Finding the key transition states and intermediates controlling net reaction rates and selectivity

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In this paper Campbell's degree of rate control is extended to introduce the concepts of degree of kinetic rate control, degree of kinetic selectivity control, degree of thermodynamic rate control and degree of thermodynamic selectivity control. It is demonstrated by applying hypothetical but realistic kinetic models of varying complexity that the new methods offers a rigorous framework to analyze the importance of kinetic and thermodynamic parameters i.e. establishing the critical parameters of the kinetic model. The methods are general and can be applied to complex reaction networks with multiple overall reactions not only in heterogeneous catalysis but for all sort of chemical kinetic models.

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INTRODUCTION

Microkinetic modeling has become an important tool in bridging the gap between experimental and theoretical surface science and heterogeneous catalysis at industrial relevant conditions [1–7] and references therein.

In microkinetic modeling the outcome of one or multiple overall reactions is modeled as a consequence of a detailed reaction mechanism. The elementary reactions and their kinetics and thermodynamics are established from "first principles" and experimental surface science. The microkinetic models are often very complex and contains many kinetic and thermodynamic parameters and possible reaction pathways. Often it turns out that only a few reaction steps control the net reaction rate and these steps are referred to as being *rate-limiting*. Furthermore, it may also occur that the net reaction rate is sensitive to the energetics of a few reaction intermediates, only. Thus, it may be sufficient to accurately determine (either by experiment or by theoretical calculation e.g. DFT) the energetics of these key intermediates along with the rate constants of the rate limiting steps. The kinetic and thermodynamic parameters of the remaining reaction steps and intermediates can be estimated with a significantly coarser accuracy without effecting the net reaction rate. The challenge in analyzing microkinetic models is to accurately pin point these rate-controlling reaction steps and intermediates. Experimentally, obtaining this information, is pivotal in order to identify which *knob* to turn in order to design the optimal catalyst.

Recently, a general concept of rate-control has been formulated by the authors [8] in which it is possible to pin point exactly which key transition states and key reaction intermediates are important by making small changes to their energies and determining the sensitivity of the net reaction rate to these changes (see also [9–11]). The concept was an extension of Campbell's degree of rate control method [4, 12, 13], yet slightly modified. In this paper we will extend the concept in order to also include selectivity effects as well. The concepts will be clearly illustrated both by algebraic derivation from simple kinetic models to numerical computations with a representative number of microkinetic models with varying complexity. The concepts presented in this paper will be completely general and can be applied on all types of chemical reactions and complex reaction networks.

Alongside our work on this topic, other authors have treated this topic in a similar manner, although different in both scope and perspective [14–17]. Furthermore, as will be evident from the material presented in the present paper, our framework is of more general nature and expandable to a wider set of problems, especially when considering selectivity limitations. The importance of having a tool for the identification of selectivity control is vital. Selectivity is a major challenge in reaction engineering. When dealing with microkinetic models this problem is rarely addressed, simply because of the complexity it imposes. Important chemicals such as ethylene oxide and formaldehyde are produced in processes with selectivity limitations as well as the product spectrum of the Fischer-Tropsch process is determined by selectivity.

We will start with a brief literature survey of reaction rates to clarify the concepts of rate limiting steps, slow and fast steps etc. In addition the literature survey will discuss some of the prevailing methods in the literature used to analyze microkinetic models. Next the formalism of reaction rates will be established. Then Campbell's degree of rate control method will be extended after which a few simple examples including Langmuir-Hinshelwood and Michaelis-Menten kinetics will be given. Finally the new methods will be used to analyze some hypothetical microkinetic models and compared to existing analysis

methods.

LITERATURE SURVEY

In the following section a brief literature survey of analyzing microkinetic models will be given.

Rate limiting steps

Much work have been performed on reaction rates of catalytic cycles, but still there seem to be some confusion and misconceptions on the subject. Such notions as rate determining step (rds), rate limiting step (rls), slow and fast steps, quasi-equilibrated steps etc. are used throughout the literature [3–5, 12, 18–20] and references therein. In a catalytic cycle of elementary reactions one or a few steps often determine the overall rate of reaction and these are referred to as rds, rls or slow steps. It has been argued that it is wrong to talk about fast and slow elementary steps in a catalytic cycle because at steady state all the elementary reactions will proceed at the same rate scaled to their stoichiometric coefficient. Hence slow and fast steps does not exist. Actually this is not entirely correct as some elementary steps often have much faster forward and backward rates than other steps and basically will be quasi-equilibrated. However the net rate of these steps will be the same as the net rate of the slow steps. Hence a fast step is a step with the potential of proceeding much faster had it not been limited by other slow steps.

Establishing rate limiting steps is very important in catalysis and many methods have been suggested.

Degree of rate control

The most essential work on rate limiting steps was done by Campbell [4, 12]. The pivotal idea of Campbell is to reveal the effect of the rate constant of a step on the overall reaction rate. Campbell defined the *d*egree of rate control ($X_{RC,s}$) as:

$$X_{RC,s} = \frac{k_s}{\mathcal{R}} \left(\frac{\delta \mathcal{R}}{\delta k_s} \right)_{K_s, k_j} \tag{1}$$

where $\mathcal{R}$ is the overall reaction rate, k_s is the rate constant of elementary step s, where the rate constants k_j for all other elementary steps ($j \neq s$), as well as the equilibrium constant for step s , K_s, remain constant. The overall reaction rate, $\mathcal{R}$, can be the consumption rate of a reactant c, the formation rate of a product c or the net rate of a catalytic cycle. For a reaction system with only one overall reaction all of the above $\mathcal{R}$'s are directly related through stoichiometry. For reaction systems with multiple overall reaction pathways different $\mathcal{R}$'s are obviously not directly related.

Campbell's degree of rate control is a theoretical method in that it should be used on microkinetic models. It is not possible to change just one rate constant without changing something else in real life. Hence it is not possible to experimentally measure degree of rate control without accurately determining the rate constants for all the kinetically-relevant elementary steps (i.e., those with non-negligible $X_{RC,s}$, and determining the rate constants for the other steps accurately enough to know that they are not kinetically relevant).

Campbell's degree of rate control is general, simple and easy to apply both in cases where analytic solutions are available, but also in cases where only numerical computer solutions are feasible. By general is meant that the method may be applied for all reaction schemes regardless of complexity not only in catalysis, but for all sorts of chemical reactions. The larger numeric value of $X_{RC,s}$ the larger degree of rate control does the rate constant of step s exhibit on the overall rate. A positive value indicates that increasing k_s will increase the overall rate and Campbell suggested that such steps are termed rate limiting steps (rls). A negative value indicates the opposite and Campbell suggested that such steps are denoted inhibition steps. A value of approximately zero indicate that the step is quasi-equilibrated. In particular Campbell found that reaction mechanisms with only one rate limiting step the value of $X_{RC,s}$ will equal unity for this step and zero for all other steps. Campbell suggested that a step with $X_{RC,s}$=1 should be defined as the rate determining step. For examples in the literature where the degree of rate control is discussed or applied refer to e.g. [14, 15, 21–50].

We strongly support Campbell's definition of rls, rds and inhibition steps and believe that following this clear definition would remove much of the confusion regarding this issue in the literature.

Campbell suggested without proof except examples that the degree of rate control is in general conserved through the sum rule:

$$\sum_s X_{RC,s} = 1 \tag{2}$$

Baranski proved that the suggested sum rule of Campbell holds for consecutive gas phase reactions [20]. Cortright and Dumesic proved that the sum rule of Campbell is true for steady-state catalytic reaction mechanisms that leads to one overall reaction [3, 18].

We have found that the sum rule apply for all steady-state kinetic models investigated in the present paper including complex reaction networks with multiple overall reactions. Thus although not mathematical proven it seems a reasonable conjecture that the sum rule is generally valid for steady-state kinetics.

Sensitivity

Cortright and Dumesic [3] defined the dimensionless sensitivity, ϕ_s, of the overall rate with respect to the rate constant k_s as:

$$\phi_s = \left(\frac{\delta \mathcal{R}}{\delta k_s}\right)_{k_j} \frac{k_s}{\mathcal{R}} \tag{3}$$

where all other parameters, both forward and backward rate constants, k_j, are held constant. At first sight the concept of sensitivity seems to be identical to the degree of rate control. However an important difference exist, because the equilibrium constant of step s is not constant when ϕ_s is determined. Hence the sensitivity is a combined measure of the importance of thermodynamics and kinetics of step s on the overall rate while the degree of rate control only concerns kinetics (rate constant). Furthermore the sensitivity has to be calculated for both the forward (ϕ_s) and backwards (ϕ_{-s}) rate constants of step s. Cortright and Dumesic's deduced some interesting relationships for sensitivities among others that the sum of all the sensitivities add to unity for a reaction scheme that leads to a single overall reaction:

$$\sum_s (\phi_s + \phi_{-s}) = 1 \tag{4}$$

and that the sum of sensitivities for a step equal the degree of rate control of that step:

$$X_{RC,s} = \phi_s + \phi_{-s} \tag{5}$$

Cortright and Dumesic suggested that the confusions regarding the concept of a rate determining step could be eliminated by denoting a step as being the maximum sensitivity step. It is not clear what is meant by the sensitivity of a step. If the authors refer to adding the sensitivity of the forward and backward rate constant of the step then the the result is Campbell's degree of rate control (Eq. 5) and the suggestion becomes trivial. On the other hand if the authors suggest that forward and backward rate constant is evaluated separately erroneous results can be obtained because a rate constant may have a large sensitivity due to thermodynamics and not because the kinetics of the step is slow. Hence the definition of Campbell for rds and rls should be preferred as also argued by Campbell [12].

There is some fundamental problems with the sensitivity concept. First of all it is not clear if a sensitivity of a step is due to kinetics, thermodynamics or both. Furthermore the overall equilibrium constant is changed in the sensitivity analysis, but should be well defined by the thermodynamics of the reactants and products. Finally the importance of thermodynamics on sensitivity is connected to an elementary step, but it would be more useful if the thermodynamics was linked to reaction intermediates. All of this causes problems which will be illustrated by examples later in this article. The sensitivity concept does answer which elementary steps are critical to a kinetic model. But as will be shown by extending Campbell's degree of rate control it is possible to obtain more detailed knowledge of critical steps and intermediates in a kinetic model without increasing the complexity of analysis.

Multiple overall reactions

The presence of multiple overall reaction paths complicates kinetic analysis considerately and introduces the complexity of selectivity. Both Campbell's degree of rate control and Dumesic and Copyright's sensitivity can be applied to analyze the individual reaction paths or individual formation/consumption rates of products/reactants in a multiple reactions network. However such an analysis will not reveal what is the most critical reactions to the overall reaction system. What is needed is a method that establishes what are the most critical parameters to the overall reaction system. For reaction systems with only a single overall net reaction the above complications does not occur as the net rates of products and reactants are proportional to their stoichiometric coefficients.

Cortright and Dumesic [3] suggested that in order to analyze such complex reaction networks a total sensitivity/degree of rate control could be calculated:

$$\phi_{s,tot} = \sum_c \left| \left(\frac{\delta \mathcal{R}_c}{\delta k_s}\right)_{k_j} \frac{k_s}{\mathcal{R}_c} \right| \tag{6}$$

$$= \sum_c \left| \left(\frac{\delta \mathcal{R}_c}{\delta k_s}\right)_{K_s,k_j} \frac{k_s}{\mathcal{R}_c} \right| \tag{7}$$

$$= X^{tot}_{RC,s} \tag{8}$$

where $\mathcal{R}_c$ refer to the rate of production of compound c. Absolute value are used in the sum since a given kinetic parameter may have a positive contribution to one product and a negative contribution for another product. Accordingly, although the parameter would not affect the overall conversion, it would change the product selectivity.

The method suggested by Cortright and Dumesic may be used to give a quick overlook of a complex reaction network. However some potential pitfalls can be imagined as the production of different products may be highly correlated and one should be very careful in identifying the c compounds to study.

Another method is to extend Campbell's degree of rate control to deal with selectivity

$$X_{SC,s} = \frac{k_s}{\mathcal{S}} \left(\frac{\delta \mathcal{S}}{\delta k_s}\right)_{K_s,k_j} \tag{9}$$

where the selectivity, $\mathcal{S}$, replaces the rate $\mathcal{R}$. This approach was used by the authors to analyze ethylene oxidation on silver resulting in a clear picture of what controls the selectivity of ethylene oxide formation [32]. In addition the degree of selectivity control is conserved following the sum rule:

$$\sum_s X_{SC,s} = 0 \tag{10}$$

FORMALISM

In this paper kinetics and microkinetic models will be discussed based on the Langmuir-Hinshelwood approach. This is done as Langmuir-Hinshelwood is the most simple and most used method to model heterogeneous catalytic reactions in the literature. The Langmuir-Hinshelwood approach has been very successful despite that some of the assumptions such as absence of lateral interactions and uniform sites are debatable. For a discussion of Langmuir-Hinshelwood mechanisms we refer to [2] and references therein. However the presented formalism of this paper can be modified to other kinetic approximations and the methods and conclusions developed in this paper will not depend on the kinetic approximation used but will be completely general.

For a systematic treatment of arbitrary large mechanisms, we need a suitable mathematical device such as a stoichiometric matrix, α. For details we refer to [2]. For a mechanism consisting of G gases, I separate surface intermediates (including free sites), and S elementary reactions, α is an S by $G+I$ matrix. The components are the stoichiometric coefficients, α_{sc} where subscript sc refers to one compound c in some elementary reaction step s of the mechanism. Note that $1 < s < S, 1 < c < G+I$. The compound c may be either a gas phase reactant, a gas phase product, a surface species reactant, or a surface species product.

By convention $\alpha_{sc} < 0$ if c is a reactant in elementary reaction s, $\alpha_{sc} > 0$ is a product of step s and $\alpha_{sc} = 0$ if c does not participate in step s.

The stoichiometric matrix has a number of important properties:

- Surface sites are conserved:

$$\sum_{s=1}^{S} r_s \alpha_{sc} = 0 \tag{11}$$

  for $c = G+1, \ldots, G+I$

- All elements in the stoichiometric matrix are integers.

- Inerts have $\alpha_{sc} = 0$ for $s = 1, \ldots, S$.

In catalysis, reaction rates should be measured and calculated as a turnover frequency, i.e. as a number of molecules produced per site per second.

The reaction rate of an elementary step s consist of a forward rate, r_{+s}, and a backward rate, r_{-s}:

$$r_s = r_{+s} - r_{-s} \tag{12}$$

$$r_{+s} = k_{+s} \prod_{\substack{c=1 \\ \alpha_{sc}<0}}^{G} \left(\frac{p_c}{p^{\ominus}}\right)^{-\alpha_{sc}} \prod_{\substack{c=G+1 \\ \alpha_{sc}<0}}^{G+I} \theta_c^{-\alpha_{sc}} \tag{13}$$

$$r_{-s} = k_{-s} \prod_{\substack{c=1 \\ \alpha_{sc}>0}}^{G} \left(\frac{p_c}{p^{\ominus}}\right)^{\alpha_{sc}} \prod_{\substack{c=G+1 \\ \alpha_{sc}>0}}^{G+I} \theta_c^{\alpha_{sc}} \tag{14}$$

where k_{+s} and k_{-s} is the forward and backward rate constant of step s, respectively. p_c is the partial pressure of c, $p^{\ominus}$ is the reference pressure, and θ_c is the coverage of intermediate c. By including the thermodynamic reference pressure in the above rate expressions a number of advantages is obtained. First of all, equilibrium constants become dimensionless in accordance with classical thermodynamics. Secondly, all the rate constants and preexponential factors hidden in the rate constants get the units of turnover frequency. Unfortunately this formalism is often not followed in the literature resulting in reported rate and equilibrium constants with many different units making it a dimensional nightmare or even impossible to compare rates obtained in different laboratories.

For each of the gases, c (where $1 < c < G$), in a mechanism we have an overall formation rate:

$$\mathcal{R}_c = \sum_{s=1}^{S} r_s \alpha_{sc} \tag{15}$$

this rate is evidently negative for reactants.

Due to the principle of microscopic reversibility (PMR) the forward and backward rate constants of an elementary step is related through the equilibrium constant, K_s, of that step:

$$k_{+s} = \frac{k_{-s}}{K_s} \tag{16}$$

This is a very important principle which means that instead of using a forward and backward rate constants in expressing elementary reaction rates we may use forward rate and equilibrium constant.

Thus reaction rates may also be written:

$$r_s = r_{+s} - r_{-s} \quad (17)$$

$$r_{+s} = k_{+s} \prod_{\substack{c=1 \\ \alpha_{sc}<0}}^{G} \left(\frac{p_c}{p^{\ominus}}\right)^{-\alpha_{sc}} \prod_{\substack{c=G+1 \\ \alpha_{sc}<0}}^{G+I} \theta_c^{-\alpha_{sc}} \quad (18)$$

$$r_{-s} = \frac{k_{+s}}{K_s} \prod_{\substack{c=1 \\ \alpha_{sc}>0}}^{G} \left(\frac{p_c}{p^{\ominus}}\right)^{\alpha_{sc}} \prod_{\substack{c=G+1 \\ \alpha_{sc}>0}}^{G+I} \theta_c^{\alpha_{sc}} \quad (19)$$

The two methods of expressing reaction rates are completely equivalent. But still we will argue that the later expression applying PMR is superior to the expression introduced earlier. There is two reasons for this. As pointed out by Cortright and Dumesic it is generally easier to estimate enthalpies and entropies to calculate equilibrium constants of elementary steps than estimating the values of activation entropies and enthalpies to calculate rate constants [3]. Another reason more important in the context of this paper is that writing the reverse rate constant as the ratio between the forward rate constant and equilibrium constant, kinetics and thermodynamics has been separated. The forward rate constant tells us about the importance of kinetics and the equilibrium constant tells us about thermodynamics. Hence a reaction mechanism becomes much easier to analyze. A simple example of this is the use of Campbell degree of rate control. Campbell suggests that both the forward and backward rate constant is increased, say 10 %, to avoid changing the equilibrium constant [4]. However using Eq. 17-19 for the rate we just changes the forward rate constant and everything works out.

It should be noted that the choice of which direction is forward or backward of an elementary step is completely arbitrary. However many prefer to move in the direction from reactants towards products.

Rate and equilibrium constants are actually not constants but vary significantly with temperature and surface coverage. Equilibrium constants may be expressed as:

$$K_s = \frac{k_{+s}}{k_{-s}} = \exp\left(\frac{\Delta S_s^{\ominus}}{R_g}\right) \exp\left(\frac{-\Delta H_s^{\ominus}}{RT}\right) = \exp\left(\frac{-\Delta G_s^{\ominus}}{R_g T}\right) \quad (20)$$

where $\Delta H_s^{\ominus}$, $\Delta S_s^{\ominus}$ and $\Delta G_s^{\ominus}$ are the changes in standard enthalpy, entropy and Gibbs free energy, respectively, for step s. R_g is the universal gas constant.

Both the forward and backward rate constants usually have Arrhenius form:

$$k_s = A_s \exp\left(\frac{-E_s^{\ddagger}}{R_g T}\right) \quad (21)$$

where A_s is the preexponential factor and $E_s^{\ddagger}$ is the activation energy of elementary step s. Experimentally it is well known that rate and equilibrium constants not only vary as a function of temperature but also as a function of surface coverage. Surface coverage dependence is ignored in the Langmuir-Hinshelwood approach followed in this paper.

Selectivity, $\mathcal{S}$, is a measure of how much is produced of a specific product compared to the production of byproducts or unwanted products. Selectivity is much more tricky to define than reaction rates because it generally depends on the specific reaction system and what is regarded as desired and undesirable products. Selectivity is always some kind of ratio between reaction rates where the nominator contains the formation rate of the wanted product and the denominator consist of the consumption rate of a key reactant or formation rates of unwanted products.

EXTENSION OF CAMPBELL'S DEGREE OF RATE CONTROL

In this section we will extend Campbell's degree of rate control in order to analyze the importance of thermodynamics and selectivity besides kinetics.

The degree of rate control ($X_{RC,s}$) is defined as:

$$X_{RC,s} = \frac{k_s}{\mathcal{R}} \left(\frac{\delta \mathcal{R}}{\delta k_s}\right)_{K_s,k_j} = \left(\frac{\delta \ln(\mathcal{R})}{\delta \ln(k_s)}\right)_{K_s,k_j} \quad (22)$$

where $\mathcal{R}$ is the overall reaction rate, k_s is the rate constant of elementary step s, where the rate constants k_j for all other steps j, as well as the equilibrium constant for step s, K_s, remain constant.

The larger numeric value of $X_{RC,s}$ the larger degree of rate control does the rate constant of step s exhibit on the overall rate. A positive value indicates that increasing k_s will increase the overall rate and step s will be denoted a rate limiting steps (rls). A negative value indicates the opposite and step s will be denoted an inhibition step. A value of approximately zero indicate that the step is quasi-equilibrated. Basically $X_{RC,s}$ investigates the sensitivity of the reaction rate on the rate constant i.e. transition state of step s.

In analogy the degree of selectivity control ($X_{SC,s}$) is defined as:

$$X_{SC,s} = \frac{k_s}{\mathcal{S}} \left(\frac{\delta \mathcal{S}}{\delta k_s}\right)_{K_s,k_j} = \left(\frac{\delta \ln(\mathcal{S})}{\delta \ln(k_s)}\right)_{K_s,k_j} \quad (23)$$

where $\mathcal{S}$ is some kind of selectivity, k_s is the rate constant of elementary step s, where the rate constants k_j for all other steps j, as well as the equilibrium constant for step s, K_s, remains constant.

A positive value indicates that increasing k_s will increase the selectivity and a negative value indicates the

opposite. A value of approximately zero indicate that the step is unimportant to selectivity. Basically $X_{SC,s}$ investigates the importance of the rate constant i.e. transition state of step s towards selectivity.

Fundamentally Eq. 22 implies changing the transition state of elementary step s while nothing else is changed in the reaction mechanism, and determining how this influences the overall rate, $\mathcal{R}$. More specifically, the standard state free energy of transition state s is changed while the energies and free energies of all other transition states, intermediates and gas phase species are kept constant. Hence Eq. 22 probes the importance of one transition state's free energy in the full potential energy surface for the reaction.

By analogy we would like to investigate the importance of intermediate stability (thermodynamics) on the overall reaction rate. To do this, we would like to determine the relative change in the net rate $\mathcal{R}$ (to one product or from one reactant), when we stabilize that intermediate (decrease its standard state free energy) by a tiny amount dG without changing anything else on the standard-state free energy surface for the net reaction. We thus define the degree of thermodynamic rate control ($X_{TRC,c}$) of intermediate c as:

$$X_{TRC,c} = \frac{1}{\mathcal{R}} \left(\frac{\delta \mathcal{R}}{\delta \left(\frac{-G_c}{R_g T} \right)} \right)_{G_j, G_n^{\ddagger}} = \left(\frac{\delta ln \mathcal{R}}{\delta \left(\frac{-G_c}{R_g T} \right)} \right)_{G_j, G_n^{\ddagger}} \tag{24}$$

G_c is the Gibbs free energy of intermediate c ($G+1 < c < G+I$). The Gibbs free energy of all other intermediates G_j and the Gibbs free energy of all transition states $G_n^{\ddagger}$ are kept constant when taking the partial derivative. $X_{TRC,c}$ is dimensionless. The degree of thermodynamics rate control has recently been introduced in [8] together with a general discussion of the concept.

Similarly the degree of thermodynamic selectivity control ($X_{TSC,c}$) is defined as:

$$X_{TSC,c} = \frac{1}{\mathcal{S}} \left(\frac{\delta \mathcal{S}}{\delta \left(\frac{-G_c}{R_g T} \right)} \right)_{G_j, G_n^{\ddagger}} = \left(\frac{\delta ln \mathcal{S}}{\delta \left(\frac{-G_c}{R_g T} \right)} \right)_{G_j, G_n^{\ddagger}} \tag{25}$$

It should be noted the degree of thermodynamic rate and selectivity control investigates the importance of intermediates stability without changing the overall equilibrium constant of the net gas phase reaction.

Campbell's degree of rate control answers the question: Suppose we could introduce a catalyst or catalyst modifier that incrementally lowered the free energy of the transition state for one elementary step s, without changing anything else. By what fraction would this change the net rate, per unit change in that step's rate (where 1 unit = that step's initial rate constant)? Similarly, the degree of thermodynamic rate control answers the closely related question: Suppose we could introduce a catalyst or catalyst modifier that incrementally lowered the free energy of one adsorbed intermediate, without changing anything else. By what fraction would this change the net rate, per unit change in free energy (in units of RT). This is a very important question, since it gives direct information about which intermediate would be most important to stabilize/destabilize (through change in the catalyst materials or addition of modifiers). In particular it has been shown in [8] that the concepts of degree of rate control and the degree of thermodynamic rate control are completely equivalent and can be compared numerically. Hence by calculating X_{RC} and X_{TRC} it can be established which transition states and intermediates that are most critical to the reaction rate and it is possible to rank the transition states and intermediates. The same goes for the selectivity.

INTERMEDIATE COVERAGE AND DEGREE OF THERMODYNAMIC RATE CONTROL

There is a simple relation between the degree of thermodynamic rate control and the coverage of intermediates:

$$X_{TRC,c} = -\sigma \theta_c \tag{26}$$

where σ is the average number of sites required in the rate limiting steps and θ_c is the coverage of intermediate c. σ typically varies between 1 to 2 depending on the nature of the rate limiting process e.g. dissociative chemisorption requires two sites, bi-molecular surface reaction requires two sites, molecular desorption requires one site etc. Certainly non-integer values are possible if a mix of different elementary reactions are rate limiting. Typically σ is more or less constant and $X_{TRC,c}$ becomes proportionate with the coverage of intermediate n. A complete mathematical proof of Eq. 26 will not be given. However in the following it will be demonstrated that Eq. 26 is valid for a Langmuir-Hinshelwood mechanism as well as for Michaelis-Menten enzyme kinetics. Furthermore all the numerical case studies of section follow Eq. 26. It should also be noted that the implications of Eq. 26 is consistent with the work of Dumesic where it was concluded based on DeDonder analysis that the stability of intermediates are unimportant to kinetics, but only the stability of transition states are of importance, except if the intermediate has a non-zero coverage [3, 51].

Langmuir-Hinshelwood example

We want to calculate the degree of thermodynamic rate control for the simple Langmuir-Hinshelwood mech-

anism:

$$A + * \rightleftharpoons A* \quad (27)$$
$$B + * \rightleftharpoons B* \quad (28)$$
$$A* + B* \rightleftharpoons AB* + * \quad (29)$$
$$AB* \rightleftharpoons AB + * \quad (30)$$

where * denotes a free site, X* denotes a surface intermediate, and X a gas phase species. We assume that the bi-molecular surface reaction (step 3) is rate limiting while all other steps are quasi-equilibrated. From equilibrium considerations we get:

$$\theta_{A*} = K_1 \frac{p_A}{p^\ominus} \theta_* \quad (31)$$
$$\theta_{B*} = K_2 \frac{p_B}{p^\ominus} \theta_* \quad (32)$$
$$\theta_{AB*} = \frac{1}{K_4} \frac{p_{AB}}{p^\ominus} \theta_* \quad (33)$$

where θ denotes coverages, K is equilibrium constants, p_i is partial pressure of i and $p^\ominus$ is the reference pressure. From the total site balance the coverage of free sites become:

$$\theta_* = \frac{1}{1 + K_1 \frac{p_A}{p^\ominus} + K_2 \frac{p_B}{p^\ominus} + \frac{1}{K_4} \frac{p_{AB}}{p^\ominus}} \quad (34)$$

The reaction rate, r, can now be written:

$$r = k_3 \theta_{A*} \theta_{B*} - \frac{k_3}{K_3} \theta_{AB*} \theta_* \quad (35)$$
$$r = \frac{k_3 \left(K_1 K_2 \frac{p_A}{p^\ominus} \frac{p_B}{p^\ominus} - \frac{1}{K_3 K_4} \frac{p_{AB}}{p^\ominus} \right)}{\left(1 + K_1 \frac{p_A}{p^\ominus} + K_2 \frac{p_B}{p^\ominus} + \frac{1}{K_4} \frac{p_{AB}}{p^\ominus} \right)^2} \quad (36)$$

Now we will calculate the degree of thermodynamic rate control for intermediate A* by applying Eq. 24 on Eq. 36. To simplify matters it is assumed that the Gibbs energy of A* is changed by changing the enthalpy of A* while the entropy remain unchanged. Hence the Gibbs free energy of Eq. 24 is substituted with enthalpy. Figure 1 shows a schematic of the potential energy surface expressed as enthalpies when the enthalpy of A* is pertubated the amount dH.

Before the enthalpy perturbation of A* we have the following enthalpies for the reaction system: H_{A*}, H_{B*}, H_{AB*}, $H^\ddagger_{AB*}$ and $E_A = H^\ddagger_{AB*} - H_{A*} - H_{B*}$ as the activation barrier of the rls.

After the enthalpy perturbation of A* we have the following enthalpies for the reaction system: $H_{A*} + dH$, H_{B*}, H_{AB*}, $H^\ddagger_{AB*}$ and $E_A = H^\ddagger_{AB*} - (H_{A*} + dH) - H_{B*}$ as the activation barrier of the rls. This results in the following changes in rate and equilibrium constants:

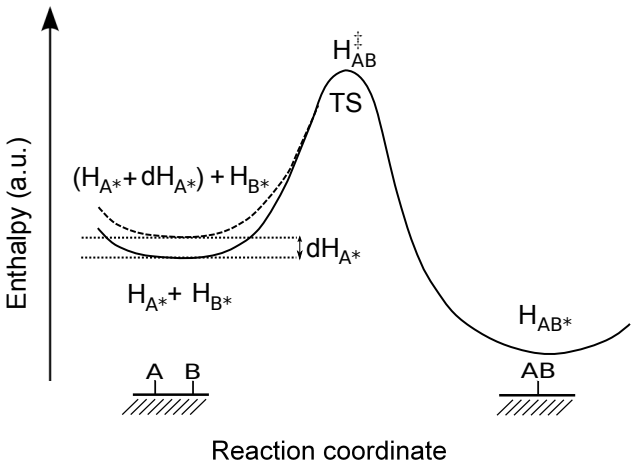


FIG. 1: Schematic potential energy surface, showing an incremental change in the standard state free energy of one adsorbed intermediate (A*) via a simple change in its enthalpy, used to estimate the degree of thermodynamic rate control of A*.

$$K_1 \rightarrow K_1 \exp\left(\frac{-dH}{RT}\right) \quad (37)$$
$$K_2 \rightarrow K_2 \quad (38)$$
$$K_3 \rightarrow K_3 \exp\left(\frac{dH}{RT}\right) \quad (39)$$
$$K_4 \rightarrow K_4 \quad (40)$$
$$k_3 \rightarrow k_3 \exp\left(\frac{dH}{RT}\right) \quad (41)$$

Now Eq. 24 is applied on 36:

$$X_{TRC,A*} = -RT \frac{\delta \left(\ln \left(\frac{k_3 \left(K_1 K_2 \frac{p_A}{p^\ominus} \frac{p_B}{p^\ominus} - \frac{1}{K_3 K_4} \frac{p_{AB}}{p^\ominus} \right)}{\left(1 + K_1 \frac{p_A}{p^\ominus} + K_2 \frac{p_B}{p^\ominus} + \frac{1}{K_4} \frac{p_{AB}}{p^\ominus} \right)^2} \right) \right)}{\delta H} \quad (42)$$
$$= -RT \frac{\delta}{\delta H} \left(\ln \left(k_3 K_1 K_2 \frac{p_A}{p^\ominus} \frac{p_B}{p^\ominus} - \frac{k_3}{K_3 K_4} \frac{p_{AB}}{p^\ominus} \right) - 2 \ln \left(1 + K_1 \frac{p_A}{p^\ominus} + K_2 \frac{p_B}{p^\ominus} + \frac{1}{K_4} \frac{p_{AB}}{p^\ominus} \right) \right) \quad (43)$$

From Eq. 37-41 it is straightforward to see that the first logarithmic term is zero. Hence we have:

$$X_{TRC,A*} = 2RT \frac{\delta \left(\ln \left(1 + K_1 \frac{p_A}{p^\ominus} + K_2 \frac{p_B}{p^\ominus} + \frac{1}{K_4} \frac{p_{AB}}{p^\ominus} \right) \right)}{\delta H}$$
$$= 2RT \frac{1}{1 + K_1 \frac{p_A}{p^\ominus} + K_2 \frac{p_B}{p^\ominus} + \frac{1}{K_4} \frac{p_{AB}}{p^\ominus}} \frac{\delta \left(K_1 \frac{p_A}{p^\ominus} \right)}{\delta H}$$
$$= 2RT \theta_* \frac{p_A}{p^\ominus} K_1 \frac{-1}{RT}$$
$$= -2\theta_{A*} \quad (44)$$

We note that the result is consistent with Eq. 26 and that the number 2 stems from the exponent of the denominator in Eq. 36, which is the number of active sites required in the RLS. By similar derivation it can be shown that $X_{TRC,B*} = -2\theta_{B*}$ and $X_{TRC,AB*} = -2\theta_{AB*}$.

Michaelis Menten kinetics

We want to calculate the degree of thermodynamic rate control for the Michaelis-Menten enzyme kinetics. The Michaelis-Menten mechanism can be written:

$$S + E \rightleftharpoons ES \tag{45}$$
$$ES+ \rightarrow P + E \tag{46}$$

where S corresponds to the substrate, E is free enzyme, ES is substrate locked to enzyme and P is the final product.

Assuming a constant amount of enzymes an enzyme balance can be written:

$$\theta_{ES} + \theta_E = 1 \tag{47}$$

where θ denotes fractions out of the total amount of enzyme.

The fraction of ES can be calculated from the steady-state approximation:

$$\frac{d\theta_{ES}}{dt} = k_1 C_S \theta_E - k_{-1}\theta_{ES} - k_2\theta_{ES} = 0 \tag{48}$$
$$\theta_{ES} = \frac{k_1}{k_{-1}+k_2} C_S \theta_E \tag{49}$$

where k_1 is forward rate constant of the first step, k_{-1} is backwards rate constant of the first step, and k_2 is the rate constant of the second step in the Michaelis-Menten mechanism.

The fraction of free enzymes can be calculated by combining Eq. 47 and Eq. 49:

$$\theta_E = \frac{1}{1 + \frac{k_1}{k_{-1}+k_2} C_S} = \frac{k_{-1}+k_2}{k_{-1}+k_2+k_1 C_S} \tag{50}$$

The rate of product formation can be written:

$$r_P = k_2\theta_{ES} = \frac{k_1 k_2 C_S}{k_{-1}+k_2+k_1 C_S} \tag{51}$$

Now the enthalpy of ES is perturbed by the amount dH in order to perturb the Gibbs free energy of ES. Before the perturbation of ES we have the following enthalpies: H_S, H_E, H_P, H_{ES}, $H^{\ddagger}_{ES}$ and $H^{\ddagger}_P$. This result in the activation barrier $E_{A,1} = H^{\ddagger}_{ES} - H_S$ for the forward step 1, $E_{A,-1} = H^{\ddagger}_{ES} - H_{ES}$ for the backward step 1 and $E_{A,2} = H^{\ddagger}_P - H_{ES}$ for the forward step 2. $H^{\ddagger}_{ES}$ is the transition state for binding the substrate to the enzyme and $H^{\ddagger}_P$ is the transition state for substrate-enzyme complex in forming P. After the perturbation of ES we have the following enthalpies: H_S, H_E, H_P, $H_{ES}+dH$, $H^{\ddagger}_{ES}$, $H^{\ddagger}_P$, $E_{A,1} = H^{\ddagger}_{ES} - H_S$, $E_{A,-1} = H^{\ddagger}_{ES} - (H_{ES}+dH)$ and $E_{A,2} = H^{\ddagger}_P - (H_{ES}+dH)$. This means that the rate constants are perturbed the following way:

$$k_1 \rightarrow k_1 \tag{52}$$
$$k_{-1} \rightarrow k_{-1}\exp\left(\frac{dH}{RT}\right) \tag{53}$$
$$k_2 \rightarrow k_2\exp\left(\frac{dH}{RT}\right) \tag{54}$$

Applying Eq. 24 on Eq. 51 for ES we obtain:

$$\begin{aligned} X_{TRC,ES} &= RT\frac{\delta}{\delta(-H_{ES})}\left(\ln\left(\frac{k_1 k_2 C_S}{k_{-1}+k_2+k_1 C_S}\right)\right) \\ &= -RT\frac{\delta(\ln k_1 + \ln k_2 + \ln C_S - \ln(k_{-1}+k_2+k_1 C_S))}{\delta(H_{ES})} \\ &= -1 + RT\frac{\delta}{\delta(H_{ES})}(\ln(k_{-1}+k_2+k_1 C_S)) \\ &= -1 + RT\frac{1}{k_{-1}+k_2+k_1 C_S}\left(\frac{k_{-1}}{RT}+\frac{k_2}{RT}\right) \\ &= -1 + \theta_E = -\theta_{ES} \end{aligned} \tag{55}$$

The calculated degree of thermodynamic rate control for the Michaelis-Menten mechanism is consistent with the result expected from Eq. 26.

Implications of Eq. 26

The simple relation between the importance of intermediate thermodynamics and the coverage of the intermediate revealed by Eq. 26 may seem surprising and does have some interesting implications. First of all, the degree of thermodynamic rate control is always negative or zero, which means that the reaction rate will decrease if an intermediate is stabilized without also stabilizing associated transition states. On the other hand, destabilizing intermediates can increase the rate significantly, unless key transition states are also destabilized. The trick in catalyst design / improvement is to destabilize key intermediates (those with large negative X_{TRC}) without destabilizing related key transition states too much, or to stabilize key transition states (those with positive X_{RC} without stabilizing key intermediates too much.

From an analysis point of view the most fundamental way to analyze a microkinetic model is to calculate the degree of rate control (probing importance of transition states) and the degree of thermodynamic rate control (probing importance of intermediates). From the apparent validity of Eq. 26 it is realized that one can calculate X_{TRC} either by using the more complex Eq. 24, or by using the calculated coverage of intermediates in the simpler Eq. 26.

TABLE I: Model 1 reaction mechanism. $*$ denotes an active site, X* denotes an adsorbed reaction intermediate and X denotes a gas phase species.

$A_2 + 2* \rightleftharpoons 2A*$	Step 1
$B + * \rightleftharpoons B*$	Step 2
$A* + B* \rightleftharpoons AB* + *$	Step 3
$AB* \rightleftharpoons AB + *$	Step 4

CASE STUDIES

In the following the usefulness of the previous introduced kinetic analysis tools: Degree of rate control, Degree of thermodynamic rate control, Degree of selectivity control and Degree of thermodynamic selectivity control are demonstrated in a series of numerical case studies on hypothetical kinetic models. Physical realistic parameters have been chosen for the components and rates of the elementary steps. The parameters are chosen in such a way that some interesting phenomena arises. The exact values are not interesting to the present investigation. The models are solved by different techniques (steady-state approximation (SSA), quasi-equilibrium approximation (QEA) and hybrid steady state approximation (HSSA)) illustrating that the analysis tools may be used for different kinetic approximations. For details on the applied kinetic approximations we refer to [2, 7]. The cases covers both simple reaction mechanisms containing a single overall reaction path and more complex reaction mechanisms with multiple reaction paths.

Single overall reaction

We start with looking at the simple reaction mechanism shown in Table I. The mechanism contains a single overall reaction:

$$A_2 + 2B \rightleftharpoons 2AB \tag{56}$$

The reaction mechanism is modeled by the SSA i.e. each elementary step is given a rate and the kinetic model will be referred to as Model 1.

The reaction rate, degree of rate control and the degree of thermodynamic rate control is calculated as a function of A_2 pressure and the results are depicted in Fig.2. It is observed from Fig. 2A that the reaction rate in the beginning increases rapidly with A_2 pressure. However a maximum rate is reached after which the rate slowly decreases with A_2 pressure.

From Fig. 2B it is clear that step 1 (A_2 dissociation) is the most rate limiting step at low A_2 pressure. However as A_2 pressure increases step 3 (bi-molecular surface reaction) becomes increasingly important. At some point step 1 even becomes an inhibition step with a negative

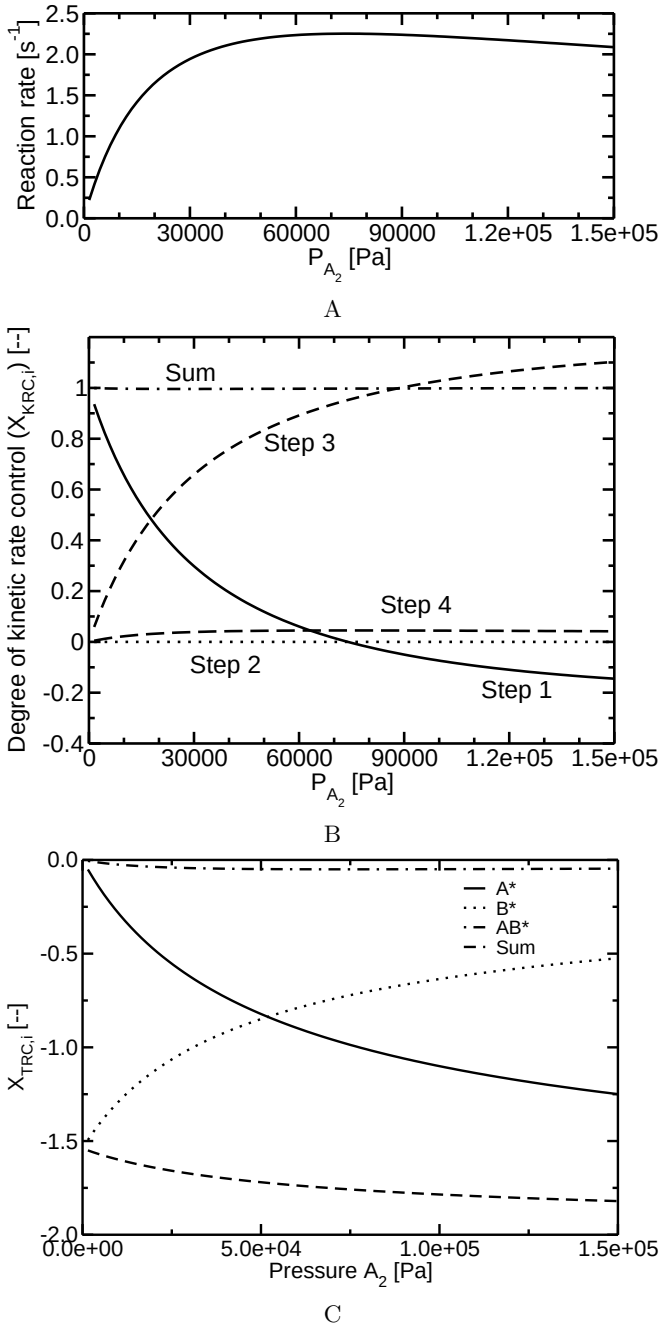


FIG. 2: Reaction rate (A), Degree of kinetic (B) and thermodynamic (C) rate control for Model 1 versus A_2 pressure. P_B = 10000 Pa, P_{AB} = 0 Pa and T = 450 K.

degree of kinetic rate control. Step 2 (B adsorption) is completely quasi-equilibrated and has a degree of rate control of zero. Step 4 (AB desorption) is close to quasi-equilibrated at the investigated conditions, but is slightly rate limiting. Note that summing all the steps leads to a constant value of one as expected. It is interesting that step 1, which is a vital step for AB production, becomes inhibiting. Actually this means that at high A_2 pressure

promoters could work by decreasing the rate of step 1 instead of increasing rates as usually expected. It is well known that dead-end steps, product inhibition etc. may be diminished by proper promotion. However in this very simple case it is observed that steps occurring before the rate limiting step may play similar inhibition roles.

It is important to note that the same elementary step can be both inhibiting and rate limiting at different reaction conditions. Hence when it is claimed that a certain step is rate limiting it should clarified at which reaction conditions.

From Fig. 2C it is apparent that increasing the stability of A* and B* have a large inhibiting effect on the rate of AB formation. Stability of A* becomes increasingly important at increasing A_2 pressure while B* stability is more critical at low A_2 pressure. The stability of AB* is uncritical (zero) at the investigated conditions (AB product is absent).

Comparing the numeric values of X_{RC} and X_{TRC} it is apparent that at low A_2 pressure the most critical parameter is B* stability which inhibits the reaction rate. Almost as important is the stability of step 1's transition state which increases the reaction rate. As A_2 pressure increases the stability of A* and step 3 transition state becomes increasingly critical to the reaction rate. It is important to notice that intermediate stability plays just as important and even in some cases more important role than the stability of the transition states. Whereas in the literature focus tends to be on transition states.

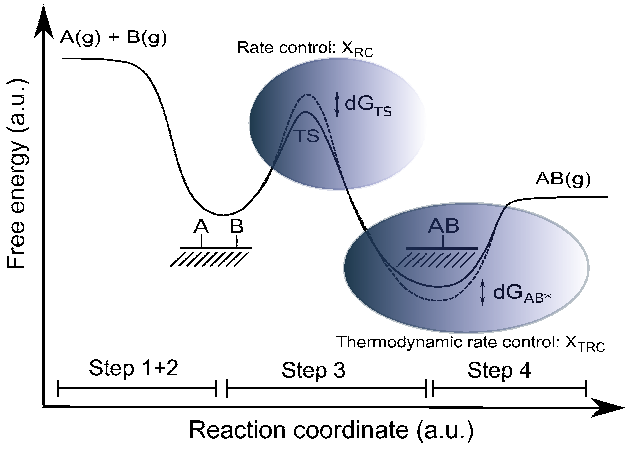


FIG. 3: Schematic potential energy surface for the model 1 reaction mechanism.

Hence the degree of rate control and the degree of thermodynamic rate control gives a clear and direct picture of which transition state and intermediate stabilities that are critical to the overall rate of AB formation. It should generally be noted when analyzing criticality of parameters of a microkinetic model that it is not enough to make an evaluation at one set of reaction conditions. Instead it is very helpful to plot the degree of rate control and thermodynamic rate control as function of reaction conditions such as temperature, reactant pressures, product pressure etc.

As mentioned earlier the sensitivity defined by Cortright and (Eq. 3) contains both kinetic and thermodynamic information for an elementary step. To compare with the information obtained from the degree of rate control and the degree of thermodynamic rate control, the sensitivity is calculated for Model 1. The sensitivity results are depicted in Fig.4 where the sensitivity of each elementary step is shown separately.

For step 1 it is apparent that both the forward and backward sensitivity is different from zero. This means that thermodynamics of the reaction plays a role. However as the sensitivities are not symmetric through the zero axis kinetics also plays a role, i.e. we have a mixed case. From the size difference between the forward and reverse sensitivities we can conclude kinetics are more important to the sensitivity, especially at low pressures. This is similar to the previous findings applying the degree of kinetic and thermodynamic rate control where the stability of A* (formed in step 1) is critical and the degree of rate control showed that step 1 is rate limiting and inhibiting. However it is not apparent from the sensitivity that stabilizing A* has a significant inhibiting effect on the reaction rate. This is due to the fact that both transition state and intermediate stability is changed when applying sensitivity.

For step 2 large numeric values of sensitivity for both forward and backward direction implying thermodynamic influence is observed. Further the sensitivities are symmetric with opposites signs i.e. sums to zero meaning that the step is quasi-equilibrated. This is similar to the previous findings applying the degree of rate control and degree of thermodynamic rate control where the stability of B* (formed in step 2) was critical and the degree of rate control showed that the step is quasi-equilibrated.

For step 3 the forward step has a significant sensitivity, while the backwards step has zero sensitivity. This means that only kinetics plays a role, i.e. the step is basically irreversible. This is similar to the previous findings applying the degree of rate control and the degree of thermodynamic rate control.

Step 4 is similar to step 3 except that the total sensitivity of the step is very low. Again this is similar to the the previous findings applying the degree of rate control and the degree of thermodynamic rate control.

Hence from Model 1 one may get the impressions that the use of sensitivity does almost as good a job as the degree of rate control and the degree of thermodynamic rate control. However this is only because Model 1 is very simple. In this case "simple" means that for all the thermodynamic important steps only one intermediate is formed. Hence it is easy to assign the sensitivity of an elementary step to an intermediate stability. However as

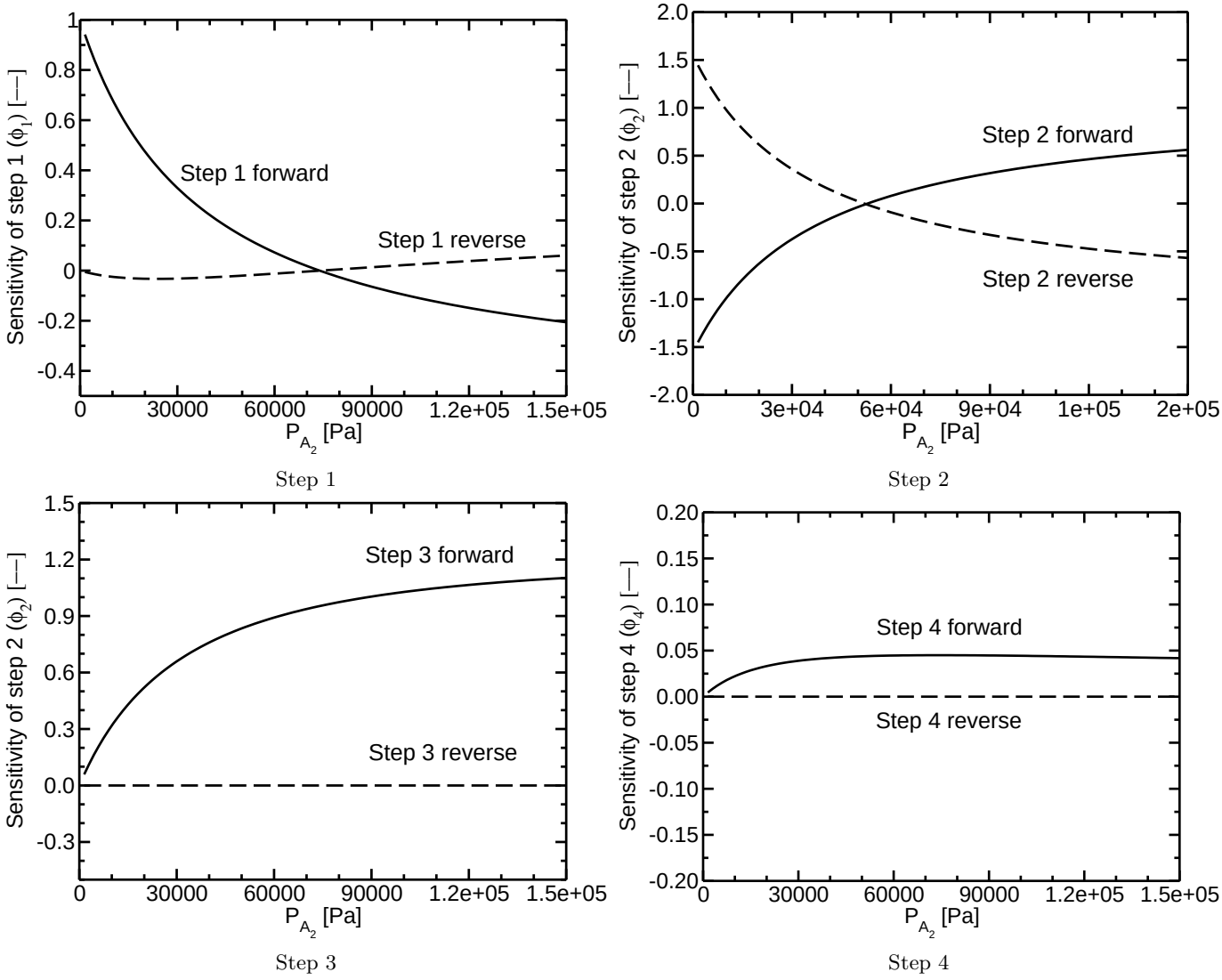


FIG. 4: Sensitivity for elementary steps of Model 1 versus A_2 pressure. $P_B = 10000$ Pa, $P_{AB} = 0$ Pa and T = 450 K.

kinetic models becomes just a bit more complicated the physics resulting in the sensitivity is not straight forward to interpret. This fact will be illustrated by analyzing the reaction mechanism shown in Table II containing a single overall reaction:

$$A_2 + 2B_2 \rightleftharpoons 2AB_2 \tag{57}$$

The reaction mechanism is modeled by the QEA i.e. with step 1 as rate limiting and all other steps quasi-equilibrated. The kinetic model will be referred to as Model 2. Due to the increased number of intermediates in the elementary steps, Model 2 is more complicated from a thermodynamics perspective.

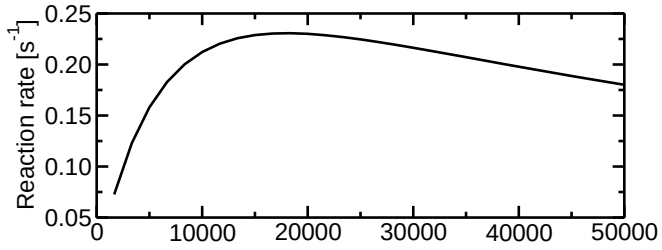
Fig.5 shows the variation of reaction rate, degree of thermodynamic rate control and sensitivity with B_2 pressure.

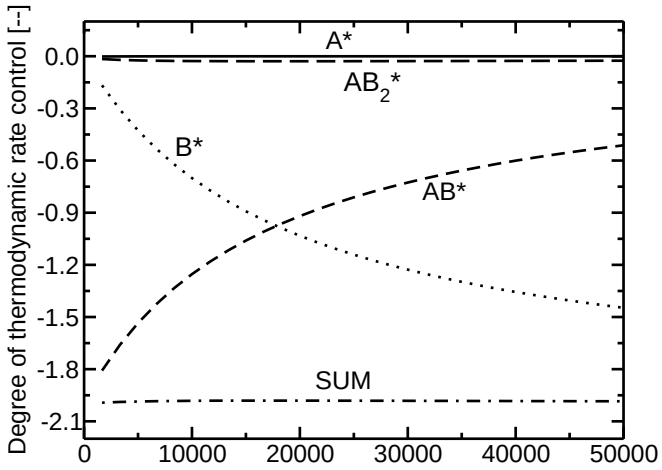
TABLE II: Model 2 reaction mechanism. $*$ denotes an active site, X* denotes an adsorbed reaction intermediate and X denotes a gas phase species.

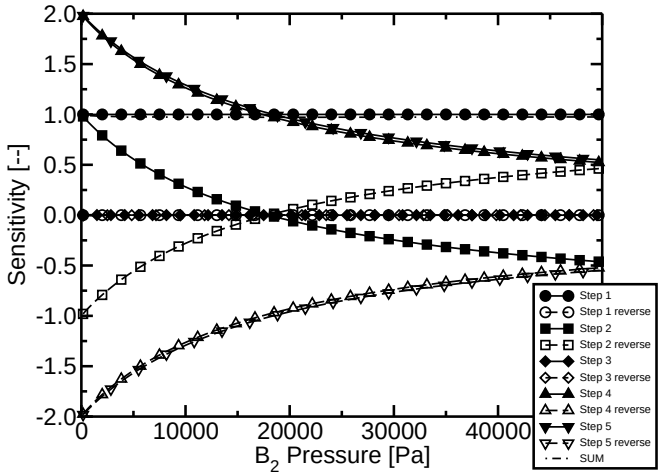
$A_2 + 2* \rightleftharpoons 2A*$ (rls)	Step 1
$B_2 + 2* \rightleftharpoons 2B*$	Step 2
$A* + B* \rightleftharpoons AB* + *$	Step 3
$AB* + B* \rightleftharpoons AB_2* + *$	Step 4
$AB_2* \rightleftharpoons AB_2 + *$	Step 5

It is observed that the reaction rate in the beginning increases rapidly with B_2 pressure. However a maximum rate is reached after which the rate decreases with B_2 pressure.

From Fig. 5B it is apparent that the stability of B* and AB* has a negative influence on AB_2 formation due







C

FIG. 5: Reaction rate(A), degree of thermodynamic rate control (B) and sensitivity (C) for Model 2 versus B_2 pressure. P_{A_2} = 10000 Pa, P_{AB_2} = 1000 Pa and T = 500 K.

to site blocking, while the stability of A* and AB_2* are uncritical at the investigated conditions.

The use of sensitivities in Fig. 5C does not result in such a clear picture. The sensitivity shows that step 1 is kinetically controlled while all other steps are quasi-equilibrated as expected since Model 2 is solved by the QEA approximation. The sensitivity method also reveals that step 2 is critical, which may readily be assigned to the stability of B*. Step 3 is uncritical even though it contains both A*, B* and AB*. Steps 4 and 5 are both critical and displays identical sensitivities. Nevertheless, it is not possible to establish if it is AB* or AB_2* stability which is critical. Hence assigning thermodynamics to a step instead of an intermediate is not a good idea. The degree of thermodynamic rate control tells us that the stability of B* and AB* is critical and should be estimated carefully for a microkinetic model. The use of sensitivity on the other hand says that the forward and backward rate constants of step 2, 4 and 5 are thermodynamically critical and has to be established as accurately as possible. Hence in conclusion sensitivity is a tool that establish which forward and backward rate constants are critical in a microkinetic model. However by calculating the degree of kinetic and thermodynamic rate control it becomes directly apparent which transition states and intermediate stabilities are important to the studied reaction rate without increasing the required amount of analysis work. Thus the degree of rate control and the degree of thermodynamic rate control gives results with a clear physical interpretation which is not the general case for the use of sensitivity.

Multiple overall reactions

In the previous section it was established that the degree of rate control and the degree of thermodynamic rate control are excellent tools to analyze and understand microkinetic models with a single overall reaction pathway. In this section focus will be on analyzing microkinetic models containing more than one overall reaction path. For such cases selectivity issues may occur and it is not clear which rate to analyze among the multiple possibilities. The answer is to perform the analysis on all the rates of interest.

TABLE III: Model 3 reaction mechanism. $*$ denotes an active site, X* denotes an adsorbed reaction intermediate and X denotes a gas phase species.

$A_2 + 2* \rightleftharpoons 2A*$ (rls)	Step 1
$B + * \rightleftharpoons B*$	Step 2
$A* + B* \rightleftharpoons AB* + *$ (rls)	Step 3
$AB* \rightleftharpoons AB + *$ (rls)	Step 4
$AB* + * \rightleftharpoons D* + *$ (rls)	Step 5
$D* \rightleftharpoons D + *$	Step 6
$B* + * \rightleftharpoons C* + *$ (rls)	Step 7
$C* \rightleftharpoons C + *$	Step 8

As an example of multiple reaction network the reaction mechanism shown in Table III is analyzed. The

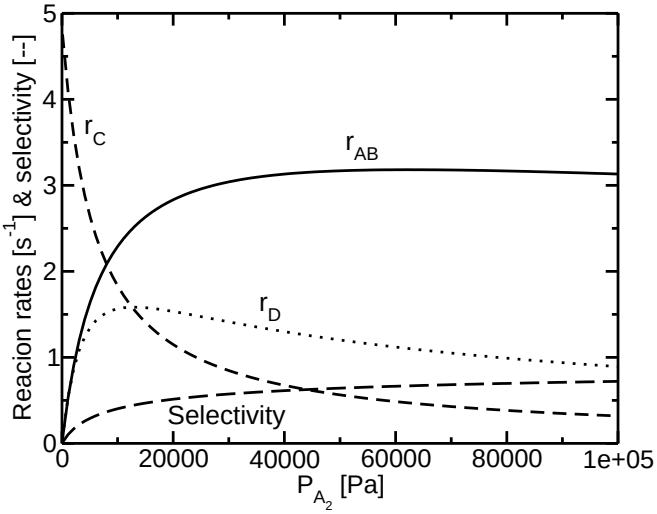


FIG. 6: Reaction rates of AB, C and D formation for Model 3 versus A_2 pressure. $P_B = 10000$ Pa, $P_{AB} = 0$ Pa, $P_C = 0$ Pa, $P_D = 0$ Pa and T = 500 K.

mechanism contains the following overall reactions:

$$A_2 + 2B \rightleftharpoons 2AB \quad (58)$$

$$AB \rightleftharpoons D \quad (59)$$

$$B \rightleftharpoons C \quad (60)$$

where AB is the desired product, C is formed in parallel to AB and D is formed in a consecutive reaction to AB.

The reaction mechanism is solved by the HSSA approximation with step 1, step 3, step 4, step 5 and step 7 as rate limiting steps. All other steps are quasi-equilibrated. In the following the kinetic model will be referred to as Model 3.

In Fig.6 the reaction rates for AB formation (desired product), D formation and C formation is calculated as a function of A_2 pressure for Model 3. The selectivity of AB formation is also shown.

From Fig.6 it is observed that initially the rate of AB formations increases rapidly with A_2 pressure but passes through a maximum and starts to decrease slowly. The rate of D formation shows a similar pattern, but decreases more rapidly after the maximum is achieved. The rate of C formation is high at low A_2 pressure but decreases fast to zero at increasing A_2 pressure. AB selectivity increases with A_2 pressure.

In Fig.7 the degree of kinetic and thermodynamic rate control is calculated for AB, C and D formation.

There is a vast amount of information in Fig.7. First it is noted that the degree of rate control is conserved summing to one for multiple reaction paths too.

For AB formation step 1 is indeed rate limiting at low A_2 pressure, but decreases fast as the pressure increases. Step 3 shows the opposite trend and is the most rate limiting step at high A_2 pressure. Step 4 has a constant

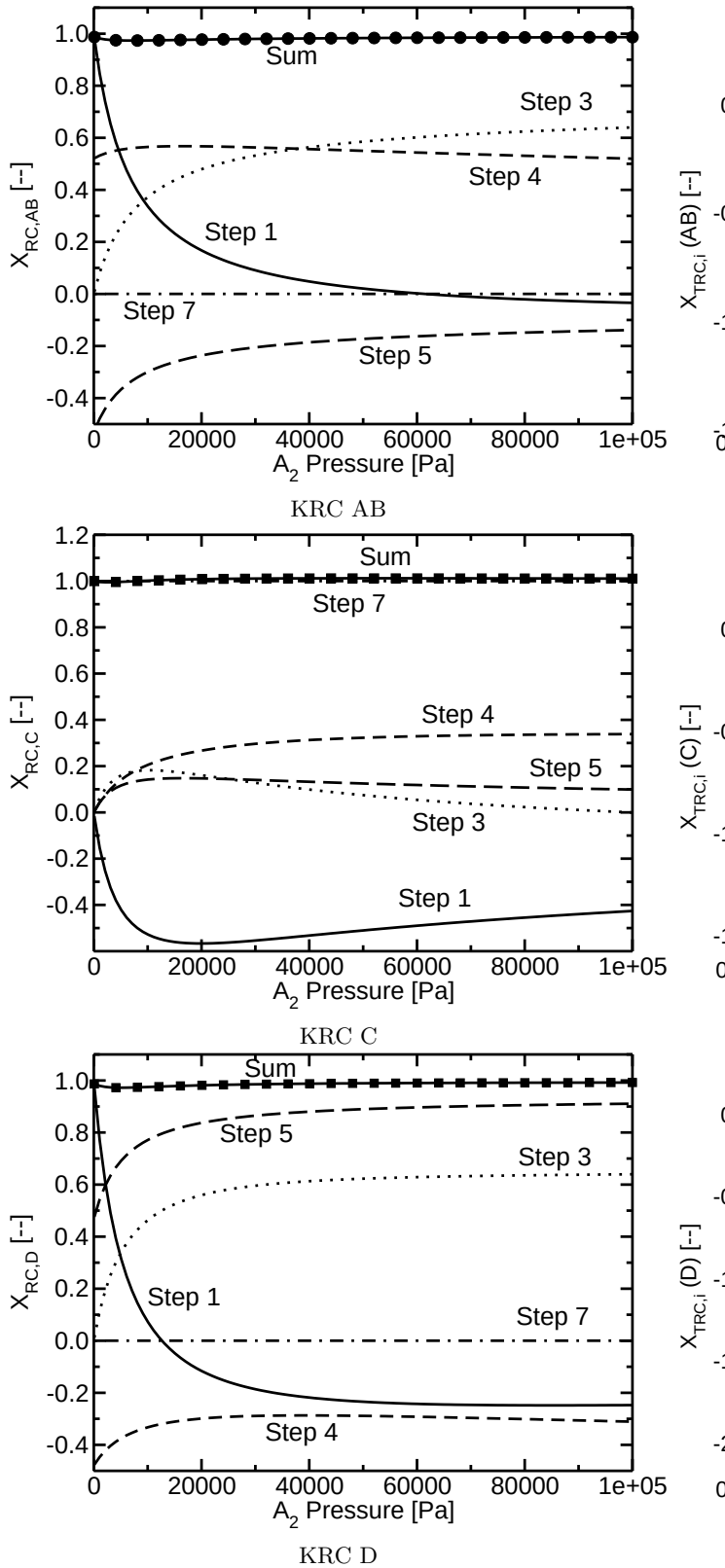


FIG. 7: Degree of kinetic and thermodynamic rate control for AB, C and D formation respectively for Model 3 versus A_2 pressure. $P_B = 10000$ Pa, $P_{AB} = 0$ Pa, $P_C = 0$ Pa, $P_D = 0$ Pa and T = 500 K.

positive degree of kinetic rate control. Step 5 has a negative effect on AB formation, while step 7 has zero effect on AB formation rate. For C formation step 7 (produces C) is rate limiting with a constant value of one. Step 3, 4, and 5 (consumes A*) have moderate positive kinetic effect, while step 1 (produces A*) has a strong negative effect. For D formation a similar kinetic picture as for AB formation is observed except that step 4 gets a negative role, while step 5 gets a positive role.

Thermodynamically all the reaction rates can be inhibited by increasing the stability of A*, B* and AB* or the rates can be increased if the stabilities are decreased. The calculated degree of thermodynamic rate control of the three reaction display the same qualitative behavior as expected from Eq. 26. However they differ quantitatively as the number of sites required for C and D formation is higher than that of AB formation.

From the above analysis it is evident that the degree of rate control and the degree of thermodynamic rate control may be used to analyze what is important to each rate separately. However a lot of analysis is involved and it will increase by the number of rates that is studied. In the current case it could be chosen to analyze the consumption rates of the reactants as well. For other cases more than three overall reaction paths may exist and the analysis becomes even more involved. The problem is that by analyzing the different rates separately it is not established which parameters are most important to the overall picture.

Cortright and Dumesic [3] suggested to sum the absolute values of the degree of rate control for all the products or chosen subset of interesting products (Eq. 8). This total degree of rate control should then reveal the most critical steps. The procedure has been followed for AB, C and D formation in Fig.8.

The method of Cortright and Dumesic may be used in a preliminary analysis to investigate what step are important for a microkinetic model. However a lot of information is lost. It is not possible to obtain the information of Fig.7 from Fig.8. It is not even possible to access if a step has a positive or negative importance or for which products a step exerts an influence. So the only advantage of this method is if you have a very complex model with many steps to determine, which steps are important and should be analyzed closer. The steps identified should than be used in calculating figures such as Fig.7. Hence lowering the number of calculations as the equilibrated steps are discarded. Furthermore the degree of rate control in Fig.8 is not conserved.

Thus a method to establish which kinetic and thermodynamic parameters are the most important to overall reaction system is still lacking. The first thing to realize for models with multiple overall reaction paths is that what is most important or critical is a subjective question. The answer depends on which product is most interesting. Hence in the present case AB is the desired

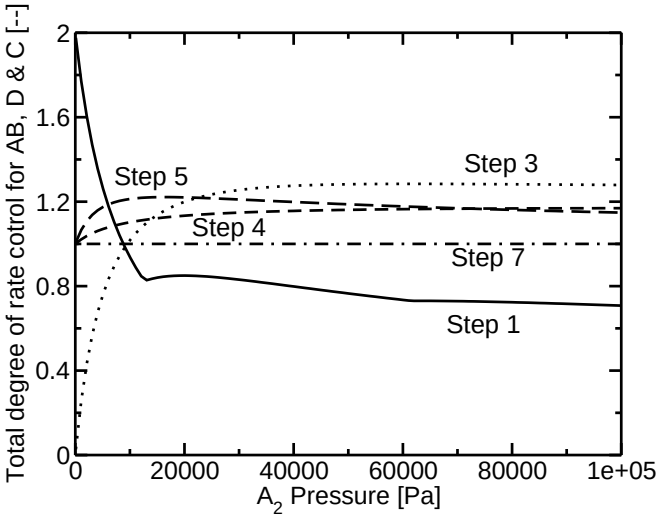


FIG. 8: The sum of absolute degree of kinetic rate control for AB, C and D formation for Model 3 versus A_2 pressure. P_B = 10000 Pa, P_{AB} = 0 Pa, P_C = 0 Pa, P_D = 0 Pa and T = 500 K.

product and the degree of kinetic and thermodynamic rate control for AB formation reveals the most critical parameters. However as useful the degree of rate control is it does not identify which parameters are important in favoring one product instead of others, i.e. selectivity. If we assume AB is the wanted product the degree of selectivity control and the degree of thermodynamic selectivity control for AB formation may be calculated as depicted in Fig.9.

It is apparent from Fig.9 that step 1 and step 4 has a positive effect on AB selectivity, while step 5 and 7 has a negative effect. It is also apparent which steps are effecting selectivity the most (positive or negative) at certain reaction conditions. Thermodynamically A*, B* and AB* stability has a positive effect on selectivity. The selectivity increases with increasing intermediate stability (increasing surface coverage) because AB formation requires less free sites than C and D formation. Note that the degree of selectivity control is conserved summing to zero.

Hence for multiple reactions, the combined use of the degree of ate and selectivity control and degree of thermodynamic rate and selectivity control results in valuable information. As minimum the rate and selectivity of the product of interest should be studied. However analyzing the rates of other products and reactants may give important clues to what is going on at the microkinetic level instead of just identifying critical parameters for the product of interest. However the most sensible approach depends on the situation.

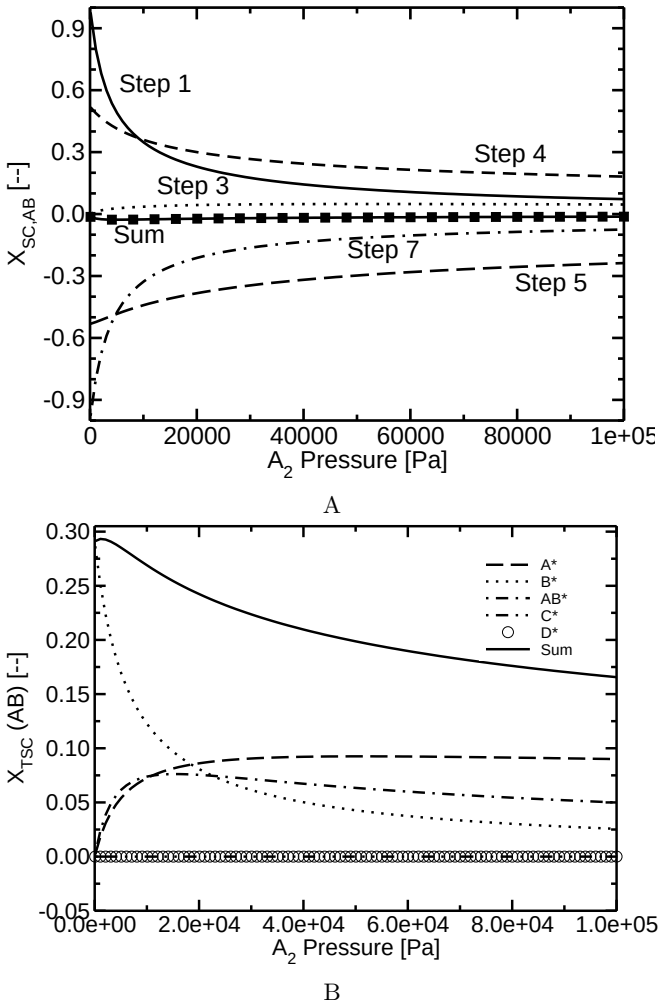


FIG. 9: Degree of kinetic (A) and thermodynamic (B) selectivity control versus A_2 pressure for Model 3. P_B = 10000 Pa, P_{AB} = 0 Pa, P_C = 0 Pa, P_D = 0 Pa and T = 500 K.

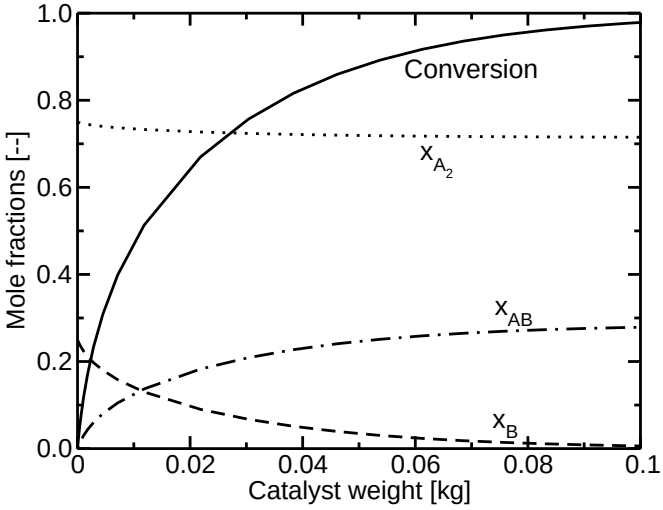


FIG. 10: Reaction conditions versus catalyst weight in an integral reactor for Model 1. P = 100000 Pa, F = 0.11 mol/s, $x^0_{A_2}$=0.75, x^0_B=0.25 and T = 500 K.

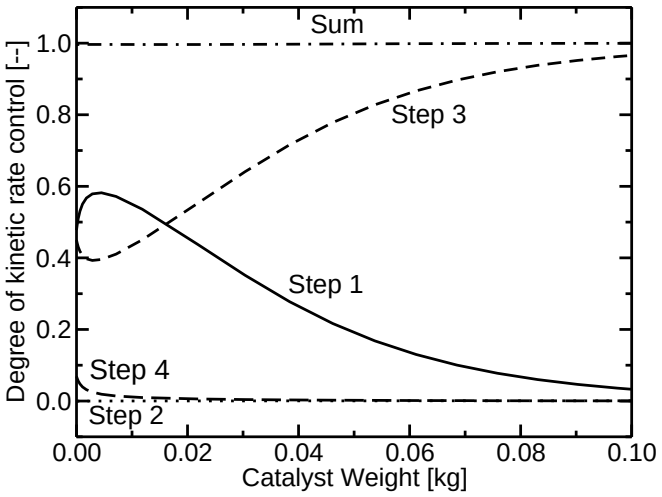


FIG. 11: Degree of rate control versus catalyst weight in an integral reactor for Model 1. P = 100000 Pa, F = 0.11 mol/s, $x^0_{A_2}$=0.75, x^0_B=0.25 and T = 500 K.

Integral reactor data

The degree of rate and selectivity control and the degree of thermodynamic rate and selectivity control are differential tools that establish the importance of parameters at the instantaneous reaction condition studied. Hence they are perfect to analyze differential reactors/instantaneous reaction conditions as done in the previous sections. However for an integral reactor reaction conditions changes and the reaction rate varies down through the reactor. In order to analyze an integral reactor, the first step is to solve the integral reactor and establishing profiles of reactor conditions i.e. partial pressure and temperatures. Afterwards each set of reaction conditions are analyzed as a differential reactor/instantaneous reaction conditions.

The above mentioned approach will now be applied for Model 1. Fig.10 displays how the reaction conditions vary down through an integral reactor for Model 1. Applying the reaction conditions of Fig.10 the degree of rate control is calculated in Fig. 11. It is apparent from Fig. 11 that step 1 and 3 are rate limiting, while step 2 and 4 is practically quasi-equilibrated. In the beginning of the reactor step 1 is the most rate limiting step. However as B is consumed Step 3 becomes the most rate limiting step.

Hence the degree of rate and selectivity control and the degree of thermodynamic rate and selectivity control is also very suitable to analyze integral reactors as well as differential reactors/instantaneous reaction conditions.

CONCLUSION

It has been clearly demonstrated by applying hypothetical microkinetic models of varying complexity that the concepts of degree of rate and selectivity control and degree of thermodynamic rate and selectivity control offers a rigorous framework to analyze kinetic models. The methods are generally applicable and can be used for all sort of chemical reaction networks and is not limited to heterogeneous catalysis. In particular the methods are suitable for multiple overall reaction networks where other methods in the literature are of limited use.

It has also been demonstrated that the introduced methods gives direct information about if it is kinetics and/or thermodynamics that is of importance. In particular it is possible to rank which transition state and intermediate stabilities there are critical to reaction rate and selectivity.

It has generally been illustrated that criticality of microkinetic model parameters may vary significantly with reaction conditions. Hence it is important that the parameters are investigated at all relevant reaction conditions. We have found it very useful to plot the degree of rate and selectivity control and the degree of thermodynamic rate and selectivity control as function of variation in reaction conditions, such as total pressure, temperature, partial pressures, catalyst weight etc.

For most cases numerical solution of the degree of rate and selectivity control and the degree of thermodynamic rate and selectivity control is required.

The importance of intermediate stability is directly related to the coverage of the intermediate. Calculating the degree of thermodynamic rate control is equivalent to establishing the coverage of the intermediates and rates always decreases by stabilizing intermediates unless key transition states are also destabilized.

On a more general note the degree of rate and selectivity control and degree of thermodynamic rate and selectivity control only establishes what transition states and intermediate stabilities are critical. Although it may appear tempting to completely discard the concepts of *rate limiting steps* and solely focus on rate limiting *states* [17] we will argue against such notion. First of all, while the rate limiting states may be appealing to physicist, the concept of rate limiting steps is printed in the mind of most chemical engineers dealing with chemical reaction analysis and reactor design. Furthermore, elementary reaction steps form the building blocks of reaction mechanisms, and as such reveal the detail of the overall reaction on a molecular level. The knowledge of which steps are rate limiting is pivotal when reducing large reaction mechanisms by various methods, such as applying the steady-state approximation or the quasi-equilibrium approximation, thereby reducing the full solution to a level which can be handled more easily, both in terms of being more comprehensible to the human brain as well being numerically well behaved. In addition to this, as also illustrated, the intermediate stability can be translated into surface coverages and may help reduce the kinetic model even further, say, if one or only few intermediates have significant coverages (see e.g. [52]). Thus, once the critical states are identified this information can be used in combination with the detailed reaction mechanism in order to provide great insight into what is going on at the microkinetic level. The method cannot however answer why certain parameters are critical. To answer this other methods such as quantum mechanics has to be used.

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[1] J.A. Dumesic, D.A. Rudd, L.M. Aparicio, J.E. Rekoske, and A.A. Treviño. *The Microkinetics of Heterogeneous Catalysis*. ACS, 1993.
[2] P. Stoltze. *Prog. Surf. Sci.*, 65:65–100, 2000.
[3] R. D. Cortright and J. A. Dumesic. *Adv. Catal.*, 46:161–264, 2001.
[4] C. T. Campbell. *Topics. Catal.*, 1:353–366, 1994.
[5] L. J. Broadbelt and R. Q. Snurr. *Appl. Catal. A.*, 200:23–46, 2000.
[6] I. E. Wachs. *Surf. Sci.*, 544:1–4, 2002.
[7] H. Lynggaard, A. Andreasen, C. Stegelmann, and P. Stoltze. *Prog. Surf. Sci.*, 77:71–137, 2004.
[8] C. Stegelmann, A. Andreasen, and C. T. Campbell. *J. Am. Chem. Soc*, 131:8077–8082, 2009.
[9] J. K. Nrskov, T. Bligaard, and J. Kleis. *Science*, 324:1655–1656, 2009.
[10] G. Armstrong. *Nature Chemistry*, 2009. `doi:10.1038/nchem.233`.
[11] W. D. Michalak, J. B. Miller, and A. J. Gellman. 2009. `http://aiche.confex.com/aiche/2011/webprogrampreliminary/Paper228774.html`.
[12] C. T. Campbell. *J. Catal.*, 204:520–524, 2001.
[13] C. T. Campbell. *Nature*, 432:282–283, 2004.
[14] S. Kozuch and S. Shaik. *J. Am. Chem. Soc.*, 128(10):3355–3365, 2006.
[15] S. Kozuch and S. Shaik. *J. Phys. Chem. A*, 112(26):6032–6041, 2008.
[16] S. Kozuch and S. Shaik. *Accounts of Chemical Research*, 44:101–110, 2011.
[17] S. Kozuch and J. M. L. Martin. *ChemPhysChem*, 12:1413–1418, 2011.
[18] J. A. Dumesic. *J. Catal.*, 204:525–529, 2001.
[19] M. Boudart and K. Tamaru. *Catal. Lett.*, 9:15–22, 1991.
[20] A. Baranski. *Solid State Ionics*, 117:123–128, 1999.
[21] P. Rotaru and S? I. Blejoiu. *Journal of the Indian Chemical Society*, 78(7):352–359, 2001.
[22] L. Olsson, H. Persson, E. Fridell, M. Skoglundh, and B. Andersson. *J. Phys. Chem. B*, 105(29):6895–6906, 2001.
[23] K. I. Gursahani, R. Alcalaá, R. D. Cortright, and J. A. Dumesic. *Appl. Catal. A*, 222(1-2):369–392, 2001.
[24] R. J. Madon, M. A Sanchez-Castillo, N. Agarwal, C. Miller, and R. D. Cortright. *J. Catal.*, 205(1):67–85,

2002.
[25] N. Agarwal, M.A. Sanchez-Castillo, R.D. Cortright, R.J. Madon, and J.A. Dumesic. *Ind. Eng. Chem. Res.*, 41(16):4016–4027, 2002.
[26] S. Sriramulu and R. S. Weber. Microkinetic analysis of automotive exhaust catalysts. volume 47, 2002.
[27] S Linic and MA Barteau. *J. Catal.*, 214(2):200–212, 2003.
[28] M. A. Sanchez-Castillo, N. Agarwal, A. Bartsch, R. D. Cortright, R. J. Madon, and J. A. Dumesic. *J. Catal.*, 218:88–103, 2003.
[29] YS Su, JY Ying, and WH Green. *J. Catal.*, 218(2):321–333, 2003.
[30] J. Hoffmann, S. Schauermann, V. Johanek, J. Hartmann, and J. Libuda. *J. Catal.*, 213(2):176–190, 2003.
[31] N. A. Koryabkina, A. A. Phatak, W. F. Ruettinger, R. J. Farrauto, and F. H. Ribeiro. *J. Catal.*, 217(1):233–239, 2003.
[32] C. Stegelmann, N. C. Schiødt, C. T. Campbell, and P. Stoltze. *J. Catal.*, 221:630–649, 2004.
[33] D. Wolf. volume 75. 2004.
[34] T Bligaard, JK Norskov, S Dahl, J Matthiesen, CH Christensen, and J Sehested. *J. Catal.*, 224(1):206–217, 2004.
[35] AA Gokhale, S Kandoi, JP Greeley, M Mavrikakis, and JA Dumesic. *Chemical Engineering Science*, 59(22-23):4679–4691, 2004.
[36] A. Bhan, S.-H. Hsu, G. Blau, J. M. Caruthers, V. Venkatasubramanian, and W. N. Delgass. *J. Catal.*, 235:35–51, 2005.
[37] J. Libuda and H. . Freund. *Surface Science Reports*, 57(7-8):157–298, 2005.
[38] M. . Bocquet and D. Loffreda. *J. Am. Chem. Soc.*, 127(49):17207–17215, 2005.
[39] L. Grabow, Y. Xu, and M. Mavrikakis. *Phys. Chem. Chem. Phys.*, 8:3369–3374, 2006.
[40] S. Kandoi, J. Greeley, M. A. Sanchez-Castillo, S. T. Evans, A. A. Gokhale, J. A. Dumesic, and M. Mavrikakis. *Topics in Catalysis*, 37(1):17–27, 2006.
[41] K Reuter and M Scheffler. *Phys. Rev. B*, 73(4), 2006.
[42] A. Hellman, E. J. Baerends, M. Biczysko, T. Bligaard, C. H. Christensen, D. C. Clary, S. Dahl, R. van Harrevelt, K. Honkala, H. Jonsson, G. J. Kroes, M. Luppi, U. Manthe, J. K. Norskov, R. A. Olsen, J. Rossmeisl, E. Skulason, C. S. Tautermann, A. J. C. Varandas, and J. K. Vincent. *J. Phys. Chem. B*, 110(36):17719–17735, 2006.
[43] Albert Poater, Xavier Solans-Monfort, Eric Clot, Christophe Coperet, and Odile Eisenstein. *J. Am. Chem. Soc.*, 129(26):8207–8216, 2007.
[44] Adrien T. Normand, Kirsty J. Hawkest, Nicolas D. Clernentt, Kingsley J. Cavell, and Brian F. Yates. *Organometallics*, 26(22):5352–5363, 2007.
[45] Vladimir P. Zhdanov. *Surface Review and Letters*, 14(3):419–424, 2007.
[46] Amit A. Gokhale, James A. Dumesic, and Manos Mavrikakis. *J. Am. Chem. Soc.*, 130(4):1402–1414, 2008.
[47] A. Bhan and W. N. Delgass. *Catal. Rev. Sci. Eng.*, 50(1):19–151, 2008.
[48] L. C. Grabow, A. A. Gokhale, S. T. Evans, J. A. Dumesic, and M. Mavrikakis. *J. Phys. Chem. C*, 112(12):4608–4617, 2008.
[49] T. C. Ho. *Catal. Rev. Sci. Eng.*, 50(3):287–378, 2008.
[50] Y. Schuurman. *Catal. Today*, 138(1-2):15–20, 2008.
[51] J. A. Dumesic. *J. Catal.*, 185:496, 1999.
[52] A. Andreasen, H. Lynggaard, C. Stegelmann, and P. Stoltze. *Appl. Catal. A.*, 289:267–273, 2005.