 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ V_{\text{surf}}k_3c_4c_5 - 2V_{\text{gas}}(v_{\text{in}}c_2^{\text{in}} - v_{\text{out}}c_2) \\ V_{\text{surf}}k_3c_4c_5 - V_{\text{gas}}(v_{\text{in}}c_1^{\text{in}} - v_{\text{out}}c_1) \\ 0 \end{bmatrix} \quad (5.5.10)$$

The dynamics of  $c_6$  has no feedback to the dynamics of  $c_{1-5}$  and may be con-

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sidered separately when the system for  $c_{1-5}$  is solved:

$$\dot{c}_6 = k_3 c_4 c_5 - V_{\text{gas}}(v_{\text{in}} c_6^{\text{in}} - v_{\text{out}} c_6).$$

For the stabilizing term, we use the thermodynamics function  $Y = -\frac{F}{RT}$ . According to (5.2.13),

$$Y = -\sum_i N_i \left( \ln \left( \frac{N_i}{N_i^*} \right) - 1 \right). \quad (5.5.11)$$

Let us calculate  $P_{\perp} \text{grad} Y$  in variables  $N$  and then rescale this term to variables  $c$ :

$$\text{grad} Y = -\ln \left( \frac{N_i}{N_i^*} \right) = -\ln \left( \frac{c_i}{c_i^*} \right).$$

For this formula, operator  $P_{\perp}$  is given by (5.5.1)

For equations in variables  $c$  (5.5.10) the stabilizing term is

$$\begin{bmatrix} \frac{1}{V_{\text{gas}}} & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{V_{\text{gas}}} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{V_{\text{surf}}} & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{V_{\text{surf}}} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{V_{\text{surf}}} \end{bmatrix} P_{\perp} \text{grad} Y \quad (5.5.12)$$

## 5.6 Quasi Steady State Approximation

This is a working tool applied in many catalyst reactions which basically defines an assumption for a fast subsystem. In the case of stepwise complex reactions, the overall reaction rate is determined by the slowest step among different fast (usually called other than the slow) steps of reactions. Various intermediate or unstable species are produced in different steps. In a simple procedure, the intermediates such as the atoms and free radicals, the concentrations of which are necessarily low, are assumed to have a constant concentration during the course of reaction.

QSSA basically split the species in two groups ([57]): The basic and the intermediate (radicals etc). Then defining the concentration space as a direct sum of

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fast  $c^f$  (intermediate species) and slow  $c^s$  (basic species) subspace i.e,

$$c = c^f \oplus c^s.$$

where as a subsystem  $c^f$  is the fast concentration at fixed values of  $c^s$ . This implies that fast subsystem relaxes to stationary state  $c^f \rightarrow c_{qss}^f(c^s)$ , then the assumption that  $c^f = c_{qss}^f(c)$  is precisely the QSS assumption. so  $J = J_s + J_f$

$$\dot{c}^f = J_f(c^s \oplus c^f), \quad c^s = const; \quad c^f \rightarrow c_{qss}^f(c^s) \quad (5.6.1)$$

$$\dot{c}^s = J_s(c^s \oplus c_{qss}^f(c^s)). \quad (5.6.2)$$

When talking about the steady state approximation, we mean that there exist a reactions which are very fast compared to the other reactions for that reason we set their correspondence rate of change to be zero but it doesn't means that they are identically zero but we are comparing their role with respect to others. According to SSA the rates of formation and consumption of the surface intermediate are approximately equal, so the time derivative of the coverage of intermediate is equal to zero or in other words it may be assumed that the rate of formation of the intermediate is equal to its rate of disappearance.

In this way, simple expressions for the concentration of intermediates can be obtained and hence an equation for the overall rate can be derived.

Consider the Michaelis-Menten mechanism:



where Z is an enzyme (catalyst) A is a substrate, AZ is the enzyme substrate intermediate complex and P is the product.

From the classical point of view enzymes are highly effective catalysts. Therefore one can say that the production or formation of enzyme and product from the enzyme substrate is a fast process. But how can we say it to be fast if it will never be the rate of reaction because in a steady state the rate of formation and degradation are approximately the same and also not be the rate constant because of having different units. So there may be another way of slowness. There exist balances and also if we could get rid of the units we will be able to resolve

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this difficulty. Thus in case of catalytic reaction the smallness parameter is the ratio of balances: Intermediate species include a catalyst, and their total amount is simply significantly smaller than the amount of all the  $c_i$ s. which allows to upgrade the QSS assumption to a singular perturbation theory rigorously [81].

The rate of the reaction for this mechanism is define as,

$$\begin{aligned}
 \dot{c}_A &= -k_1^+ c_A c_Z + k_1^- c_{AZ}, \\
 \dot{c}_Z &= -k_1^+ c_A c_Z + k_1^- c_{AZ} + k_2^+ c_{AZ} - k_2^- c_Z c_P, \\
 \dot{c}_{AZ} &= k_1^+ c_A c_Z - k_1^- c_{AZ} - k_2^+ c_{AZ} + k_2^- c_Z c_P, \\
 \dot{c}_P &= k_2^+ c_{AZ} - k_2^- c_Z c_P
 \end{aligned} \tag{5.6.4}$$

Whereas the mass conservation law gives us two equations (balance equations).

$$\begin{aligned}
 B_Z &= c_Z + c_{AZ}, \\
 B_A &= c_A + c_P + c_{AZ}.
 \end{aligned} \tag{5.6.5}$$

Note that these balances also satisfy the above differential equations (rate equations). Whereas the main idea of the SSA is that the concentration of highly reactive intermediate like AZ eventually goes to a rough balance between the production and destruction i.e at that point the net change of AZ is comparatively very small. In order to give evidence of our arguments, we have to choose new measuring scales for each of the variables ( $c_\bullet$ ) such that each is of unit magnitude or in other words we can say we have to define the new variables ( $\zeta_\bullet$ ) by

$$\zeta_A = c_A/B_A, \quad \zeta_P = c_P/B_A, \quad \zeta_Z = c_Z/B_Z, \quad \zeta_{AZ} = c_{AZ}/B_Z, \tag{5.6.6}$$

due to the balancing terms

$$\zeta_A + \zeta_P + \frac{B_Z}{B_A} \zeta_{AZ} = 1; \quad \zeta_Z + \zeta_{AZ} = 1; \quad \zeta_\bullet \geq 0.$$

We are left with only,

$$\begin{aligned}\dot{\zeta}_A &= B_Z[-k_1^+ \zeta_A \zeta_Z + \frac{k_1^-}{B_A} \zeta_{AZ}], \\ \dot{\zeta}_Z &= B_A[-k_1^+ \zeta_A \zeta_Z + \frac{k_1^-}{B_A} \zeta_{AZ} - k_2^- \zeta_P \zeta_Z + \frac{k_2^+}{B_A} \zeta_{AZ}].\end{aligned}\quad (5.6.7)$$

such that fast subsystem is regarded as a slow system for all the foregoing subsystems. For  $B_Z < B_A$  such that the catalyst is much smaller than the substrate the slowness of  $\zeta_A, \zeta_P$  is evident from the above equation.

The idea of slowness is similar for the radicals in which the amount of radical is less than the basic species. However, the calculation of this small parameter is not through the balances but through the thermodynamical approach in which the function  $G$  decreases in the course of a reaction, and we obtain the estimate of concentrations of any species:

$$c_i \leq \max_{G(c) \leq G(c(0))} c_i, \quad (5.6.8)$$

where  $c(0)$  is the initial concentration. If the concentration of the radical remains small initially as well as in equilibrium, then it is assumed that it remains small at all times, and, as in the case of ideal gas system under constant temperature and pressure, the following inequality is valid

$$c_R[\ln(c_R(t)/c_R^{eq}) - 1] \leq G(c(0)). \quad (5.6.9)$$

The above inequality gives the idea of the thermodynamic estimate of  $c^R(t)$  in terms of  $G(c(0))$  and  $c_R^{eq}$  uniformly for  $t > 0$ . A complete theory of thermodynamic estimates of dynamics has been developed by Gorban (1984). One can also do computations without a priori estimations, if one accepts the QSS assumption as long as the values  $c^f$  stay sufficiently small.

By knowing the pre estimate it is possible to normalize the value  $c_i$ , and with the help of the new variable, which takes the value from the unit segment  $[0, 1]$ , i.e  $\tilde{c}_i = c_i/c_{i \max}$ , the system will take a form

$$\frac{d\tilde{c}_i}{dt} = \frac{1}{c_{i \max}} J_i(c). \quad (5.6.10)$$

Various realization of the QSS approximation are possible through the system of dimension-less parameters  $\epsilon_i = c_i / \max_i c_i$ , which define a hierarchy of relaxation times. The simplest version is the standard QSS assumption: Parameters  $\epsilon_i$  are separated into two groups: the smaller ones and those of the order 1. Accordingly, the concentration vector is split into  $c^s \oplus c^f$ . Various hierarchical QSS are possible. With this, the problem becomes more tractable analytically.

## 5.7 How to find Equilibrium

Let us consider a system of chemical reactions defined as



where

$$(\alpha_r, A) = \sum_i \alpha_{ri} A_i, \quad (\beta_r, A) = \sum_i \beta_{ri} A_i$$

$i = 1 \dots n$ ,  $r$  is the reaction number,  $A_i$  are the chemical species and  $\alpha_r, \beta_r$  are the stoichiometric coefficients. The stoichiometric vector can be define as

$$\gamma = \beta_r - \alpha_r.$$

The kinetic equation under isochoric conditions will become

$$\dot{c}_i = J(c), \quad J(c) = \sum_r \gamma_s W_r \quad (5.7.2)$$

where  $W_r$  is reaction rate of step  $r$  and the linear stoichiometric conservation law is a system of linear function

$$b(c) = \sum_j b_j c_j, \quad j = 1, 2, \dots, l \quad (5.7.3)$$

that annuls all stoichiometric vectors for a given reaction mechanism

$$b(\gamma_r) = 0, \quad \forall r.$$

## ILLUSTRATION

Stoichiometric conservation law is strictly positive if all  $b_i > 0$ . This assumption plays an important role in Mass Action Law kinetics. Phase space  $V$  has now dimension  $m = n - l$  in the given  $n$ -dimension space (5.7.1) due to the  $l$ -dimensional (5.7.3) set of conservation laws

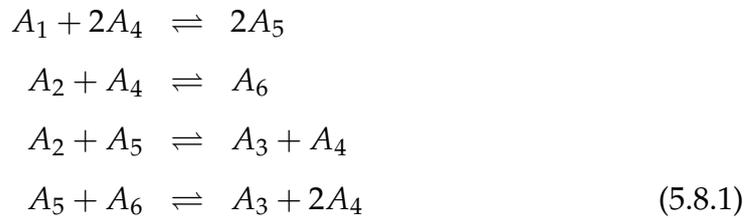
Thus we are left with a kinetic system in the form

$$\dot{c}_m = F(c, b). \quad (5.7.4)$$

This reduced mechanism can be easily solved by any direct solver to get an equilibrium of the system. Let us illustrate the above idea with the following example.

## 5.8 Illustration

CO oxidation over Pt metal group(Pt,Pd,Ir,Ru,Rh) is a complex reaction. A detailed mechanism is a combination of impact (Eley-Rideal) and adsorption (Langmuir-Hinshelwood) mechanism and involves the following steps of the reaction:



These chemical species (substances) are defined as  $O_2 = A_1, CO = A_2, CO_2 = A_3, Pt = A_4, PtO = A_5, PtCO = A_6$ , where oxygen, carbon monoxide and carbon dioxide are gases, and platinum and its oxides are surfaces. Their stoichiometric vectors can be defined step wise

$$\gamma_1^g = \begin{bmatrix} -1 \\ 0 \\ 0 \end{bmatrix}, \gamma_2^g = \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix}, \gamma_3^g = \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix}, \gamma_4^g = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \quad (5.8.2)$$

ILLUSTRATION

$$\gamma_1^s = \begin{bmatrix} -2 \\ 2 \\ 0 \end{bmatrix}, \gamma_2^s = \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix}, \gamma_3^s = \begin{bmatrix} 1 \\ -1 \\ 0 \end{bmatrix}, \gamma_4^s = \begin{bmatrix} 2 \\ -1 \\ -1 \end{bmatrix}, \quad (5.8.3)$$

or we can write their stoichiometric vectors as

$$\begin{aligned} \gamma_1 &= (-1, 0, 0, -2, 2, 0), \\ \gamma_2 &= (0, -1, 0, -1, 0, 1), \\ \gamma_3 &= (0, -1, 1, 1, -1, 0), \\ \gamma_4 &= (0, 0, 1, 2, -1, -1). \end{aligned} \quad (5.8.4)$$

The kinetic equation of the six component vector for concentrations  $c = (c_1, c_2, c_3, c_4, c_5, c_6)^T$  is given by the equation

$$\dot{c} = J(c) = \gamma_1 W_1 + \gamma_2 W_2 + \gamma_3 W_3 + \gamma_4 W_4, \quad (5.8.5)$$

$$J(c) = \begin{bmatrix} J_1 & J_2 & J_3 & J_4 & J_5 & J_6 \end{bmatrix}^T$$

and is in the form

$$\begin{aligned} \dot{c}^g &= \frac{S}{V}(\gamma_1^g W_1 + \gamma_2^g W_2 + \gamma_3^g W_3 + \gamma_4^g W_4) + \frac{v_{in} c_{in}^g}{V} + \frac{v_{out} c^g}{V}. \\ \dot{c}^s &= \frac{S}{V}(\gamma_1^s W_1 + \gamma_2^s W_2 + \gamma_3^s W_3 + \gamma_4^s W_4). \end{aligned} \quad (5.8.6)$$

Or we can write it as

$$\begin{aligned} \dot{c}_1 &= \frac{S}{V}(-W_1) + \frac{v_{in} c_{1in}}{V} + \frac{v_{out} c_1}{V}, \\ \dot{c}_2 &= \frac{S}{V}(-W_2 - W_3) + \frac{v_{in} c_{2in}}{V} + \frac{v_{out} c_2}{V}, \\ \dot{c}_3 &= \frac{S}{V}(W_3 + W_4) + \frac{v_{in} c_{3in}}{V} + \frac{v_{out} c_3}{V}, \\ \dot{c}_4 &= (-2W_1 - W_2 + W_3 + 2W_4), \\ \dot{c}_5 &= (2W_1 - W_3 - W_4), \\ \dot{c}_6 &= (W_2 - W_4), \end{aligned} \quad (5.8.7)$$

ILLUSTRATION

and an equation for  $v_{out}$  is given as

$$\begin{aligned} v_{out} &= v_{in} + S(W_1V_1 + W_2V_2 + W_3V_3 + W_4V_4) \\ V_1 &= -\frac{RT}{P}, V_2 = -\frac{RT}{P}, V_3 = \frac{RT}{P}, V_4 = 0. \end{aligned} \quad (5.8.8)$$

Ultimately we have,

$$v_{out} = v_{in} + \frac{SRT}{P}(-W_1 - W_2 + W_3) \quad (5.8.9)$$

while their rate functions can be calculated through the law of mass action given by the equations (3.3.1)

$$\begin{aligned} W_1 &= W_1^+ - W_1^- = k_1^+ c_1 c_4^2 - k_1^- c_5^2. \\ W_2 &= W_2^+ - W_2^- = k_2^+ c_2 c_4 - k_2^- c_6. \\ W_3 &= W_3^+ - W_3^- = k_3^+ c_2 c_5 - k_3^- c_3 c_4. \\ W_4 &= W_4^+ - W_4^- = k_4^+ c_5 c_6 - k_4^- c_3 c_4^2. \end{aligned} \quad (5.8.10)$$

The balances are obtained through the detailed balances (laws of conservation) with respect to oxygen, carbon and platinum

$$Dc = Const.$$

$$\begin{bmatrix} 2 & 1 & 2 & 0 & 1 & 1 \\ 0 & 1 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix} = \begin{bmatrix} const_1 \\ const_2 \\ const_3 \end{bmatrix} \quad (5.8.11)$$

where the *const* are balances of oxygen, carbon and platinum, i.e:

$$\begin{aligned} const_1 &= b_{O=oxygen} = b_1, \\ const_2 &= b_{C=carbon} = b_2, \\ const_3 &= b_{Z=platinum} = b_3. \end{aligned}$$

## ILLUSTRATION

The above kinetic equation (5.8.5) can be written as

$$J(c) = \begin{bmatrix} k_1^- c_5^2 - k_1 c_1 c_4^2 \\ k_2^- c_6 - k_2 c_2 c_4 + k_3^- c_3 c_4 - k_3 c_2 c_5 \\ k_3 c_2 c_5 - k_3^- c_3 c_4 + k_4 c_5 c_6 - k_4^- c_3 c_4^2 \\ 2 k_1^- c_5^2 - 2 k_1 c_1 c_4^2 + k_2^- c_6 - k_2 c_2 c_4 + k_3 c_2 c_5 - k_3^- c_3 c_4 + 2 k_4 c_5 c_6 - 2 k_4^- c_3 c_4^2 \\ -2 k_1^- c_5^2 + 2 k_1 c_1 c_4^2 - k_3 c_2 c_5 + k_3^- c_3 c_4 - k_4 c_5 c_6 + k_4^- c_3 c_4^2 \\ -k_2^- c_6 + k_2 c_2 c_4 - k_4 c_5 c_6 + k_4^- c_3 c_4^2 \end{bmatrix} \quad (5.8.12)$$

## How to Calculate Equilibrium Numerically

Let us calculate an equilibrium for the system (5.8.1) involving six chemical species for which the following set of parameters is defined

$$k_1^+ = 1, k_2^+ = 1, k_3^+ = 1, k_4^+ = 10,$$

$$c_1^{eq} = 0.01, c_2^{eq} = .02, c_3^{eq} = 0.97, c_4^{eq} = 0.97, c_5^{eq} = 0.01, c_6^{eq} = 0.02$$

Laws of conservation give 3-balances defined by oxygen, carbon, and platinum (5.8.11),

$$b_{O=oxygen} = 1.21,$$

$$b_{C=carbon} = 1.01,$$

$$b_{Z=platinum} = 0.21.$$

The system is reduced to 3-dimension, and by solving a new system of kinetic equations we obtain a unique equilibrium point

$$c_1^* = 0.00000, c_2^* = 0.720503, c_4^* = 0.120496$$

## 5.9 How to Calculate and Use the QE Manifold of the System

Let us describe the procedure in two steps

- calculate the ‘initial layer’, also called the initial trajectories of the system.
- solve the slow system.

Consider a system of chemical reactions at constant volume and temperature. Under these condition the free energy  $F(N, T) = Vf(N, T)$  decreases.

Define a kinetics of  $n$  chemical species in the form

$$\frac{dN}{dt} = k_{sl}(N) + \frac{1}{\epsilon} k_{fs}(N). \quad (5.9.1)$$

The initial layer, defined by the fast subspace  $L$ , is spanned by their stoichiometric vectors, whose equations are represented as

$$(\alpha_i, A) \leftrightarrow (\beta_i, A) \quad i = 1 \dots m. \quad (5.9.2)$$

linear function form by the slow coordinates has dimension  $s = n - \dim L$  which can be chosen by any basis of the subspace here we take the orthogonal ones  $L^\perp$  define the basic function as  $b_j(N) = (b_j, N)$ ,  $j = 1 \dots p$  along with the remaining set of reactions are

$$(\alpha_l, A) \leftrightarrow (\beta_l, A) \quad l = m + 1 \dots m + q. \quad (5.9.3)$$

Now when the subsystem defined by the fast species  $N^f$  relaxes to the stationary states i.e,

$$N^f(A) \rightarrow N_{qss}^f(A)$$

During the initial layer the slow variables remain unchanged so the vector field becomes

$$J = J_s + J_f,$$

$$\dot{N}^f = J(N^s \oplus N^f), \quad N^s = \text{const}; \quad N^f \rightarrow N_{qss}^f(N^s)$$

so,

$$\dot{N}^s = k_{sl}(N)$$

will be transformed into

$$\dot{N}^s = J_s(N^s \oplus_{q_{ss}}^f(N^s)). \quad (5.9.4)$$

By careful analysis we come across (through an experiment) that when the system of fast reactions reaches to an equilibrium i.e,

$$k_s^+(T) \prod_{i=1}^n c_i^{\alpha_i} = k_s^-(T) \prod_{i=1}^n c_i^{\beta_i}, \quad (5.9.5)$$

there arises an additional balance of slow variable such that

$$(b_j^*, N) = Constants \quad (5.9.6)$$

$j = p + 1 \dots p + v$  then by knowing all these balances (atomic + additional ones) say  $M$  and through the equilibrium of fast reactions we can calculate the value of  $c(b_i)$  and the variation of slow variable  $b^*(t)$  obtained from the initial kinetics. In the next section we consider an example to clear the idea discussed here.

## 5.10 One dimensional Invariant Grid for CO on Pt oxidation (Implementing the idea)

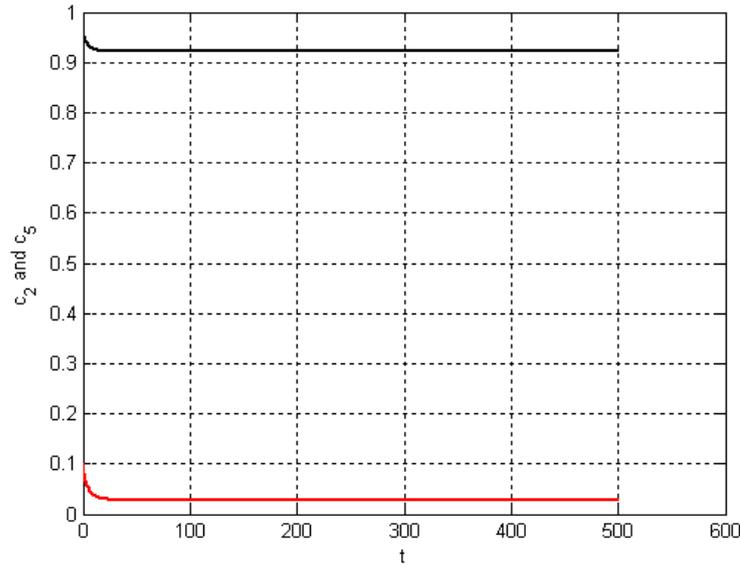
Consider a complex chemical reaction (5.8.1) involving six chemical species  $A_1 = O_2, A_2 = CO, A_3 = CO_2, A_4 = Pt, A_5 = PtO, A_6 = PtCO$ . Among this 4-step chemical reactions let us assume the first pair of reactions to be fast (1st case) i.e,



The subspace  $L$ , spanned by the stoichiometric vectors

$$\gamma_1 = (-1, 0, 0, -2, 2, 0), \quad \gamma_2 = (0, -1, 0, -1, 0, 1).$$

ONE DIMENSIONAL INVARIANT GRID FOR CO ON PT OXIDATION  
(IMPLEMENTING THE IDEA)



**Figure 5.4:** Initial layer defined by the fast system.

is two dimensional, whereas orthogonal complement to  $L^\perp$  is a three dimensional subspace spanned by vectors  $(2, 1, 2, 0, 1, 1)$ ,  $(0, 1, 1, 0, 0, 1)$ ,  $(0, 0, 0, 1, 1, 1)$ . So the balance equations defined by the oxygen, carbon, and platinum balances are

$$\begin{aligned} 2N_1 + N_2 + 2N_3 + N_5 + N_6 &= b_1, \\ N_2 + N_3 + N_6 &= b_2, \\ N_4 + N_5 + N_6 &= b_3. \end{aligned} \tag{5.10.2}$$

Consider a homogenous system. In this six dimensional system we still need some additional terms to solve the problem, which are provided by the fast subsystem (5.10.1). When it reaches to an equilibrium

$$\begin{aligned} k_1^+ c_1 c_4^2 &= k_1^- c_5^2, \\ k_2^+ c_2 c_4 &= k_2^- c_6, \end{aligned} \tag{5.10.3}$$

there arises an additional balance orthogonal to the fast system

$$2N_1 + N_5 = b_4. \tag{5.10.4}$$

ONE DIMENSIONAL INVARIANT GRID FOR CO ON PT OXIDATION  
(IMPLEMENTING THE IDEA)

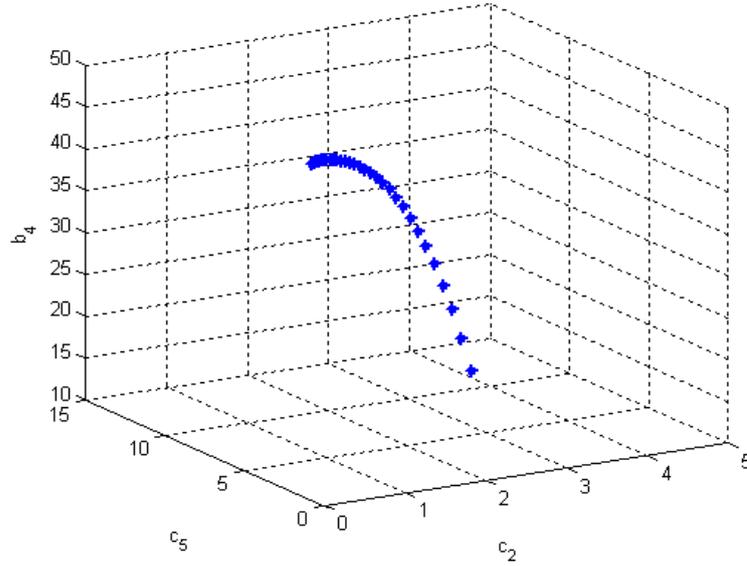


Figure 5.5: Slow system trajectory

Now we have four balances,

$$M = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \end{bmatrix} = \begin{bmatrix} 2N_1 + N_2 + 2N_3 + N_5 + N_6 \\ N_2 + N_3 + N_6 \\ N_4 + N_5 + N_6 \\ 2N_1 + N_5 \end{bmatrix}. \quad (5.10.5)$$

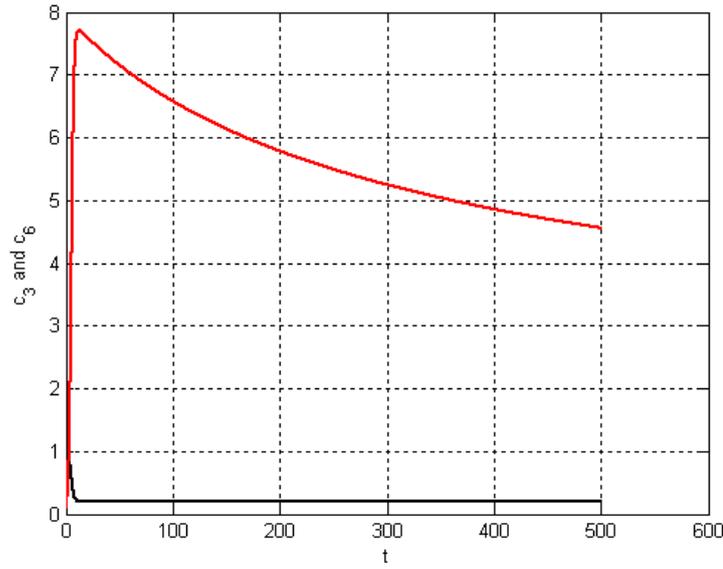
Note that

$$(M, \gamma) = 0.$$

Thus along with the fast kinetics, we solve the system and proceed with the slow variables. But before that, let us discuss the initial trajectories defined by the fast subsystem.

**Initial Layer:** Kinetic equation for the system is described in (5.2.18), The system is decomposed into fast and slow motions. During the fast motion the slow variable remains unchanged. Similarly during the slow motion fast variable variation is negligible. We solve the kinetics for the CO and PtO to obtain initial trajectories of the system, which can be seen in Figure 5.4 i.e, after a short interval of time the system goes to its steady state. We used the following parameters:

$$k_1^+ = 1, k_2^- = 1, k_3^+ = 1, k_4^+ = 10,$$



**Figure 5.6:** Initial layer trajectories of the fast system

$$c_1^{eq} = 0.01, c_2^{eq} = .02, c_3^{eq} = 0.97, c_4^{eq} = 0.97, c_4^{eq} = 0.01, c_6^{eq} = 0.02$$

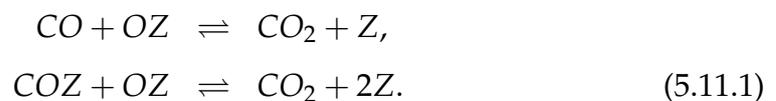
**Slow variable trajectories:** For the slow variables the equations are

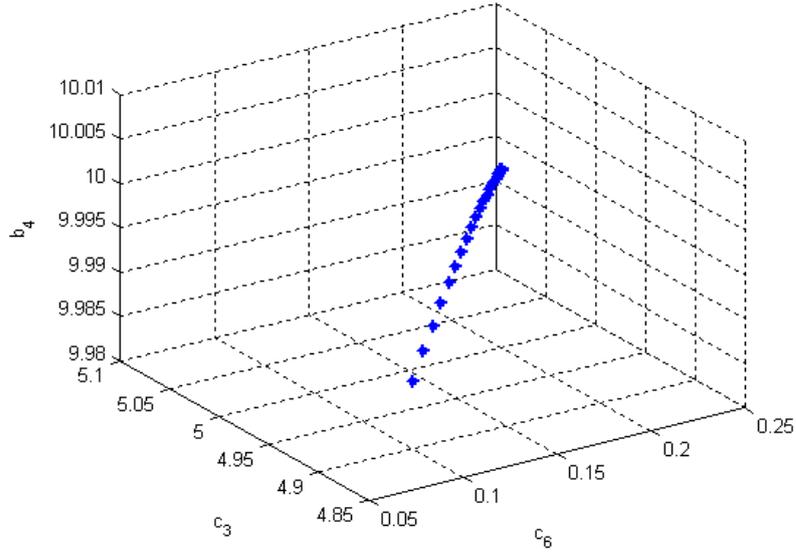
$$\begin{aligned} \dot{b}_1 &= 2\dot{N}_1 + \dot{N}_2 + 2\dot{N}_3 + \dot{N}_5 + \dot{N}_6, & \dot{b}_2 &= \dot{N}_2 + \dot{N}_3 + \dot{N}_6, \\ \dot{b}_3 &= \dot{N}_4 + \dot{N}_5 + \dot{N}_6, & \dot{b}_4 &= 2\dot{N}_1 + \dot{N}_5 \end{aligned}$$

together with initial layer when reaches to steady state. The system of slow variables can be solved in the same way under given parameters. Three dimensional trajectory between  $CO$ ,  $PtO$  and  $b_4$  is shown in Figure 5.5.

## 5.11 Stiff-non-stiff Transformation For Several Settings

There are six possibilities of choosing a pair of reactions to be fast in this 4-step chemical reaction (5.8.1). Here we consider a second pair of reactions as a fast pair





**Figure 5.7:** Slow trajectory of the system

A two dimensional subspace  $L$  is spanned by the stoichiometric vectors

$$\gamma_1 = (0, -1, 1, 1, -1, 0), \quad \gamma_2 = (0, 0, 1, 2, -1, -1),$$

while the balancing equations are defined by the orthogonal complement  $L^\perp$ , which is 3-dimensional (5.10.2). Additional balance,  $N_3 + N_5 = b_4$ , given by the fast equilibria

$$\begin{aligned} k_3^+ c_2 c_5 &= k_3^- c_3 c_4, \\ k_4^+ c_5 c_6 &= k_4^- c_3 c_4^2, \end{aligned} \quad (5.11.2)$$

makes a system non-stiff and easy to solve. Proceeding in the same manner as discussed in first case, we calculate its initial layer from the fast system defined by  $CO_2$  and  $Pt$  variables as shown in Figure 5.6 and slow manifold w.r.t  $b_4, CO_2, PtCO$  by choosing the same initial parameters we obtain a slow trajectory shown in Figure 5.7.

## 5.12 Higher dimensional Case

More than one dimensional case makes the system easier to solve. While analyzing the system from beginning to initial equilibrium one can select from the given number of reactions which one to be equilibrated. Just as we have cho-

## HIGHER DIMENSIONAL CASE

sen the adsorption reaction in a complex chemical reaction (oxidation of carbon monoxide over platinum) as our first case and then the equilibrium manifold is defined through this choice. Now, by considering the same system with only one reaction to be fast among all (as a second case) i.e,

$$(\alpha_1^*, A) \rightleftharpoons (\beta_1^*, A), \quad (5.12.1)$$

the remaining ones will form a slow system, i.e

$$(\alpha_i, A) \rightleftharpoons (\beta_i, A), \quad (5.12.2)$$

where  $i= 2\dots q + 1$ . In addition, balancing equation is given by the law of thermodynamics

$$(b_j, N) = Constants, \quad j = 1\dots p. \quad (5.12.3)$$

plus additional balances arise, when the fast system reaches an equilibrium state

$$(b_j^*, N) = Constants, \quad j = p + 1\dots p + v. \quad (5.12.4)$$

An initial layer is obtained from the fast system (equation in that case) projected onto the trajectory given by the slow variables. Same is the case for the high dimensional problem for this case therefore we focussed on the 1-d case.

# Intrinsic Low Dimensional Manifold

Now a days, computational challenges are in every field of Science. In the field of chemical kinetics, we deal with it in a **detail transport, complex chemical kinetics** which can either be simplified by the simplified transport calculation i.e, Naiver Stock's Method for detail transport. In case of complex chemical kinetics, it can be simplified by a number of ways discussed in Section 6.1. In order to understand the behavior of chemical species  $(N_i, c_i)$  in a system of complex reactions, people are impelled to transform the chemical system into mathematical form in order to express the interrelation among the species to help monitor and control the system behavior.

This mathematical form of the system generally involves a nonlinear system which cannot be solved analytically so the other way left is to solve it numerically by assuming an initial condition for each concentration variable and then assuming small time interval  $\delta t$  to replace the infinitesimal  $dt$  to calculate concentration at the next time step.

This can be done with the help of modern computers but with certain limitations. Alternatively we can apply a model reduction techniques for which various methods have been developed so for.

## 6.1 Model Reduction

Different chemical species move with different time scales in a chemical reactions, so time scales describe their rate of decay and characterize their solutions. For numerical purpose and because of their dominant cause of variation of fast time scale in their earliest time of reaction, small time scale is required near the initial conditions. After some time the change in the solution due to their rate of decay becomes zero and the values of dependent variable approach towards the equilibrium state. "The state where further increase in the independent variable (fast ones) does not affect (too much) the dependent variables (slow variable)" which requires a lot of computational work while moving from the initial to equilibrium state.

There are several essentially different approaches to asymptotic and scale separation in kinetics and each of them has its own area of applicability. It is also important to find a reduce system in such a ways that it may not affect the accuracy and complete description of the solution of the system which can either be achieved by quasi equilibrium method or by quasi steady state which are discussed in detail in previous chapter (5).

These methods are quite important to understand which leads to lower dimension manifold in a composition space and are directly related with the rate of some vectors vanishes in direction of composition space, just like in the case of quasi equilibrium assumption. Similarly in the steady state assumption force, it is the rate of production of some species to vanish. In reduce mechanism method (RMM) the most common of them are: Quasi Equilibrium Approximation (QEA), Quasi Steady State Approximation (QSSA), Dynamic Dimension Reduction (DDR) (including methods of invariant manifolds), Sensitivity Analysis (SA), method of Limiting Step (LS), Computational Singular Perturbation (CSP), Intrinsic Low Dimension Manifold (ILDM).

### Quasi Equilibrium Approximation

Most of the works on non equilibrium thermodynamics deal with the QE approximations and corrections to them, or with applications of these approximations (with or without corrections). There are two basic formulation of the QE

approximation: the thermodynamic approach, based on entropy maximum, or the kinetic formulation, based on selection of fast reversible reactions. The very first use of the entropy maximization dates back to the classical work of Gibbs [26], but it was first claimed for a principle of informational statistical thermodynamics by Janes [39]. A very general discussion of the maximum entropy principle with applications to dissipative kinetics is given in the review [5]. Corrections of QE approximation with applications to physical and chemical kinetics were developed in [27, 28].

The basic assumption behind the quasi-equilibrium is the hypothesis of the decomposition of motions into fast and slow. The quasi-equilibrium approximation itself describes slow motions. However, sometimes it becomes necessary to restore the whole system, and to take into account the fast motions as well. With this, it is desirable to keep intact one of the important advantages of the quasi-equilibrium approximation - its independence of the rate constants of fast reactions. For this purpose, the detailed fast kinetics is replaced by a model equation (single relaxation time approximation)[22].

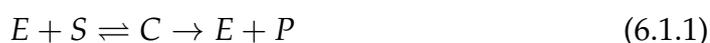
The QE approximation in a Chemical Kinetics implies that some intermediates (enzymes or catalyst) rapidly establish equilibrium state after the start of reaction and has no disturbing affect on the catalyzed reaction. QE is a common technique used in enzyme kinetics and is usually applied for reversible chemical reactions. It has a combined character with steady state of the system but the reason for its wide use is its simplicity in resulting the kinetics equations and its easily derivation. It basically establishes a condition for the maintenance of constant value of substrate and product concentration during the catalyzed reaction by giving an idea that whether the reaction proceed or not if the ratio of intermediate concentration is in equilibrium. And the result of all is that in the equilibrium segment the intermediate concentration negligibly depends on the catalyzed reaction proceed or not.

## Quasi Steady State Approximation

QSS was proposed by Bodenstein in 1913 [6], and the important Michaelis and Menten work [47] was published simultaneously. It appears that no kinetic theory of catalysis is possible without QSS. This method was elaborated into

an important tool for analysis of chemical reaction mechanism and kinetics [58, 13, 36]. The classical QSS is based on the *relative smallness of concentrations* of some of “active” reagents (radicals, substrate-enzyme complexes or active components on the catalyst surface) [7, 1, 60].

QSSA is an important technique for mathematician, used to derive many of the equations that describe enzyme kinetics. It states that after an initial transient the concentration of a chemical specie will not change significantly with respect to the remaining concentrations of the system. We indicate the general process by working through a standard example (Michaelis-Menten mechanism):



discussed in detail (5.2). Where as in this mechanism  $E$  is enzyme and  $S$  is substrate  $C$  is enzyme substrate, intermediate complex and  $P$  is the product.

Chemical kinetics systems often have invariants [51]. These invariants express mass conservation laws such as the one in the case (6.1.1). The advantage of this method is that the dimensionality of the system is reduced through by the conservation laws which basically leads to the more simplification by setting the concentration with respect to time to zero, because of the assumption that it is negligible. Applying the QSSA reduces the order of the system of differential equations by an amount equal to the number of chemical species to which an assumption is applied.

## Dynamic Dimension Reduction

Reducing dimension of a system may cause a loss of useful information but searching in multiple dimensions has been extensively researched in the database and computational geometry literature. From the geometrical point of view, the behavior of chemical species and their trajectories are attracted towards the surface of increasingly lower dimension, that are usually called the slow invariant manifold SIM. Although there exists several procedures for detecting the useful data structures such as R-trees, hB-trees, SS-trees and SR-trees which are used in fast searching in large multi-dimensional databases which are quite efficient for small dimensional system (of order upto 1-10). However, as the dimensionality

of data increases, the query performance of these structures degrades rapidly.

## Sensitivity Analysis

It deals with the principal component of the reaction, measured by normalization of each reaction and separate the reaction which has little effect on overall reaction mechanism or which has a low sensitivity. So left with only principal component representing one way of getting reduced mechanism. For a number of reasons, sensitivity analysis is useful in computer and mathematical modeling. In more general terms uncertainty and sensitivity analysis investigate the robustness of a study when the system involves complexity. It supports decision making or the development of recommendations, making it more credible, understandable, compelling or persuasive increased understanding or quantification of the system (e.g. understanding relationships between input and output variables) and model development (e.g. searching for errors in the model).

## Lumping Procedure

In this technique, an assumption was made that the chemically similar species behave at the same rate in chemical reactions. They are considered to be a single compound rather than considering it to be separately. But in this procedure a useful information of detail reaction has been lost by compromising the detail mechanism with global mechanism.

Lumping analysis aims to combine reagents into "quasicomponents" for dimension reduction [68, 42, 43, 62].

Wei and Prater [69] demonstrated that for (pseudo) monomolecular systems, there exist linear combinations of concentrations which evolve in time independently. These linear combinations (quasicomponents) correspond to the left eigenvectors of kinetic matrix: if  $lK = \lambda l$  then  $d(l, c)/dt = (l, c)\lambda$ , where the standard inner product  $(l, c)$  is concentration of a quasicomponent. They also demonstrated how to find these quasicomponents in a properly organized experiment.

This observation gave rise to a question: how to lump components into proper quasicomponents to guarantee the autonomous dynamics of the quasicompo-

nents with appropriate accuracy? Wei and Kuo studied conditions for exact [68] and approximate [42] lumping in monomolecular and pseudomonomolecular systems. They demonstrated that under certain conditions large monomolecular system could be well-modelled by lower-order system.

More recently, sensitivity analysis and Lie group approach were applied to lumping analysis [43, 62], and more general nonlinear forms of lumped concentrations were used (for example, concentration of quasicomponents could be rational function of  $c$ ).

Lumping analysis was placed in the linear system theory and the relationships between lumpability and the concepts of observability, controllability and minimal realization was demonstrated [12]. The lumping procedures were considered also as efficient techniques leading to nonstiff systems and demonstrated efficiency of developed algorithm on kinetic models of atmospheric chemistry [19]. An optimal lumping problem can be formulated in the framework of a mixed integer nonlinear programming (MINLP) and can be efficiently solved with a stochastic optimization method [45].

## Limiting Step

The concept depending on limit simplification defines the behavior of whole network of the system and behave as a single step. This is the most popular approach for model simplification in chemical kinetics and in many areas beyond kinetics. In the form of a *bottleneck* approach, this approximation is very popular from traffic management to computer programming and communication networks. Recently, the concept of the limiting step is extended to the asymptotically of multiscale reaction networks ([29, 2]).

## Computational Singular Perturbation

An iterative method used to reduce the dimensionality of system of ordinary differential equation with multiple time scale defined by fast and slow dynamics of trajectories. Also common for clear understanding and analysis of complex kinetics behavior. By reducing the number of dependent variables reduces the resource required for the computational work, which make the system less

stiff.

## Intrinsic Low Dimension Manifold

Maas and Pope (1992) introduced a method which automatically applies the steady-state and quasi equilibrium approximation over all possible thermochemical states of system. Using the same fact, during a reaction a large number of chemical processes are so fast that they are not rate limiting and can be decoupled. Then these decoupled  $n_f$  fast reactions which are faster than the flow time scales can be ignored while those with slow time scales are tracked using progress variables. What ILDM method does is to identify attracting intrinsic low dimensional manifolds in  $n_s = n - n_f$  dimensional state space with the property that after a short time the thermodynamical state of the system has relaxed onto the low-dimensional manifold  $n_s$ . Since the  $n_s$  progress variables completely describe the system, only these variables must be calculated which leads to a dramatic reduction of CPU time for solving the chemistry in a reacting flow calculation. Importance and further explanation of this method is discussed in the next section.

## 6.2 Advantages and Disadvantages

There are a number of advantages and disadvantages related to each method (discussed above) are hereby discussed in detail as a comparison. Although these methods are easy to implement (RMM) but some drawbacks are also related with them, namely the explicitly imposed assumption:

- The major one is that even for a couple of reaction the number of differential equations generated can be very high. Which requires a lot of computational time, (QEM, QSSA, SA).
- Because of the lack of understanding of correlation between the chemical species, the interpretation of simulation results are difficult, (QEM, QSSA, SA).
- In order to understand and then implement the mechanism one must need to do case to case study of each reaction, (QEM, LA, QSSA, SA).

## ADVANTAGES AND DISADVANTAGES

- Then according to the nature of the reaction their composition at different temperature , different quasi equilibrium and quasi steady state have to be specified.
- The species which are in quasi steady state in domain of composition space , but might be improper outside the specified domain.
- RMM i.e, (QEM, QSSA, SA, LP, LS) works in a limited range. The reason for it is that it depends greatly on physical conditions, change in reaction path as combustion moves from fuel rich to fuel-lean conditions.

Therefore we need such a method which allows us to specify only the desired dimension of the reaction subspace. Which does not depend upon the experience or intuition from the person applying it and describe the most essential and interesting detail of the system. Such a system can be achieved which depend upon the analysis of eigenvalue and eigenvectors obtained from the Jacobian of their system equations such as in ILDM. For the combustion system it was firstly introduced by Mass and Pope in 1992 but the idea about manifold has been in the literature for much longer and has several advantages.

- The ILDM used to describe reduce chemical kinetics in such a way to extract automatically the required information from the full system.
- Most of the detail chemistry is maintained in this method ,still gives computation speed up in chemical reaction.
- Depending on time scale, it reduces the effort made for simplifying the reaction mechanism by eliminating reaction or species.
- Ignoring the fast time scale (yet depending in detail kinetics), gives the opportunity to calculate only slow time scale.
- It is also important in a sense that it requires system and the desired dimension only for an initial input. It doesn't depend on the rate and speed of the reaction with which it moves to produce or to be consumed during the reaction.
- More over as long as there exists an attracting stable manifold there is no chance of this method to fail. which make it to be more reliable than the others to be easily applicable and accurately calculated.

## Decoupling fast time scale

Separation of the chemical species according to their time scale gives a useful information about the reaction's. A large negative value indicates that the reaction is governed by the fast chemical reaction and is in local equilibrium. Thus the time scale  $\tau_{flow}$  associated with each reacting flow based on a resolution of the transport calculation and their frequency  $1/\tau_{flow}$ , shown in following table.

<b>Eigenvalues</b>	<b>Frequency</b>	<b>eigenvectors</b>	<b>eigenspace</b>
$Re(\lambda_i) >$	$1/\tau_{flow}$	$e_i(\lambda_i) \in$	Slow Space
$Re(\lambda_i) <$	$1/\tau_{flow}$	$e_i(\lambda_i) \in$	Fast Space
$Re(\lambda_i) =$	0	conserved variables	i.e pressure in isobaric system

The eigenvectors belonging to fast subspace can be decoupled from the reaction system and the remaining one (i.e which can not be decoupled) form a reduced system. This is also common in laminar or turbulent combustion calculation.

### 6.3 Stiffness Measure

In a chemical combustion where each elementary reaction behaves differently with respect to time. Therefore, in a system of ODE with time independent variables are characterized by local set of time scale. In order to capture their different time scale (due to elementary reaction) the useful information is obtained through the eigenvalue of the Jacobian of the system of ODEs. The reciprocal of the real part of eigenvalue are the time scale for the system behavior near the point and if there exists imaginary part of it then it describes the frequency with which solution oscillates at a point.

The real part of the eigenvalue describes the exponential decay for stable systems or exponentially grow for unstable systems of the solution which defines the time scale. It is also important to note that as the Jacobian of the system changes with time, their time scale also evolves along it which are indicated as  $J_0$  such that jacobian at a point 0. The reason for such a calculation is that the concentration of chemical species are not same. Some species (chemical species) evolve more quickly than the others in the initial period of time but as

the time passes the other species (remaining ones) become dominant call the slower time scale terms. By careful analysis, it has been observed that there is specific range of time scale in the solution for the evolution of different species. The stiffness of the system has been calculated through the ratio of fastest to the slowest time scale of the species i.e, if  $\lambda_1, \lambda_2, \dots, \lambda_n$  are the eigenvalues of Jacobian  $J$  of the system, then stiffness  $S$  is given by

$$S = \frac{\|Re(\lambda)\|_{max}}{\|Re(\lambda)\|_{min}}. \quad (6.3.1)$$

The larger value of  $S$  is the indication of stiffness in a system which can be transformed into nonstiff system by adopting the certain techniques discussed in detail in Chapter 5. Reduce the mechanism, as it done in the quasi equilibrium and quasi steady state technique or implement a method ILDM.

When the rates of fast to slow time scale differ by several order of magnitudes, then the useful information can be obtained within the solution part of the slowest time scale which approaches towards the equilibrium for all initial conditions. Slow time scales are important to describe the kinetics of the system for the time of interest rather than the fast time scale variation which is assumed to be in steady state without significant loss of the system kinetic description. Here no assumptions were made about their specific behaviors.

## 6.4 Dimension of the Manifold

The dimension of the manifold is directly related to the amount of time passed after the continuation of reaction and before the manifold is in a good description of the solution. The number of variables in the reduced set determine the dimension of the manifold. The system can be defined dimensionally as

- Equilibrium point, zero dimension attracting manifold for the system in a phase space, all the trajectories approach to one common point.
- The time when solution trajectories attract towards and away from the equilibrium point to some other region within an infinitesimal period of time, the slowest time scale term becomes dominant than all other terms at each point. Then solution approaches to a one dimension path in a

phase space representing one dimensional manifold, all trajectories approach to a common trajectory where only slow time scale governs the chemical reaction.

- When the next slowest time scale term dominates all fast terms rather than slowest time scale term, then the solution will move along the two dimensional surface in phase space representing two dimensional manifold for a system.

Once a thermodynamic system is on the manifold it will never leave the system until there exist any perturbation in a system, whether it is through physical process like molecular diffusion, heat convection and mixing or by any other means. If the system is perturbed at a time scale slower than the fastest time scale of the manifold, then it does not affect the dynamics of the system. But if the perturbation happens at a time scale that is faster than the existing manifold, a higher dimensional manifold should be employed (Blasenbrey, et al. 1998). Similarly, other formulations can be defined for higher dimensional manifold if there exists in a system, in order to capture a larger number of time scales which simply means that more number of progress variables must be added to the manifold.

## 6.5 Mathematical Model

In this section we discuss how to find invariant manifold by using an ILDM technique. Let us consider an  $n$ -dimensional system of ordinary differential equations represented as

$$\frac{dX}{dt} = \phi(X) \quad (6.5.1)$$

Their function describes the rate of change of dependent variable with respect to dependent variable and other constant parameter. To find the low dimension manifold for the system, it is necessary to know the time scale associated with the solution at each point in the solution space. If there are  $n_s$  characteristic time scales (the eigenvalue of their Jacobian) then there exists  $n_s$  characteristic direction (eigenvector) associated with it. Its Jacobian  $J$  at each point in the

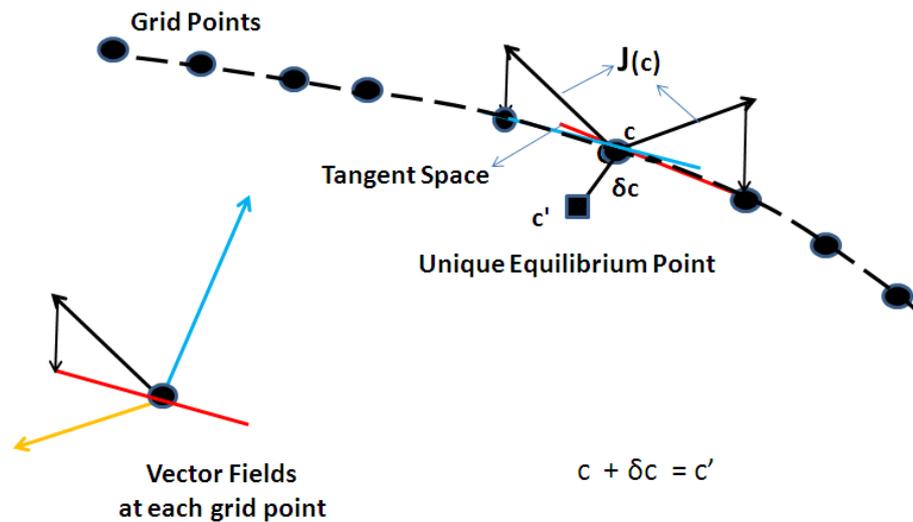


Figure 6.1: General idea of constructing 1D ILDM, starting near its equilibrium  $c'$  in the forward and backward direction.

solution space is represented as a

$$J = \begin{bmatrix} \frac{\partial \phi_1}{\partial x_1} & \cdot & \cdot & \cdot & \frac{\partial \phi_1}{\partial x_n} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \frac{\partial \phi_n}{\partial x_1} & \cdot & \cdot & \cdot & \frac{\partial \phi_n}{\partial x_n} \end{bmatrix}_0 \quad (6.5.2)$$

'0' indicates the point where Jacobian is evaluated. Now the perturbed system can easily be analyzed within these eigenspaces.

- Positive eigenvalues indicates the increasing perturbation in the direction of the eigenvector.
- Negative eigenvalues indicates the relaxing perturbation at some point.
- Zero eigenvalue represents the conserved variables.

The manifolds in their state space can be defined by dividing their space into two subgroups at each point of the system. Fast subspace and slow subspace. Slow subspace arises from the fast one when the fast subspace represent the steady state  $n_f$  gives the slow manifold  $n_s = n - n_f$ .

$$\max\{Re[\lambda_i], i = 1, \dots, n_f\} \ll \tau < \min\{Re[\lambda_i], i = n_f + 1 \dots n\}, \quad \tau < 0. \quad (6.5.3)$$

The reason behind this partition is that, to eliminate the possibility that the solution trajectories travel along the fast time scale direction or in other words the low dimension manifold contains only the slow time scale term of the solution. In order to eliminate the characteristic direction associated with the fast time scale at each point this can be easily achieved by considering them to be in orthogonal directions. Normally the eigenvectors we obtain through diagonalization are not orthogonal, so the best way is to apply Schur decomposition on Jacobian  $J$  at each point in a phase space. The Schur decomposition of a matrix  $M$  whose elements are real number are represented as

$$J = Q^T T Q \quad (6.5.4)$$

The transition matrix  $Q(X)$  from the local basis to a standard one obtained through the eigenvector of Jacobian and its inverse  $Q(X)^{-1}$  can be represented in a block matrix form as

$$Q = (Q_f, Q_s); \quad Q^{-1} = \begin{pmatrix} \tilde{Q}_f \\ \tilde{Q}_s \end{pmatrix}.$$

$$\begin{pmatrix} \tilde{Q}_f \\ \tilde{Q}_s \end{pmatrix} \cdot (Q_f, Q_s) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = I \quad (6.5.5)$$

where as  $Q_f$  represents a  $(n \times n_f)$  Matrix of fast eigenvectors and  $Q_s$  represents  $(n \times n_s)$  Matrix of slow eigenvectors,  $\tilde{Q}_f$  implies  $(n_f \times n)$  Matrix of fast eigenvectors,  $\tilde{Q}_s$  implies  $(n_s \times n)$  Matrix of slow eigenvectors.

Now Schur decomposition exists at every point in the solution space where the system  $\phi(X)$  is continuous and can be accurately calculated at each point of  $T$  contain the eigenvalues of  $J$  in descending order of magnitude.

According to the Mass and Pope, the intrinsic low dimension manifold is determined by an undetermined system of  $n_f$  equation for  $n$ -variables

$$\tilde{Q}_f \cdot \phi(X) = 0, \quad (6.5.6)$$

which vanishes the large part of Jacobian matrix corresponding to fast time scale. Here  $\tilde{Q}_f$  denotes the  $(n_f \times n)$  matrix, whose rows partitioning are the

transpose of Schur matrix.

## 6.6 The Scheme

The basic idea behind this scheme is to find a maximum number of points that define the manifold at discrete location in the phase space. As the analytical solution for the system of non-linear equation  $\phi$  is not possible in the case. Therefore the procedure adopted here is Schur decomposition applied on the jacobian at each point for which, one must have to move to the point near to the equilibrium point and then by making the correction through by an ILDM proceed it further as shown in Figure 6.1. An approximate guess for the next step on the manifold is obtain by moving a small distance along the tangent to the manifold at that point.

$$x_i^g = x_i^p + \Delta x_i \quad (6.6.1)$$

where  $p$  represent the previous point and  $g$  is the next guess made. Similarly for the next points, an assumption can be made by solving this expression

$$Q^T(x_i^g - x_i^p) = 0 \quad (6.6.2)$$

Once  $x^g$  is found, the above equation can be solved by any of the iterative root solver where as the iteration starts by using the  $x^g$  as initial guess for the next manifold point and continuous until the convergence can be achieved with in a specified tolerance. Similarly adopting the same procedure before and after the equilibrium point to get the attracting trajectory of one dimensional manifold.

## 6.7 One Dimensional ILDM for Oxidation of CO/Pt

In order to implement the idea discussed above we consider again a system of our case study, Oxidation of CO/Pt. Consisting of four steps chemical reaction involving six species  $O_2 = A_1, CO = A_2, CO_2 = A_3, Pt = A_4, PtO =$

$$A_5, PtCO = A_6.$$

$$\begin{aligned} A_1 + 2A_4 &\rightleftharpoons 2A_5, \\ A_2 + A_4 &\rightleftharpoons A_6, \\ A_2 + A_5 &\rightleftharpoons A_3 + A_4, \\ A_5 + A_6 &\rightleftharpoons A_3 + 2A_4. \end{aligned} \quad (6.7.1)$$

The equations for the oxygen, carbon, platinum balance can be obtain through conservation law is defined in 5.8.11. This time, there is no need to make a partition of the system (as we did in our previous methods in previous chapters) consider a whole mechanism. Our system is reduced to three dimensions due to the balances and we are left with only two gas and one surface equation in the form of

$$\begin{aligned} c^g &= \frac{S}{V}(\gamma_1^g W_1 + \gamma_2^g W_2 + \gamma_3^g W_3 + \gamma_4^g W_4) + \frac{v_{in} c_{in}^g}{V} + \frac{v_{out} c^g}{V}. \\ c^s &= \frac{S}{V}(\gamma_1^s W_1 + \gamma_2^s W_2 + \gamma_3^s W_3 + \gamma_4^s W_4). \end{aligned} \quad (6.7.2)$$

Let us call this reduced system to be  $F(c_i, b_i) = \phi(X)$  and introduce the following parameters for it.

$$k_1^+ = 1, k_2^+ = 1, k_3^+ = 1, k_4^+ = 10,$$

$$c_1^{eq} = 0.1, c_2^{eq} = .40, c_3^{eq} = 0.40, c_4^{eq} = 0.40, c_5^{eq} = 0.34, c_6^{eq} = 0.21,$$

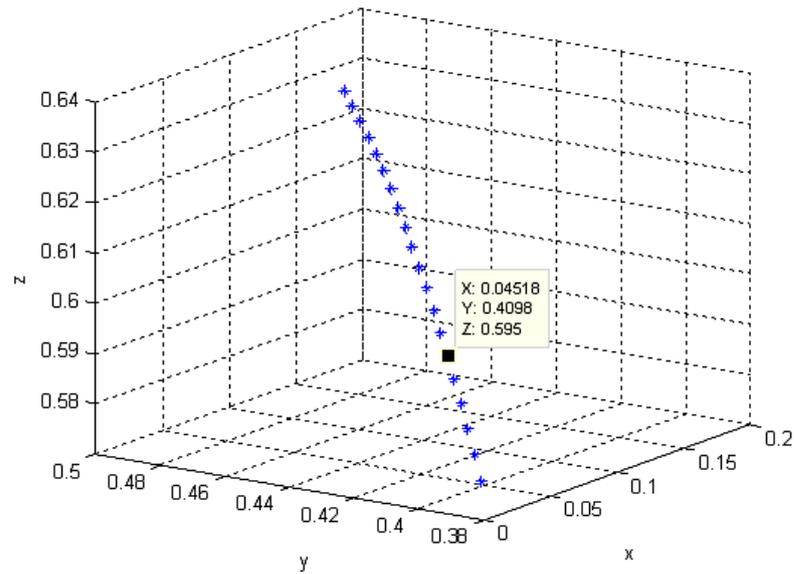
and by solving the reduced system of kinetic equations with respect to following parameters, we obtain a unique equilibrium point for the system, i.e

$$c_1^* = 0.04518, c_2^* = 0.4098, c_4^* = 0.595.$$

The differential of the system gives Jacobian which is to be calculated at each point, is represented as

$$J_p = \frac{\partial \phi}{\partial x_j}. \quad (6.7.3)$$

where,  $j = 1, 2, 3$  and  $J_p$  indicate Jacobian at a point  $p$ . The eigenspace span by the system is calculated at each defined time interval. By applying Schur decomposition at each point and reducing the model, it is possible to solve it



**Figure 6.2:** One dimensional intrinsic low dimension manifold, square represents equilibrium point.

analytically, or even by hand calculations in order to get the guesses for the next manifold point  $x^8$ . But for a large system the numerical solution is perfect. And it is possible to get the whole solution of it which is then verified by comparing them with the actual solution points. Also being a reduced system, it no longer remains stiff and it is possible to get the whole solution for the system easily. It is also important to verify that the point on the manifold represents an intrinsic low-dimensional attractive manifold and are well described after being the fast time scale of the solution have been decayed.

As shown in a Figure 6.2 this technique is applied on both the side of the equilibrium point and moves along the tangent by correcting each term, indicates that as the time passes the solution approaches to an equilibrium point. The fast time scale part of the solution decays and solution approaches the manifold, called the intrinsic low dimensional manifold.

## Conclusion and outlook

In this thesis we presented in detail the modern techniques of model reduction in a complex chemical reaction. These model reduction techniques are based on constructing accurate approximations of invariant manifolds for the system of kinetic equations. Given the approximate slow invariant manifold of a dynamical system, the reaction is described as a slow motion along the manifold and a fast motion towards the manifold.

The main ideas behind the construction of the slow invariant manifold (SIM), are based on finding initial approximation using Quasi Equilibrium Manifold (QEM) and Quasi Steady State Approximation (QSSA) and finally the Intrinsic Low Dimensional Manifold (ILDM) and then refining it by any of the methods discussed in Chapter 2.

We present the general formalism of the Quasiequilibrium approximation (QE) with the proof of the persistence of entropy production in the QE approximation (Section 2.3). We demonstrate how to apply this formalism to chemical kinetics, and give several examples for the Mass Action law kinetic equation. We discuss the difference between QE and QSS and analyze the classical Michaelis–Menten and Briggs–Haldane model reduction approaches (Section 2.6). After that, we use ideas of Michaelis, Menten and Stueckelberg to create a general approach to kinetics. The method of invariant grids is utilized for reducing the kinetics of a simple two-dimensional system (Section 2.8) as a first case in order to obtain an one-dimensional description (by refinement). Different initial approximations have been calculated and refined.

What are the main results of our discussion? First of all, we believe that this

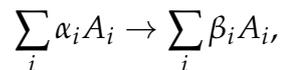
is the finish of the Michaelis–Menten–Stueckelberg program. The approach to modeling of the reaction kinetics proposed by Michaelis and Menten in 1913 [47] for enzyme reactions was independently in 1952 applied by Stueckelberg [59] to the Boltzmann equation. Some consequences of the Stueckelberg approach were rediscovered for the Mass Action law kinetics by Horn and Jackson in 1972 [25] and supplemented by the ‘zero deficiency theorem’ [50]. This is the history.

In our work, we develop the Michaelis–Menten–Stueckelberg approach to general kinetics. This is a combination of the QE (fast equilibria) and the QSS (small amounts) approaches to the real or hypothetical intermediate states. These intermediate states (compounds) are included in all elementary reactions (4.1.3) as it is illustrated in Figure 4.2. Because of the small amount, the free energy for these compounds  $B_i$  is perfect (4.1.5), the kinetic of compounds is the first order Markov kinetics and satisfies the Master equation. After that, we use the combination of QE and QSS approximations and exclude the concentrations of compounds. For the general kinetics the main result of this approach is the general kinetic law (4.2.2). Earlier, we just postulated this law because of its convenient and natural form ([30],[9]), now we have the physical framework where this law can be proved.

What is the most attractive feature of this approach to general non-ideal kinetics? We do not assume anything about reaction rates of the main reactions (2.2.4). We use only thermodynamic equilibrium, the hypothesis about fast equilibrium with compounds and the smallness of concentration of compounds. This smallness implies the perfect entropy and the first order kinetics for compounds. After that, we get the reaction rate functions from the qualitative assumptions about compounds and the equilibrium thermodynamic data.

For example, if we relax the assumption about fast equilibrium and use just smallness of compound concentrations (the Briggs-Haldane QSS approach) then we immediately need the formulas for reaction rates of compound production. Equilibrium data become insufficient. If we relax the assumption about the smallness of concentrations then we lose the perfect entropy and the first order Markov kinetics. So, only the combination  $QE + QSS$  gives the desired result.

The general kinetic law has a simple form: for an elementary reaction,



the reaction rate is  $r = \varphi \Omega$ , where  $\Omega > 0$  is the Boltzmann factor,  $\Omega = \exp(-\sum_i \alpha_i \mu_i)$ ,  $\mu_i = \partial S / \partial N_i$  is the chemical potential divided by  $RT$ , and  $\varphi \geq 0$  is the kinetic factor. Kinetic factors for different reactions should satisfy some conditions. Two of them are connected to the basic physics:

- The detailed balance: the kinetic factors for mutually reverse reaction should coincide,  $\varphi^+ = \varphi^-$ . This identity is proven for systems with microreversibility (Section 4.3.5).
- The complex balance: the sum of kinetic factors for all elementary reactions of the form  $\sum_i \alpha_i A_i \rightarrow \dots$  is equal to the sum of kinetic factors for all elementary reactions of the form  $\dots \rightarrow \sum_i \alpha_i A_i$  (4.2.19). This identity is proven for all systems under the Michaelis-Menten-Stueckelberg assumptions about the existence of intermediate compounds which are in fast equilibria with other components and are present in small amounts.

For the general kinetic law we studied several sufficient conditions of accordance between thermodynamics and kinetics: detailed balance, complex balance and G-inequality. In the practice of modeling, a kinetic model may, initially, do not respect thermodynamic conditions. For these cases, we solved a problem: is it possible to add a linear function to entropy in order to provide agreement with the given kinetic model and deformed thermodynamics? The answer is constructive (Section 4.3) and allows us to prove the general algebraic conditions for the detailed and complex balance. In Section 5.3, we propose to revise the model reduction problem statement. What is our main problem: to reduce dimension or to remove stiffness? Of course, it is desirable to solve both problems but if it is impossible then let us study the problem of stiffness removal. We demonstrate how to use the QE approximation for stiffness removal and give an example, the CO oxidation on Pt.

Thermodynamics play an important role for constructing an invariant manifold in the case of QEM and QSSA, where we consider that the extensive parameters in the absence of any internal constraints are those that maximize the entropy

over the manifold of constrained equilibrium states. The entropy is continuous and differentiable and is monotonically increasing function of the energy and vanishes in the state where variation of energy w.r.t entropy is zero, (i.e. where temperature  $T = 0$ ). This is known as the 'entropy maximum postulate'. In open systems the concepts of thermodynamics and the quasi equilibrium manifold are important for the cases of constructing slow invariant manifolds. Thermodynamic projector plays an important role. It transforms an arbitrary vector field equipped with a given Lyapunov function into a vector field with a same Lyapunov function on any manifold which is not tangent to the level of the Lyapunov function. The quasi chemical approximation is a very important working tool for assembling the equations. It enables us to construct and study wide classes of evolution equations with prescribed Lyapunov functions.

While in the final case the method used is ILDM which is independent of all these measures (discussed above), and is fast in the sense of computation. Depending on eigenspace it determines the required dimensions of the manifold.

Thus we can say that it is possible to construct invariant manifolds. The problem of constructing invariant manifolds can be formulated as the invariance equation, subject to additional conditions of slowness (stability). The Newton method with incomplete linearization, relaxation methods, the method of natural projector, and the method of invariant grids enables well-read approximations to the slow invariant manifolds. These methods were tested on a recently discovered class of exactly solvable reduction problems [54]-[56]. It becomes further clearer at the present time that the constructive methods of invariant manifold are useful for a wide range of subjects, spanning from applied hydrodynamics to physical and chemical kinetics [22].

There are a number of reasons for constructing slow invariant manifold that is necessary for the model reduction. Specifically in the case of complex kinetic systems with a known detailed description of the system we normally solve the initial value problem for the system. But the idea fails when we know only small part of the interacting system (like in a complex chemical reaction system). Finally, the modern technique we applied to calculate initial approximation of the system can be further used to find the SIM by using any method discussed in chapter 2.

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# Appendix

## Appendix 1

### 1 D invariant manifold for CO oxidation over Pt

Here we consider a 1st pair of reaction to be fast as discuss in section (**One dimensional(1D)Invariant Grid for CO on Pt oxidation (Implementing the idea)  $O_2 + 2Z \rightleftharpoons 2ZO, CO + Z \rightleftharpoons ZCO$** ) and apply the Quasi Steady State Approximation (QSSA) on it in order to get rid of stiffness arises in the system.

where as  $O_2, CO, CO_2, Z, ZO, ZCO$  are  $c_i = c_{1-6}$  :

The model we have to solve consist of ,

$$\Phi(\mathbf{c}, \mathbf{b}) := \begin{bmatrix} k_1^+ \cdot c_1 \cdot c_4 - k_1^- \cdot c_5^2 \\ k_2^+ \cdot c_2 \cdot c_4 - k_2^- \cdot c_6 \\ 2 \cdot V_g \cdot c_1 + V_g \cdot c_2 + 2V_g \cdot c_3 + V_s \cdot c_5 + V_s \cdot c_6 - b_1 \\ V_g \cdot c_2 + V_g \cdot c_3 + V_s \cdot c_6 - b_2 \\ V_s c_4 + V_s c_5 + V_s \cdot c_6 - b_3, \\ 2 \cdot V_g \cdot c_1 + V_s \cdot c_5 - b_4 \end{bmatrix}$$

For simplification we transform the system into system of three nonlinear equations of the form,

$$F_1 := f(\mathbf{c}, \mathbf{b}); \quad F_2 := g(\mathbf{c}, \mathbf{b}); \quad F_3 := h(\mathbf{c}, \mathbf{b});$$

which can be solved implicitly , for which we can proceed as follow,

$$c_2' := \left( \frac{\begin{pmatrix} F_{1c_5} \cdot F_{2b_4} - F_{1b_4} \cdot F_{2c_5} \\ F_{1c_2} \cdot F_{2c_5} - F_{1c_5} \cdot F_{2c_2} \end{pmatrix} \cdot F_3}{\begin{pmatrix} F_{1c_2} \cdot F_{2c_5} - F_{1c_5} \cdot F_{2c_2} \end{pmatrix}} \right) : \quad \text{where as } F_{x's} \text{ are the}$$

differential of  $F_i$  w.r.t  $c_i$ 's,  $b_i$ 's &  $k_i = \frac{k_i^-}{k_i^+}$  :

$$\begin{aligned} & \left( (4 c_5 b_4 c_2 - 4 c_5 b_1 c_2 + 2 c_2 b_3 k_2 - 8 b_2 b_3 c_2 - 4 c_2 b_4 b_1 - 8 c_2^2 b_2 + 4 c_2^2 b_3 + 4 \right. \\ & \quad c_2^2 b_1 + 2 b_4^2 c_2 - b_4^2 k_2 + c_2^2 k_2 - 4 c_2^2 c_5 + 2 b_3^2 c_2 + b_3^2 k_2 + 2 b_1^2 c_2 + b_1^2 k_2 + 8 b_2^2 c_2 \\ & \quad + 4 b_2^2 k_2 + 2 c_5^2 c_2 + 3 c_5^2 k_2 - 4 c_2^2 b_4 - 4 c_5 b_3 c_2 + 2 c_5 b_4 k_2 + 4 b_1 b_3 c_2 \\ & \quad + 2 b_1 b_3 k_2 + 4 k_1 c_5 k_2 - 4 c_2 b_4 b_3 - 4 b_2 b_3 k_2 + 8 c_2 b_4 b_2 + 8 c_5 b_2 k_2 \\ & \quad + 4 k_1 c_5 c_2 + 2 c_2 b_1 k_2 - 4 c_2 c_5 k_2 - 4 c_5 b_1 k_2 - 8 b_1 b_2 c_2 - 4 c_5 b_3 k_2 - 4 b_1 b_2 k_2 \\ & \quad + 8 c_5 b_2 c_2 - 4 c_2 b_2 k_2 + 2 c_2^3) \left( -c_5 b_4 - 2 c_5 b_2 + c_5 b_1 - k_3 c_5 b_1 - k_3 b_2 b_3 \right. \\ & \quad - k_4 b_4 b_3^2 + 2 k_4 b_1^2 b_3 - 3 k_4 b_4 b_1^2 - 2 k_4 c_5 b_1^2 - k_4 b_4 c_2^2 + 3 k_4 b_1 b_4^2 - 2 k_4 c_5 b_4^2 \\ & \quad - 3 k_3 b_1 b_2 + k_3 c_5 b_2 - 5 k_4 b_1^2 b_2 - k_3 b_3 b_4 + 4 k_4 c_2 b_2^2 - 4 k_4 c_5 b_2^2 + k_3 c_5 b_4 \\ & \quad + k_4 b_1 b_3^2 - 5 k_4 b_2 b_4^2 - k_4 b_2 c_2^2 + k_4 b_1 c_2^2 - 2 k_3 b_1 b_4 + 8 k_4 b_1 b_2^2 - k_3 c_2 b_4 \\ & \quad - k_3 c_2 b_2 + k_3 b_4^2 + 2 k_4 b_3 b_4^2 + 3 k_3 b_2 b_4 + 2 k_4 c_2 b_1^2 - k_4 b_4 c_5^2 - k_4 b_2 b_3^2 \\ & \quad - 8 k_4 b_4 b_2^2 + k_4 c_5^2 b_1 - k_4 c_5^2 b_2 + 4 k_4 b_2^2 b_3 + k_3 c_2 b_1 + 2 k_4 c_2 b_4^2 + 2 k_4 b_1 c_2 b_3 \\ & \quad + 2 k_4 c_5 c_2 b_2 - 2 k_4 b_4 c_2 b_3 + 6 k_4 b_4 b_2 b_3 + 6 k_4 c_5 b_1 b_2 + 2 k_4 b_4 c_5 b_3 \\ & \quad - 4 k_4 b_4 c_2 b_1 - 2 k_4 c_5 c_2 b_1 + 2 k_4 c_5 b_2 b_3 - 6 k_4 b_1 b_2 b_3 - 6 k_4 b_1 c_2 b_2 \\ & \quad - 2 k_4 b_2 c_2 b_3 + 6 k_4 b_4 c_2 b_2 - 6 k_4 b_4 c_5 b_2 + 2 k_4 b_4 c_2 c_5 + 10 k_4 b_4 b_1 b_2 \\ & \quad + 4 k_4 b_4 c_5 b_1 - 4 k_4 b_4 b_1 b_3 - 2 k_4 c_5 b_1 b_3 + k_3 b_1^2 + 2 k_3 b_2^2 - k_4 b_4^3 - 4 k_4 b_2^3 + k_4 \\ & \quad \left. b_1^3 + k_3 b_1 b_3 \right) \Big/ \left( -8 b_2^3 + 8 c_5 b_4 c_2 + 4 k_1 c_5 b_1 - 8 k_1 c_5 b_2 + 4 k_1 c_5 b_3 \right. \\ & \quad - 4 k_1 c_5 b_4 + b_4^3 + b_1^3 + 6 c_5 b_4 b_1 - 12 c_5 b_4 b_2 + 6 c_5 b_4 b_3 - 10 c_5 b_1 b_3 \\ & \quad - 2 b_1 b_3 b_4 - 12 c_5 b_1 c_2 + 2 c_2 b_3 k_2 - 16 b_2 b_3 c_2 - 4 c_2 b_4 b_1 - 12 b_1 b_2 b_3 \\ & \quad + 4 b_1 b_2 b_4 - 10 c_2^2 b_2 + 5 c_2^2 b_3 + 5 c_2^2 b_1 - b_4^2 k_2 + c_2^2 k_2 - 7 c_2^2 c_5 + 4 b_3^2 c_2 + b_3^2 k_2 \\ & \quad + 4 b_1^2 c_2 + b_1^2 k_2 + 16 b_2^2 c_2 + 4 b_2^2 k_2 + 8 c_5^2 c_2 + 3 c_5^2 k_2 - 3 c_2^2 b_4 - 6 b_1^2 b_2 + 12 b_1 \\ & \quad b_2^2 + 12 b_2^2 b_3 - 6 b_2 b_3^2 - b_4^2 c_5 - b_4^2 b_1 + 2 b_4^2 b_2 - b_4^2 b_3 - 5 c_5^2 b_4 + 7 c_5^2 b_1 - 5 c_5 \\ & \quad b_1^2 - 5 b_3^2 c_5 + 3 b_3^2 b_1 - b_3^2 b_4 - 14 c_5^2 b_2 - 20 c_5 b_2^2 + 3 b_1^2 b_3 - b_1^2 b_4 - 4 b_2^2 b_4 + 7 \\ & \quad c_5^2 b_3 - 4 k_1 c_5^2 + 20 b_2 b_3 c_5 + 4 b_2 b_3 b_4 - 12 c_5 b_3 c_2 + 2 c_5 b_4 k_2 + 8 b_1 b_3 c_2 \\ & \quad + 2 b_1 b_3 k_2 + 4 k_1 c_5 k_2 - 4 c_2 b_4 b_3 - 4 b_2 b_3 k_2 + 8 c_2 b_4 b_2 + 8 c_5 b_2 k_2 \\ & \quad \left. + 8 k_1 c_5 c_2 + 2 c_2 b_1 k_2 - 4 c_2 c_5 k_2 - 4 c_5 b_1 k_2 - 16 b_1 b_2 c_2 + 20 b_1 b_2 c_5 \right) \end{aligned}$$

$$-4 c_5 b_3 k_2 - 4 b_1 b_2 k_2 + 24 c_5 b_2 c_2 - 4 c_2 b_2 k_2 + 2 c_2^3 + b_3^3 - 3 c_5^3) :$$

$$c_5' := \left( \frac{\left( \begin{array}{cc} F_{1c_2} \cdot F_{2b_4} - F_{1b_4} \cdot F_{2c_2} \\ F_{1c_5} \cdot F_{2c_2} - F_{1c_2} \cdot F_{2c_5} \end{array} \right) \cdot F_3}{\left( \begin{array}{cc} F_{1c_2} \cdot F_{2b_4} - F_{1b_4} \cdot F_{2c_2} \\ F_{1c_5} \cdot F_{2c_2} - F_{1c_2} \cdot F_{2c_5} \end{array} \right)} \right) :$$

$$\left( \begin{array}{l} -8 b_2^3 + 8 c_5 b_4 c_2 + 4 b_4 b_2 k_2 - 2 c_2 b_4 k_2 - 2 b_4 b_3 k_2 - 2 b_4 b_1 k_2 - 3 b_4^3 + b_1^3 \\ + 6 c_5 b_4 b_1 - 12 c_5 b_4 b_2 + 6 c_5 b_4 b_3 - 2 c_5 b_1 b_3 - 10 b_1 b_3 b_4 - 4 c_5 b_1 c_2 \\ + 2 c_2 b_3 k_2 - 16 b_2 b_3 c_2 - 12 c_2 b_4 b_1 - 12 b_1 b_2 b_3 + 20 b_1 b_2 b_4 - 10 c_2^2 b_2 + 5 \\ c_2^2 b_3 + 5 c_2^2 b_1 + 8 b_4^2 c_2 + b_4^2 k_2 + c_2^2 k_2 - 3 c_2^2 c_5 + 4 b_3^2 c_2 + b_3^2 k_2 + 4 b_1^2 c_2 + b_1^2 k_2 \\ + 16 b_2^2 c_2 + 4 b_2^2 k_2 + c_5^2 k_2 - 7 c_2^2 b_4 - 6 b_1^2 b_2 + 12 b_1 b_2^2 + 12 b_2^2 b_3 - 6 b_2 b_3^2 - 5 \\ b_4^2 c_5 + 7 b_4^2 b_1 - 14 b_4^2 b_2 + 7 b_4^2 b_3 - c_5^2 b_4 - c_5^2 b_1 - c_5 b_1^2 - b_3^2 c_5 + 3 b_3^2 b_1 - 5 \\ b_3^2 b_4 + 2 c_5^2 b_2 - 4 c_5 b_2^2 + 3 b_1^2 b_3 - 5 b_1^2 b_4 - 20 b_2^2 b_4 - c_5^2 b_3 + 4 b_2 b_3 c_5 \\ + 20 b_2 b_3 b_4 - 4 c_5 b_3 c_2 + 2 c_5 b_4 k_2 + 8 b_1 b_3 c_2 + 2 b_1 b_3 k_2 - 12 c_2 b_4 b_3 \\ - 4 b_2 b_3 k_2 + 24 c_2 b_4 b_2 + 4 c_5 b_2 k_2 + 2 c_2 b_1 k_2 - 2 c_2 c_5 k_2 - 2 c_5 b_1 k_2 \\ - 16 b_1 b_2 c_2 + 4 b_1 b_2 c_5 - 2 c_5 b_3 k_2 - 4 b_1 b_2 k_2 + 8 c_5 b_2 c_2 - 4 c_2 b_2 k_2 + 2 c_2^3 + \\ b_3^3 + c_5^3) \left( \begin{array}{l} -c_5 b_4 - 2 c_5 b_2 + c_5 b_1 - k_3 c_5 b_1 - k_3 b_2 b_3 - k_4 b_4 b_3^2 + 2 k_4 b_1^2 b_3 \\ - 3 k_4 b_4 b_1^2 - 2 k_4 c_5 b_1^2 - k_4 b_4 c_2^2 + 3 k_4 b_1 b_4^2 - 2 k_4 c_5 b_4^2 - 3 k_3 b_1 b_2 + k_3 c_5 b_2 \\ - 5 k_4 b_1^2 b_2 - k_3 b_3 b_4 + 4 k_4 c_2 b_2^2 - 4 k_4 c_5 b_2^2 + k_3 c_5 b_4 + k_4 b_1 b_3^2 - 5 k_4 b_2 b_4^2 \\ - k_4 b_2 c_2^2 + k_4 b_1 c_2^2 - 2 k_3 b_1 b_4 + 8 k_4 b_1 b_2^2 - k_3 c_2 b_4 - k_3 c_2 b_2 + k_3 b_4^2 + 2 k_4 b_3 \\ b_4^2 + 3 k_3 b_2 b_4 + 2 k_4 c_2 b_1^2 - k_4 b_4 c_5^2 - k_4 b_2 b_3^2 - 8 k_4 b_4 b_2^2 + k_4 c_5^2 b_1 - k_4 c_5^2 b_2 \\ + 4 k_4 b_2^2 b_3 + k_3 c_2 b_1 + 2 k_4 c_2 b_4^2 + 2 k_4 b_1 c_2 b_3 + 2 k_4 c_5 c_2 b_2 - 2 k_4 b_4 c_2 b_3 \\ + 6 k_4 b_4 b_2 b_3 + 6 k_4 c_5 b_1 b_2 + 2 k_4 b_4 c_5 b_3 - 4 k_4 b_4 c_2 b_1 - 2 k_4 c_5 c_2 b_1 \\ + 2 k_4 c_5 b_2 b_3 - 6 k_4 b_1 b_2 b_3 - 6 k_4 b_1 c_2 b_2 - 2 k_4 b_2 c_2 b_3 + 6 k_4 b_4 c_2 b_2 \\ - 6 k_4 b_4 c_5 b_2 + 2 k_4 b_4 c_2 c_5 + 10 k_4 b_4 b_1 b_2 + 4 k_4 b_4 c_5 b_1 - 4 k_4 b_4 b_1 b_3 \\ - 2 k_4 c_5 b_1 b_3 + k_3 b_1^2 + 2 k_3 b_2^2 - k_4 b_4^3 - 4 k_4 b_2^3 + k_4 b_1^3 + k_3 b_1 b_3) \right) / \left( \begin{array}{l} -8 b_2^3 \\ + 8 c_5 b_4 c_2 + 4 k_1 c_5 b_1 - 8 k_1 c_5 b_2 + 4 k_1 c_5 b_3 - 4 k_1 c_5 b_4 + b_4^3 + b_1^3 + 6 c_5 b_4 b_1 \\ - 12 c_5 b_4 b_2 + 6 c_5 b_4 b_3 - 10 c_5 b_1 b_3 - 2 b_1 b_3 b_4 - 12 c_5 b_1 c_2 + 2 c_2 b_3 k_2 \\ - 16 b_2 b_3 c_2 - 4 c_2 b_4 b_1 - 12 b_1 b_2 b_3 + 4 b_1 b_2 b_4 - 10 c_2^2 b_2 + 5 c_2^2 b_3 + 5 c_2^2 b_1 \\ - b_4^2 k_2 + c_2^2 k_2 - 7 c_2^2 c_5 + 4 b_3^2 c_2 + b_3^2 k_2 + 4 b_1^2 c_2 + b_1^2 k_2 + 16 b_2^2 c_2 + 4 b_2^2 k_2 + 8 \end{array} \right)$$

$$\begin{aligned}
& c_5^2 c_2 + 3 c_5^2 k_2 - 3 c_2^2 b_4 - 6 b_1^2 b_2 + 12 b_1 b_2^2 + 12 b_2^2 b_3 - 6 b_2 b_3^2 - b_4^2 c_5 - b_4^2 b_1 \\
& + 2 b_4^2 b_2 - b_4^2 b_3 - 5 c_5^2 b_4 + 7 c_5^2 b_1 - 5 c_5 b_1^2 - 5 b_3^2 c_5 + 3 b_3^2 b_1 - b_3^2 b_4 - 14 c_5^2 b_2 \\
& - 20 c_5 b_2^2 + 3 b_1^2 b_3 - b_1^2 b_4 - 4 b_2^2 b_4 + 7 c_5^2 b_3 - 4 k_1 c_5^2 + 20 b_2 b_3 c_5 + 4 b_2 b_3 b_4 \\
& - 12 c_5 b_3 c_2 + 2 c_5 b_4 k_2 + 8 b_1 b_3 c_2 + 2 b_1 b_3 k_2 + 4 k_1 c_5 k_2 - 4 c_2 b_4 b_3 \\
& - 4 b_2 b_3 k_2 + 8 c_2 b_4 b_2 + 8 c_5 b_2 k_2 + 8 k_1 c_5 c_2 + 2 c_2 b_1 k_2 - 4 c_2 c_5 k_2 - 4 c_5 b_1 k_2 \\
& - 16 b_1 b_2 c_2 + 20 b_1 b_2 c_5 - 4 c_5 b_3 k_2 - 4 b_1 b_2 k_2 + 24 c_5 b_2 c_2 - 4 c_2 b_2 k_2 + 2 c_2^3 \\
& + b_3^3 - 3 c_5^3) :
\end{aligned}$$

where  $F_3$  is,

$$\begin{aligned}
F_3 := & c_5 k_1 \left( 3 \sqrt{2} c_5^2 - 4 c_5 \sqrt{(b_4 - c_5) k_1} - 4 \sqrt{2} c_5 b_4 - \sqrt{2} c_5 b_3 + k_2 \sqrt{2} c_5 \right. \\
& + \sqrt{2} b_4^2 + 2 \sqrt{2} c_5 b_2 - \sqrt{2} c_5 b_1 - k_2 \sqrt{2} b_4 - 2 \sqrt{2} b_2 b_4 + \sqrt{2} b_1 b_4 \\
& \left. + \sqrt{2} b_3 b_4 \right) \left( 4 b_4^2 b_1^2 c_5^2 + 4 b_2 c_5^4 k_1 - 4 b_4^2 b_1 c_5^3 + k_2^2 k_4 b_1 b_3^2 c_5^2 - k_2^2 k_4 b_2 b_3^2 c_5^2 \right. \\
& - 3 b_4^3 b_1^2 c_5 - 6 b_4^4 b_2 c_5 + 8 b_4^2 b_2 c_5^3 + 3 b_4^4 b_1 c_5 + 4 b_2 c_5^4 b_3 - 2 b_2 c_5^3 b_3^2 - 2 b_1 \\
& c_5^4 k_1 - 8 b_2^3 b_4^2 c_5 + 16 b_4^2 b_2^2 c_5^2 + 2 c_5^4 b_4 k_1 - 2 b_4^3 b_3 c_5^2 - k_2^2 b_4^2 k_4 b_2 b_3^2 + 8 b_2^2 c_5^3 b_3 \\
& - k_2^2 b_4^2 k_4 b_2 c_5^2 - 2 b_4^3 b_1 c_5^2 - 2 c_5^3 b_4^2 k_1 + 2 b_4^2 b_3^2 c_5^2 + 2 b_4^4 b_3 c_5 - 2 b_1 c_5^4 b_3 \\
& - 2 k_2 b_4 k_3 b_1^2 c_5^2 - 2 k_2 b_4^3 k_3 b_1 c_5 + 3 k_2 b_4^2 k_3 b_1 b_3 b_2 + k_2^2 b_4^2 k_4 b_1 b_3^2 \\
& + 2 k_2 b_4 k_3 b_1 b_3^2 c_5 - 12 b_4^3 b_2^2 c_5 + k_2 k_3 b_1^2 c_5^3 + k_2 b_4 k_3 c_5^4 - k_2^2 b_4^3 k_4 c_5^2 + k_2^2 k_4 b_1 c_5^4 \\
& - k_2^2 b_4 k_4 c_5^4 - c_5 b_4^5 - k_2^2 k_4 b_2 c_5^4 + b_1 c_5^5 + b_1^3 c_5^3 - 8 b_1 c_5^3 b_2 b_3 - k_2 b_4^2 k_3 c_5^3 - k_2 \\
& b_4^4 k_3 b_3 + k_2 b_4^4 k_3 c_5 + k_2 b_4^3 k_3 b_3^2 - k_2 b_4^3 k_3 c_5^2 - 2 \\
& k_2^2 b_4 k_4 b_1 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 - 4 c_5^3 b_4 b_1 b_2 - 2 b_1 b_4 b_3 \\
& c_5^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + k_2 k_3 b_2 c_5^4 - k_2 k_3 b_1 c_5^4 - 2 k_3 k_2 b_1 b_3 \\
& c_5^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 2 k_2^2 b_4 k_4 b_2 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 - 3 k_2 b_4^3 k_3 b_2 b_3 - \\
& b_4^3 b_3^2 c_5 - 2 k_3 k_2 c_5^3 b_4 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 4 b_4^3 b_2 c_5^2 - c_5^5 b_4 - 8 b_1 \\
& c_5^3 b_2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} - 8 b_4^2 b_2 c_5^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + k_2 b_4^2 k_3 b_1^2 c_5 + 2 c_5^3 b_4^3 \\
& + k_2 b_4 k_3 b_1^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 + 16 b_1 b_4 b_2 c_5^2 b_3 - 4 b_2 \\
& c_5^3 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} - 2 b_1^2 c_5^4 - 8 b_2^2 c_5^4 - 8 b_2^3 c_5^3 - 8 b_1 b_4^2 b_2 b_3 c_5 - c_5^3 b_4 b_3^2 \\
& - 2 b_2 c_5^5 - k_2 b_4 k_3 b_2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^2 + 4 b_2 b_4 b_3^2 c_5^2 - 2 k_2^2 k_4 b_1 b_3 c_5^3 - 4 \\
& k_2^2 b_4^2 k_4 b_3 c_5^2 - 6 b_1^2 c_5^3 b_2 + 8 b_1 c_5^4 b_2 + 2 k_2^2 b_4^3 k_4 b_3 c_5 + 2 b_1
\end{aligned}$$

$$\begin{aligned}
& c_5^3 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 2 k_2^2 k_4 b_2 b_3 c_5^3 + 8 b_4^3 b_2 b_3 c_5 + 2 k_3 k_2 b_1 k_1 c_5^3 - 2 \\
& k_2^2 b_4 k_4 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^2 + 2 k_2^2 b_4 k_4 k_1 c_5^3 - 2 k_2^2 b_4^2 k_4 k_1 c_5^2 - 2 \\
& c_5^3 b_4 b_1 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 2 k_2^2 b_4^2 k_4 b_3^2 c_5 + 2 k_2 k_3 b_1 b_3 c_5^3 + 2 k_3 k_2 k_1 c_5^2 b_4^2 \\
& - 2 k_2 k_3 b_2 k_1 c_5^3 + 2 k_2^2 b_4^2 k_4 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 - 2 k_3 k_2 k_1 c_5^3 b_4 + 12 b_1 b_4^2 \\
& b_2^2 c_5 - 2 k_2 k_3 b_2^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^2 + 8 b_1 b_4 b_2 c_5^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} - 2 \\
& k_2^2 k_4 b_1 k_1 c_5^3 + 2 k_2^2 k_4 b_2 k_1 c_5^3 + 4 k_2^2 b_4 k_4 b_1 b_3 c_5^2 + 2 k_2^2 b_4 k_4 b_2 b_3^2 c_5 - 12 b_4^2 b_2 \\
& c_5^2 b_3 - k_2^2 b_4^3 k_4 b_3^2 - 2 k_2 b_4^2 k_3 b_1 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 + 3 k_2 k_3 b_1 b_3 c_5^2 b_2 + 2 k_2^2 \\
& b_4^2 k_4 c_5^3 + 2 c_5^4 b_4 b_3 + b_1 c_5^3 b_3^2 - 3 k_2 k_3 b_1 c_5^3 b_2 - k_2 k_3 b_1^2 b_3 c_5^2 - 2 k_2 b_4 k_3 b_1 b_3 c_5^2 \\
& - 2 k_2 k_3 b_2^2 b_3 c_5^2 - 2 k_2 b_4^2 k_3 b_3^2 c_5 + 3 k_2 b_4^3 k_3 b_2 c_5 + 3 k_2 \\
& b_4^2 k_3 b_2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 + 8 b_2^2 b_4^2 b_3 c_5 + 2 k_2 k_3 b_2^2 c_5^3 + 2 k_3 k_2 b_3 b_4 \\
& c_5^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} - 2 b_1^2 b_4 c_5^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} - 6 k_2 b_4 k_3 b_1 b_3 b_2 c_5 - 4 \\
& c_5^4 b_4 b_2 - 2 k_2^2 k_4 b_2 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^2 + 12 b_1 c_5^3 b_2^2 + k_2^2 b_4^2 k_4 b_1 c_5^2 \\
& + 6 k_2 b_4 k_3 b_1 c_5^2 b_2 + 2 b_1 c_5^3 k_1 b_4 + 2 k_2^2 b_4^2 k_4 b_2 b_3 c_5 + 2 b_4^2 b_3 \\
& c_5^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 2 k_2 k_3 b_2 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^2 - 4 b_2 c_5^3 k_1 b_4 + 3 k_2 \\
& b_4^2 k_3 b_1 c_5^2 + 2 c_5^4 b_4 b_1 - 8 b_2^2 b_4 c_5^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 2 b_1^2 c_5^3 b_3 - 2 k_2 k_3 b_2 b_3 c_5^3 \\
& + 3 k_2 k_3 b_1 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^2 b_2 - 2 k_2 k_3 b_2 c_5^3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 4 b_4^2 b_1 \\
& c_5^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 16 b_2^3 b_4 c_5^2 - 2 k_3 k_2 b_3 b_4^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 \\
& - 2 k_3 k_2 b_1 k_1 c_5^2 b_4 + 2 k_2 k_3 b_2 k_1 c_5^2 b_4 - k_2 k_3 b_1^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^2 + 8 b_2^2 \\
& c_5^3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + b_1^3 b_4^2 c_5 + 2 k_2 b_4 k_3 b_2^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 \\
& - 2 k_2 b_4 k_3 b_2 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 + 2 k_2^2 k_4 b_1 k_1 c_5^2 b_4 + 2 k_2^2 b_4 k_4 b_2 c_5^3 + 2 \\
& c_5^4 b_4 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 2 b_1^2 c_5^3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} - 2 b_1 \\
& c_5^4 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 4 b_2 c_5^4 \sqrt{2} \sqrt{(b_4 - c_5) k_1} - 2 c_5^2 b_4^3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} \\
& - 2 k_2^2 k_4 b_2 k_1 c_5^2 b_4 + c_5^3 b_4 b_1^2 + 4 k_2 b_4 k_3 b_2^2 b_3 c_5 - 2 c_5^3 b_4 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} \\
& + 4 c_5^3 b_4 b_2^2 + 2 k_2 b_4^2 k_3 b_2^2 c_5 + 2 k_2 b_4 k_3 b_1^2 b_3 c_5 + 2 \\
& k_2^2 k_4 b_1 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^2 - 2 k_2^2 b_4 k_4 b_1 c_5^3 - 2 k_2^2 k_4 b_1 \sqrt{2} \sqrt{(b_4 - c_5) k_1} \\
& c_5^3 - 2 k_2^2 b_4^2 k_4 b_1 b_3 c_5 + 4 c_5^3 b_4 b_2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 2 k_2 b_4^3 k_3 b_1 b_3 + k_2 k_3 b_2 \\
& b_3^2 c_5^2 - 2 k_2 b_4 k_3 b_2 b_3^2 c_5 + 2 k_2 b_4 k_3 b_1 b_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 + 2 k_2^2 k_4 b_2 \\
& c_5^3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 2 k_3 k_2 b_1 c_5^3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} - 2 k_2 b_4 k_3 b_3 c_5^3 \\
& + k_2 b_4 k_3 b_3^2 c_5^2 + k_2 b_4^2 k_3 b_2 b_3^2 - 16 b_4^2 b_1 c_5^2 b_2 - k_2^2 b_4 k_4 b_3^2 c_5^2 - 5 k_2 b_4^2 k_3 b_2 c_5^2
\end{aligned}$$

$$\begin{aligned}
& -2 b_1 b_4 b_3^2 c_5^2 - 24 b_1 b_4 b_2^2 c_5^2 - 4 k_2^2 b_4 k_4 b_2 b_3 c_5^2 - k_2 b_4^2 k_3 b_1 b_3^2 - 2 k_2 \\
& b_4^2 k_3 b_1 b_3 c_5 - 2 k_2^2 b_4 k_4 b_2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^2 - 2 k_2^2 b_4^2 k_4 \sqrt{2} \sqrt{(b_4 - c_5) k_1} \\
& c_5^2 + k_2 b_4^3 k_3 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 - k_2 b_4^2 k_3 b_1^2 b_3 - 4 b_1^2 b_4 c_5^2 b_3 + k_2 b_4 k_3 b_2 b_3 c_5^2 \\
& - 2 k_2^2 b_4 k_4 b_1 b_3^2 c_5 + 6 b_4^2 b_1 c_5^2 b_3 - 16 b_2^2 b_4 c_5^2 b_3 \\
& - 3 k_2 b_4 k_3 b_1 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5 b_2 - 4 b_4^3 b_1 b_3 c_5 - 3 k_2 b_4^2 k_3 b_1 c_5 b_2 \\
& + k_2 b_4 k_3 b_2 c_5^3 - 2 k_2 b_4^2 k_3 b_2^2 b_3 + 2 b_1^2 b_4^2 b_3 c_5 - 2 b_1^3 b_4 c_5^2 + 4 b_2 b_4 b_3 \\
& c_5^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 2 k_2^2 b_4 k_4 b_1 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^2 + 3 k_2 b_4^2 k_3 b_3 c_5^2 \\
& + k_3 k_2 c_5^2 b_4^2 \sqrt{2} \sqrt{(b_4 - c_5) k_1} + 12 b_1^2 b_4 c_5^2 b_2 + 12 b_4^3 b_1 b_2 c_5 - 4 k_2 b_4 k_3 b_2^2 c_5^2 \\
& + 2 k_2^2 b_4 k_4 \sqrt{2} \sqrt{(b_4 - c_5) k_1} c_5^3 - 2 b_4^2 b_3 c_5^3 + b_1 b_4^2 b_3^2 c_5 - 2 b_2 b_4^2 b_3^2 c_5 - 6 b_1^2 \\
& b_4^2 b_2 c_5 - k_2 k_3 b_1 b_3^2 c_5^2 + 2 k_2^2 b_4 k_4 b_3 c_5^3 + 4 k_2 b_4^2 k_3 b_2 b_3 c_5) :
\end{aligned}$$