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Thermodynamic Analysis of Reaction Schemes with Empty Routes

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Steady-State Kinetics of Complex Reactions

Catalytic reactions represent complex networks, consisting of a variety of participating species. Kinetic modeling of these reaction networks has been extensively discussed in the literature for homogeneous catalytic, biochemical, and heterogeneous catalytic reactions.[1-4] Overall reaction equations, which are linear combinations of chemical equations of steps, are obtained by the addition of chemical equations of stages multiplied by certain numbers (positive, negative, or zero). Following Horiuti these numbers (which could be also fractional) are called *stoichiometric* and must be chosen in such a way that the overall equations contain no intermediates. A set of stoichiometric numbers of the stages producing an overall reaction equation is called after Horiuti a *reaction route*. Routes must be essentially different and it is impossible to obtain one route from another through multiplication by a number, although their respective overall equations can be identical. Although the basis of routes (such as a set of linear independent reaction routes, none of which can be represented as a linear combination of others) can be chosen in different ways, the number of basis routes for a given reaction mechanism is determined in a unique way.

Once the reaction network is established it is essential for kinetic modeling to specify kinetic and thermodynamic parameters.[1] Because parameters in a mechanistic model have a physicochemical meaning, there are certain constraints. For instance the rates of forward and reverse reactions are related through thermodynamics (de Donder equation[5]). Combining the de Donder equation with the principle of microscopic reversibility it can be demonstrated that for the so-called molecular loop the overall Gibbs energy is equal to zero, and thus the equilibrium constant is equal to unity.[6] The overall equilibrium constant is a multiplication of equilibrium constants of reaction steps, which are equal to the ratio of forward and reverse constants. In the present communication the principle of microscopic reversibility is discussed with respect to complex reaction networks.

Networks with Empty Routes: Partial Oxidation of Methane to Synthesis Gas

Linear independence of routes does not mean that corresponding overall equations are linearly independent. The number of routes can be higher than the number of reactions,[3] which means that some routes could be empty because they do not result in any chemical transformation. In the case of reactions with empty routes the main focus is as expected in analyzing the kinetic equations for nonempty routes. At the same time the presence of intermediates—which are not directly involved in these nonempty routes, but appear in empty routes—through a complex relation influences the surface coverage of all species, thus having a profound impact on the overall kinetics. Herein we consider a recent example from the literature with several empty routes[7] and demonstrate the importance of thermodynamic consistency in selection of kinetic parameters.

The partial oxidation of methane in catalytic monoliths at short contact times offers a promising route for the conversion of natural gas into more useful chemicals such as synthesis gas (syngas), a mixture of hydrogen and carbon monoxide. Syngas can subsequently be converted into methanol or higher hydrocarbons. The previously presented kinetic model for partial oxidation of methane,[7] which includes 19 reversible reactions with six gas-phase species and 11 adsorbed species, was claimed to be suitable for complete and partial oxidation of

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methane on rhodium surfaces. In this short communication we cannot give a complete overview of the literature on methane partial oxidation and, therefore, refer not to the original publications on the mechanism, but rather to the work that uses this mechanism. The presence of 19 steps, one balance equation (which relates coverage of surface species), and 12 intermediates results according to the Horiuti–Temkin rule[3] in eight routes. Six gas-phase species give rise to the following overall chemical equations, describing such phenomena as complete oxidation of methane, steam reforming of methane, and water–gas shift reaction, respectively: $CH_4 + O_2 = 2H_2O + CO_2$, $CH_4 + H_2O = CO + 3H_2$, $CO + H_2O = CO_2 + H_2$. The reaction mechanism that we consider below (the Eq. 1 system) can thus be presented by three routes describing these three reactions, as well as six empty routes. In fact, the choice of these reactions depends on selection of the basis of reaction routes. In another set of routes one could have, say, a route leading not to steam, but to dry reforming of methane.

	Step	$N^{(1)}$	$N^{(2)}$	$N^{(3)}$	$N^{(4)}$	$N^{(5)}$	$N^{(6)}$	$N^{(7)}$	$N^{(8)}$	
1	$H_2+2Z \leftrightarrows 2HZ$	0	−3	−1	0	0	0	0	0	
2	$O_2+2Z \leftrightarrows 2OZ$	2	0	0	0	0	0	0	0	
3	$CH_4+Z \leftrightarrows CH_4Z$	1	1	0	0	0	0	0	0	
4	$H_2O+Z \leftrightarrows H_2OZ$	−2	1	1	0	0	0	0	0	
5	$CO_2+Z \leftrightarrows CO_2Z$	−1	0	−1	0	0	0	0	0	
6	$CO+Z \leftrightarrows COZ$	0	−1	1	0	0	0	0	0	
7	$H_2OZ+Z \leftrightarrows OHZ+HZ$	0	1	1	0	0	0	0	1	
8	$CO+Z \leftrightarrows CZ+OZ$	−1	−1	0	0	0	0	0	0	
9	$CO_2+Z \leftrightarrows COZ+OZ$	−1	0	−1	0	0	0	0	0	
10	$CH_4Z+Z \leftrightarrows CH_3Z+HZ$	0	1	0	1	1	0	0	0	
11	$CH_3Z+Z \leftrightarrows CH_2Z+HZ$	0	1	0	1	0	1	0	0	
12	$CH_2Z+Z \leftrightarrows CHZ+HZ$	0	1	0	1	0	0	1	0	
13	$CHZ+Z \leftrightarrows CZ+HZ$	0	1	0	1	0	0	0	0	
14	$OZ+HZ \leftrightarrows OHZ+Z$	0	−1	−1	4	1	1	1	1	
15	$OHZ+OHZ \leftrightarrows H_2OZ+ZO$	2	0	0	0	0	0	0	1	
16	$CH_4Z+ZO \leftrightarrows CH_3Z+OHZ$	1	0	0	−1	−1	0	0	0	
17	$CH_3Z+OZ \leftrightarrows CH_2Z+OHZ$	1	0	0	−1	0	−1	0	0	
18	$CH_2Z+OZ \leftrightarrows CHZ+OHZ$	1	0	0	−1	0	0	−1	0	
19	$CHZ+OZ \leftrightarrows CZ+OHZ$	1	0	0	−1	0	0	0	0	(1)

$N^{(1)}$: $CH_4+O_2=2H_2O+CO_2$; $N^{(2)}$: $CH_4+H_2O=CO+H_2$; $N^{(3)}$: $CO+H_2O=CO_2+3H_2$; $N^{(4)}$, $N^{(5)}$, $N^{(6)}$, $N^{(7)}$, $N^{(8)}$: $0=0$.

The basis of routes, presented above, was chosen arbitrarily. Just to illustrate this point, simple manipulations $N^{(9)} = N^{(4)} - N^{(5)} - N^{(6)} - N^{(7)}$ result in a reaction route with all the steps having stoichiometric numbers equal to zero with the exception of steps 13, 14, and 19, where these numbers are 1, 1, and −1, respectively. Now we can express this reaction route $N^{(9)}$ following the principle of microscopic reversibility[6]:

$$K_{eq}^{N^{(9)}} = K_{13}K_{14}/K_{19} = \frac{k_{13}}{k_{-13}}\frac{k_{14}}{k_{-14}}\frac{k_{-19}}{k_{19}} \tag{2}$$

Similarly for some other empty routes one obtains

$$K_{eq}^{N^{(5)}} = K_{10}K_{14}/K_{16} \qquad K_{eq}^{N^{(6)}} = K_{11}K_{14}/K_{17}$$
$$K_{eq}^{N^{(7)}} = K_{12}K_{14}/K_{18} \qquad K_{eq}^{N^{(8)}} = K_7K_{14}K_{15} \tag{3}$$

The values of the equilibrium constants for these empty routes should be equal to unity as discussed above, providing the possibility of verifying the thermodynamic consistency of reported kinetic parameters.[7] Because the main aim of the present contribution is not in doing complete analysis of the kinetic parameters for complete and partial oxidation given by the Eq. 1 system, but rather in demonstrating the necessity of thermodynamic considerations of empty routes, we will limit the discussion to just one route, $N^{(7)}$:

$$K_{eq}^{N^{(7)}} = K_{12}K_{14}/K_{18} = \frac{k_{12}}{k_{-12}}\frac{k_{14}}{k_{-14}}\frac{k_{-18}}{k_{18}} \tag{4}$$

The values of rate constants for these steps are provided in the literature[7] and summarized in Table 1.

Calculation of the equilibrium constant for Eq. 4 gives $K_{eq}^{N^{(7)}} = 166 \exp(43{,}600/RT)$, which is considerably far from being equal to unity and is also temperature dependent. Similar analysis can be performed for other empty routes—$N^{(4)}$, $N^{(5)}$, $N^{(6)}$, and $N^{(8)}$—that also give substantial deviations from unity.

As an example when the thermodynamic consistency of reaction schemes with empty routes was taken into account, we mention the published study by Vlachos and coworkers on methane oxidation over Pt.[8]

In the reaction mechanism described by the Eq. 1 system all the steps of empty routes did not include the gaseous species, only species adsorbed on the surfaces. A more general case can include the gaseous species as well.

Table 1. Values of Kinetic Parameters*

Parameter	Numbering according to Bizzi et al.[7]	A	E_a (kJ/mol)
k_{12}	27	$3.70 \times 10^{+24}$	100.0
k_{14}	13	$5.00 \times 10^{+22}$	83.7
k_{18}	35	$3.70 \times 10^{+24}$	158.4
k_{-12}	28	$3.70 \times 10^{+21}$	68.0
k_{-14}	14	$3.00 \times 10^{+20}$	37.7
k_{-18}	36	$3.70 \times 10^{+21}$	36.8

Adopted from Bizzi et al.[7]

Surface Nonuniformity

It should be noted that the rate coefficients in Bizzi et al.[7] were considered in a general form, also suitable for nonuniform surfaces: the coverage dependency was introduced in the expressions for the dependency of the rate constants, although the absolute values were not presented and it remained unclear whether surface nonuniformity[3,4] is essential for kinetic modeling of methane partial oxidation.

In this section we attempt to demonstrate that the general conclusions on the thermodynamic restrictions for empty routes are also valid in the case of so-called surface nonuniformity or appearance of lateral interactions in the adsorbed layer. For the nonideal surfaces when the nonlinearity of macroscopic rate laws manifests itself, the rate constants of adsorption and desorption depend on surface coverage arising from lateral interactions. Imagine that in the reaction mechanism there are steps of types i: AZ + Z → products and j: AZ + BZ → products. The reaction rates for steps of types i and j could be given by the following expressions[4]:

$$r_i = k_i \theta_A \theta_0 \exp[(1 - \alpha_i)\lambda \sum \theta]$$
$$r_j = k_j \theta_A \theta_B \exp[(2 - \alpha_j)\lambda \sum \theta] \quad (5)$$

where θ_0 stands for coverage of vacant sites, rate constants k_i and k_j obey the conventional Arrhenius temperature dependency, and α is the Polanyi parameter that relates the Gibbs activation energy and Gibbs energy of a particular reaction and serves as a bridge between kinetics and thermodynamics. The interaction parameter λ, which is positive for repulsive and negative for attractive interactions in the adsorbed layer, for the sake of clarity is considered to be the same for all interactions between adsorbed species.

The equilibrium constants for steps 13, 14, and 19 in the Eq. 1 system take the following forms:

$$K_{13} = \frac{k_{13} e^{(1-\alpha_{13})\lambda\Sigma\theta}}{k_{-13} e^{(2-\alpha_{13})\lambda\Sigma\theta}} \qquad K_{14} = \frac{k_{14} e^{(2-\alpha_{14})\lambda\Sigma\theta}}{k_{-14} e^{(1-\alpha_{14})\lambda\Sigma\theta}}$$
$$K_{19} = \frac{k_{19} e^{(2-\alpha_{19})\lambda\Sigma\theta}}{k_{-19} e^{(2-\alpha_{19})\lambda\Sigma\theta}} = \frac{k_{19}}{k_{-19}} \quad (6)$$

By combining these expressions, for the reaction route $N^{(9)}$ we obtain

$$K_{eq}^{N^{(9)}} = K_{13}K_{14}/K_{19} = \frac{k_{13}}{k_{-13}} e^{-\lambda\Sigma\theta} \frac{k_{14}}{k_{-14}} e^{\lambda\Sigma\theta} \frac{k_{-19}}{k_{19}} = \frac{k_{13}}{k_{-13}} \frac{k_{14}}{k_{-14}} \frac{k_{-19}}{k_{19}} = 1 \quad (7)$$

which is similar to Eq. 2.

Thus for a case of nonuniform surfaces (such as lateral interactions in the adsorbed layer) the equilibrium constant for the reaction route is expressed with a classical equation for the equilibrium constant, which is determined as the ratio of constants of the forward and reverse reactions; these constants do not include the lateral interactions in the adsorbed layer. Thus analysis of the kinetic parameters in terms of their thermodynamic consistency can also be performed for reaction mechanisms with empty routes, independent of the presence of lateral interactions. The same conclusion is valid for intrinsically inhomogeneous surfaces (so-called biographical nonuniformity), where the rate is obtained by summation of rates on active catalytic centers with different affinities to reactants and products. At the same time the equilibrium constant is equal to unity in the case of empty routes for each site.

Conclusions

Complex reaction networks have been discussed in the literature for a variety of catalytic reactions. It is essential for kinetic modeling to specify values of kinetic parameters, which should have physicochemical meaning. Analysis of thermodynamic consistency is especially important for nonlinear reaction mechanisms (including nonideal surfaces in heterogeneous catalysis) because, in the general case, rate expressions cannot be derived in explicit form. Quite often complex reaction schemes contain empty routes, such as a sequence of elementary steps that do not result in chemical transformations. In the case of such networks the main focus is as expected in analyzing the kinetic equations for nonempty routes. At the same time the presence of intermediates—which are not directly involved in these nonempty routes, but appear in empty routes—through a complex relation influences concentrations of catalyst–substrate complexes (or coverage of all surface species), thus having a profound impact on the overall kinetics. Thermodynamic analysis of empty routes requires that the overall Gibbs energy along these routes is zero, meaning also that the equilibrium constant K is equal to unity. An example of heterogeneous catalytic partial oxidation of methane with five empty routes is discussed and the importance of thermodynamic consistency in selection of kinetic parameters is demonstrated. It is shown that analysis of the kinetic parameters in terms of their thermodynamic consistency is also valid for reaction mechanisms with empty routes for intrinsically inhomogeneous surfaces and surfaces with lateral interactions.

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