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COMPUTER CONSTRUCTION OF CHEMICAL REACTION MECHANISMS

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A computer program was developed which permits the design of all possible mechanisms of a certain class of chemical reactions proceeding according to a step scheme via intermediate components and a brutto-reaction. The application of the program for concrete reactions is described.

Keywords: chemical reaction, reaction mechanism, algorithm, intermidiate substances, Maple program

Introduction

It is of great importance to find a mechanism of a chemical reaction in accordance with measurements. The solution of this problem is based on the formulation of all possible step schemes describing the experimental peculiarities of the reaction. It is based also on choosing a mechanism consisting of intermediate components in the various steps which is confirmed by the corresponding physico-chemical methods. In the publications [1-3] the systematization of all possible three- and four-step mechanisms of catalytic reactions is carried out. For these mechanisms the relaxation time [1] and autooscillations [2,3] were investigated. As a base for generating these mechanisms, transient steps of intermediate components on a catalyst surface are taken without referring to special chemical reactants. In the present paper a program for the automatic generation of stoichiometric factors of a certain class of reactions will be presented.

The algorithm and the program

The computer program which allows the design of step schemes of chemical reactions like

$$\sum_l c_{il}^{+} A_l = \sum_l c_{il}^{-} A_l , \qquad (1)$$

$$(i = 1,...,s_A;\ l = 1,...,n_A),$$

is described in this paper. They proceed via the following steps

$$\sum_j a_{ij}^{+} X_j = \sum_j a_{ij}^{-} X_j , \ d_{ri} \qquad (2)$$

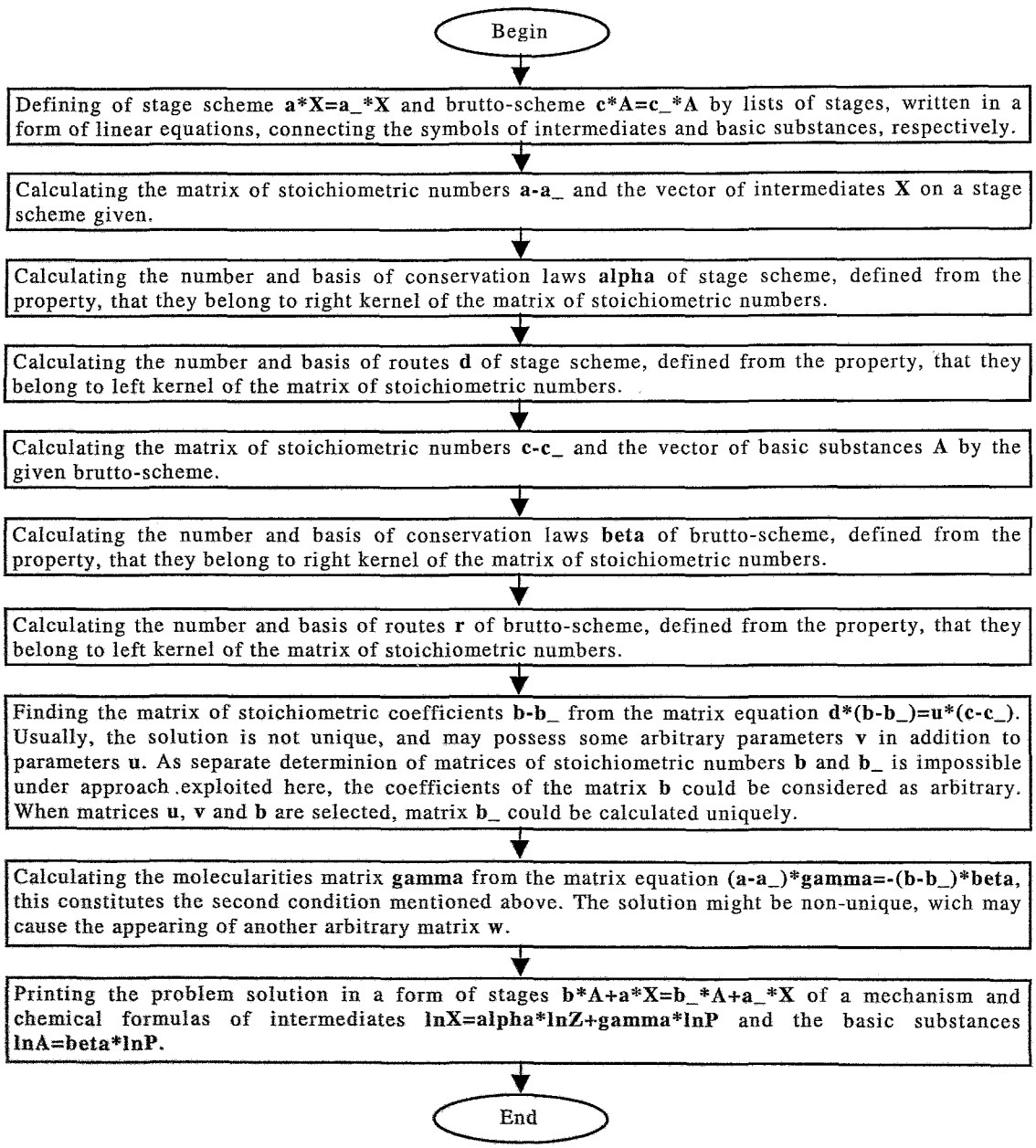
$$(i = 1,...,s_K,\ j = 1,...,n_K;\ r = 1,...,q),$$

where A_l, X_j are reactants and intermediate substances; n_A, n_K are the numbers of reactants and intermediate substances; s_A, s_K are the number of brutto-reactions (1) and steps (2) in the mechanism, respectively; $a_{ij}^{\pm} \geq 0$ and $c_{ij}^{\pm} \geq 0$ are stoichiometric coefficients; $d_{ri} > 0$ are stoichiometric numbers of the *i-th* step in the *r-th* route (a route is a linear combination of elementary steps which lead to the final brutto reaction of the reactants); q is the number of routes. The goal of the program is to determine all possible mechanisms of step scheme (2) in the form

$$\sum_l b_{il}^{+} A_l + \sum_j a_{ij}^{+} X_j = \sum_l b_{il}^{-} A_l + \sum_j a_{ij}^{-} X_j \qquad (3)$$

taking into account brutto-reactions of eq. (1). It is worth noting that the scheme (2) is supposed to be given and the program provides the selection of basic substances for this scheme. The program searches not only for the stoichiometric coefficients $b_{il}^{\pm}$, but also guarantees the satisfaction of the laws of conservation

Table 1 The block diagram of algorithm of the program



for reactants and intermediate substances and the chemical formulas of the species X_j and reactants A_l.

The algorithm is as follows. The chemical formulas of intermediates X_j are written in the form

$$X_j = \prod_k Z_k^{\alpha_{jk}} * \prod_k P_k^{\beta_{jk}}, \qquad (4)$$

where Z_k and P_k are the types of catalyst and types of reactant atoms. The chemical formulas of the reactants A_l have the following form

$$A_l = \prod_k P_k^{\gamma_{lk}}, \qquad (5)$$

where α_{jk} are numbers of adsorption sites of catalyst atoms of type Z_k where the intermediates X_j are adsorbed; β_{jk} are numbers of adsorbing reactants of type P_k on the adsorbing sites Z_k; γ_{lk} are the numbers which connect of numbers α_{jk}, β_{jk} and the stoichiometric coefficients by the following relations

$$\sum_j (a_{ij}^+ - a_{ij}^-)\alpha_{jk} = 0,$$

$$\sum_l (b_{il}^+ - b_{il}^-)\gamma_{lk} = 0,$$

$$\sum_{i,j} d_{ri}(b_{ij}^+ - b_{ij}^-)\beta_{jl} = 0,$$

$$\sum_l (c_{il}^+ - c_{il}^-)\gamma_{lk} + \sum_j (a_{ij}^+ - a_{ij}^-)\beta_{jk} = 0. \qquad (6)$$

The solution of these linear equations (unknown values are α_{jk}, β_{jk}, γ_{lk}, b_{il}^+ and b_{il}^-) results in the mechanism (3) which is in accordance with the step scheme (2) and the brutto-reactions (1).

This algorithm is realized in a program written in Maple programming language.

The problem that this program solves is summarized below:

***Given*:**

1. Step scheme **a*X=a_*X**
2. Routes **d*(a-a_)=0**
3. Conservation laws **(a-a_)*alpha=0**
4. Chemical formulas **lnX=alpha*lnZ**
5. Brutto-reaction **c*A=c_*A**
6. Routes **r*(c-c_)=0**
7. Conservation laws **(c-c_)*beta=0**
8. Chemical formulas **lnA=beta*lnP**

The following set of linear equations has to be solved to find **alpha, beta, gamma, b and b_**.

Find **b, b_, alpha, beta, gamma** such that:

1. Mechanism is **b*A+a*X=b_*A+a_*X,**
2. Chemical formulas are
   lnX=alpha*lnZ+gamma*lnP,
   and the following conditions are fullfilled:
   a) on routes: **d*(b-b_)*beta=0**
   b) on conservation laws:
   (b-b_)*beta+(a-a_)*gamma=0

Here **a** and **a_** are matrices of stoichiometric coefficients of the intermediates in eq. (2); **c**, **c_** and **b**, **b_** are matrices of stoichiometric coefficients of the reactants in eqs. (1) and (3), respectively; **d** is the matrix of stoichiometric numbers of steps in different routes (see eq.(2)); alpha, beta, gamma are matrices of coefficients α_{jk}, β_{jk}, γ_{lk} (see eqs. (4),(5)); **A**, **X**, **Z**, **P** are vectors of A_i, X_j, Z_k, P_k (see eqs.(4), (5)). Brief comments on the algorithm will be given.

The first condition represents equality of all **d**-routes of the mechanism (i.e. routes, obtained using stoichiometric coefficients of matrix **d**) to the set of steps of the brutto-scheme. We mean an equality with respect to linear combinations of steps, i.e. equality of linear spans of vectors of stoichiometric numbers of steps. This condition could be written also in a form **d*(b-b_)=u*(c-c_)**, where **u** is an arbitrary matrix of the corresponding size. It follows from the orthogonality of matrices **d*(b-b_)** and **c-c_** to the same matrix **beta**.

The second condition describes the balance of each step of the mechanism of atoms **P** of reactants (the balance on atoms **X** of intermediates is satisfied automatically). The main steps of the program are given in a block scheme (see *Table 1*).

Application of the program

Let us analyze the applications of the program for concrete chemical reactions.

For example, the reaction $2CO + O_2 = 2CO_2$ proceeds via a four-step scheme

$$1.\ 2X_1 = 2X_2,$$
$$2.\ X_1 = X_3,$$
$$3.\ X_2 + X_3 = 2X_1,$$
$$4.\ X_2 = X_1.$$

The initial data will look like

*StepScheme:=[2*x1=2*x2,x1=x3,x2+x3=2*x1,x2=x1];*
*BruttoScheme:=[2*CO+O2=2*CO2];*

The step scheme in mechanism set (9) given below in the appendix becomes the simplest one if the parameter values are the following

$$b_{12} = b_{21} = b_{41} = 1,$$
$$b_{11} = b_{13} = b_{22} = b_{23} = b_{31} = b_{32} = b_{33} = b_{42} = b_{43} = 0,$$
$$u_{11} = v_{11} = w_{11} = 1,$$
$$v_{31} = v_{32} = -1,\ u_{21} = v_{21} = v_{12} = v_{22} = w_{21} = 0.$$

The following mechanism is the simplest:

$$1.\ O_2 + 2K = 2KO,$$
$$2.\ CO + K = KCO,$$
$$3.\ KO + KCO = 2K + CO_2,$$
$$4.\ CO + KO = K + CO_2, \qquad (7)$$

which corresponds to a two-route scheme of carbon monoxide oxidation on platinum catalysts [4]. This model is important because mechanism (7) has two routes which are characterized by a similar brutto-reaction ($2CO + O_2 = 2CO_2$).

If a three-step mechanism

$$1.\ 2X_1 = X_2 + X_3,$$
$$2.\ X_2 = X_1,$$
$$3.\ X_3 = X_2,$$

is supposed to be realized for the reaction $2CO + 2NO = 2CO_2 + N_2$, the initial data for the program will be as follows:

StepScheme:=[2*x1=x2+x3,x2=x1,x3=x2];
BruttoScheme:=[2*CO+2*NO=2*CO2+N2].

The program gives not one, but a set of mechanisms (10) which is characterized by the parameters

$b_{ij}, w_{ij}, v_{ij}, u_{ij}$. The selection of fixed values of these parameters like

$$b_{13} = b_{21} = b_{33} = 1,$$
$$b_{11} = b_{12} = b_{14} = b_{22} = b_{23} = b_{24} = b_{31} = b_{32} = b_{34} = 0,$$
$$u_{11} = v_{11} = v_{32} = 1,\ v_{21} = v_{42} = -1,$$
$$v_{31} = v_{41} = v_{12} = v_{22} = w_{11} = w_{21} = w_{31} = 0$$

allows one to write down a mechanism and chemical formulas of reactants and intermediate substances in the following form

$$NO + 2X_1 = X_2 + X_3,\ CO + X_2 =$$
$$= CO_2 + X_1,\ NO + X_3 = N_2 + X_2,$$
$$X_1 = Z_1,\ X_2 = Z_1P_2P_3^{-1},\ X_3 = Z_1P_1P_2^{-1}P_3,$$
$$CO = P_3,\ CO_2 = P_2,\ NO = P_1,\ N_2 = P_1^2P_2^{-2}P_3^2.$$

This is a mechanism

$$1.\ NO + 2K = KO + KN,$$
$$2.\ CO + KO = K + CO_2,$$
$$3.\ NO + KN = KO + N_2. \qquad (8)$$

It coincides with the known mechanism [5] of carbon monoxide interaction with nitrogen oxide on platinum catalysts.

Conclusion

It is known that the structure of a mechanism to determine the dependence of the reaction rate as a function of concentration of reactants or time [6]. Reactions proceeding via linear mechanisms are characterized by monotonous dependences of stationary rates vs. initially taken substance concentrations. Reactions proceeding via nonlinear mechanisms are characterized by critical phenomena like multiplicity of stationary states (MSS) and autooscillations. There are papers in which step schemes describing autooscillations [3] and MSS [6] are published. Thus, if a given reaction proceeds in an autooscillation regime, its mechanism can be established by the step schemes which are given in the paper [3]. For each scheme it is possible with the aid of our program to determine the chemical structure of intermediate components and the amount of reactants in each step. Some other schemes are formed in the same manner. As a result, a set of mechanisms is formed. In the end that mechanism containing intermediate components must be chosen, which is confirmed by experimental methods.

Thus, the developed program enables one to construct mechanisms of chemical reactions with the aid of a computer. This program gives the ability to search for chemical formulas of reactants and intermediate components in each step of a reaction mechanism. The program can be used for the solution of the step scheme identification problem, which is connected with a unique mechanism determination of a reaction which is characterized by a definite kinetic behavior.

REFERENCES

1. ALEXEEV B. V., FEDOTOV V. KH. and KOLTSOV N. I.: Chem. Phys., *1982*, 1, 776-779 (in Russian)
2. FEDOTOV V. KH., ALEXEEV B. V. and KOLTSOV N. I.: Izv. Vuzov. Chemistry and Chem. Technology, *1985*, 28, 66-68 (in Russian)
3. KOLTSOV N. I., ALEXEEV B. V. and FEDOTOV V. KH.: Dokl. Akad. Nauk SSSR, *1994*, 337, 761-764 (in Russian)
4. IVANOV V. P., ELOKHIN V. I., YABLONSKII G. S., SAVCHENKO V. I. and TATAUROV V. L.: Kinet. Katal., *1981*, 22, 1040-1042 (in Russian)
5. DRUZHININ D. L., IVANOVA A. N. and FURMAN G. A.: Chem. Phys., *1986*, 5, 1410-1412 (in Russian)
6. KOLTSOV N. I., FEDOTOV V. KH. and ALEXEEV B. V.: Kinet. Katal., *1995*, 36, 42-46 (in Russian)

APPENDIX

The program written in MAPLE and examples

Program

```
with(linalg):
# Step1 Step scheme a*X=a_*X & brutto-scheme c*A=c_*A
# StepScheme:=[x1=x2,x2=x3,2*x1+x3=3*x1];
# StepScheme:=[2*x1=2*x2,x1=x3,x2+x3=2*x1,x2=x1];
# BruttoScheme:=[2*CO+O2=2*CO2];
# O2+2K=2KO, KO+KCO=2K+CO2, CO+K=KCO,
  CO+KO=K+CO2
# StepScheme:=[2*x1=x2+x3,x2=x1,x3=x2];
  BruttoScheme:=[2*CO+2*NO=2*CO2+N2];
# NO+2K=KO+KN, CO+KO=K+CO2, NO+KN=KO+N2
StepScheme:=[x1=x2,x2=x3,x3=x1];
BruttoScheme:=[2*CO+2*NO=2*CO2+N2];
# NO+2K=KO+KN, CO+KO=K+CO2, NO+KN=KO+N2
# Step 2 Stoichiometric matrix a-a_ & vector X
Steps:=nops(StepScheme): lprint(`Intermediate reaction step
scheme given`,StepScheme);
IntermediatesVector:=transpose(matrix([[op(indets(StepSche
me))]])): Intermediates:=rowdim(IntermediatesVector):
lprint(`Steps founded`,Steps);
if Steps=0 then ERROR(`At least one step must be given`) fi;
lprint(`Intermediates founded`,Intermediates):
lprint(`Intermediates vector`): print(IntermediatesVector):
if Intermediates=0 then ERROR(`At least one intermediate
must be founded`) fi;
a:=matrix(Steps,Intermediates,['coeff(op(1,StepScheme[i]),
IntermediatesVector[j,1])'$'j'=1..Intermediates]'$'i'=1..Steps]):
a_:=matrix(Steps,Intermediates,['coeff(op(2,StepScheme[i]),
IntermediatesVector[j,1])'$'j'=1..Intermediates]'$'i'=1..Steps]):
`a-a_`:=matadd(a,a_,1,-1):
lprint(`Stoichiometric matrices of intermediate reaction step
scheme,a,a_,a-a_`);
print(a,a_,`a-a_`);
# Step 3 Conservation laws alpha
alpha:=transpose(matrix([op(kernel(`a-a_`))])):
Laws:=coldim(alpha): lprint(`Intermediates conservation laws
founded`,Laws);
if Laws=0 then ERROR(`At least one conservation law must
```

```
exist`) else lprint(`Intermediates conservation laws matrix,
alpha`); print(alpha);
# Step 4 Routes d
d:=matrix([op(kernel(transpose(`a-a_`)))]):
Routes:=rowdim(d): lprint(`Routes founded`,Routes);
if Routes>0 then lprint(`Routes matrix, d`); print(d); fi fi:
# Step 5 Matrix c-c_ & vector A
lprint(`Brutto reaction step scheme given`,BruttoScheme);
Brutos:=nops(BruttoScheme): lprint(`Steps founded`,Brutos);
SpeciesVector:=transpose(matrix([[op(indets(BruttoScheme))]
])): Species:=rowdim(SpeciesVector): lprint(`Species
founded`,Species): lprint(`Species vector`):
print(SpeciesVector): if ({op(IntermediatesVector)} intersect
{op(SpeciesVector)})<>{} then ERROR(`Intermediates
vector`,IntermediatesVector,`of step scheme`,
StepScheme,`and species vector`,SpeciesVector,`of brutto
reaction`,Brutto,`must have zero intersection`,
{op(IntermediatesVector)} intersect {op(SpeciesVector)}) fi;
`c-c_`:=matrix(Brutos,Species,[seq([seq(coeff(op(1,
BruttoScheme[i])-op(2,BruttoScheme[i]),
SpeciesVector[j,1]),j=1..Species)],i=1..Brutos)]):
lprint(`Stoichiometric matrix of brutto reaction step scheme,
c-c_`); print(`c-c_`);
# Step 6 Conservation laws beta
beta:=transpose(matrix([op(kernel(`c-c_`))])):
BruttoLaws:=coldim(beta): lprint(`Brutto conservation laws
founded`,BruttoLaws);
if BruttoLaws>0 then lprint(`Conservation laws matrix, beta`);
print(beta) fi:
# Step 7 Routes r
r:=matrix([op(kernel(transpose(`c-c_`)))]):
BruttoRoutes:=rowdim(r): lprint(`Brutto routes founded`,
BruttoRoutes); if BruttoRoutes>0 then lprint(`Brutto routes
matrix`); print(r) fi;
# Step 8 Stoichiometric matrix b-b_
RowSp:=matrix([op(rowspan(`c-c_`))]):
u:=array(1..Routes,1..rowdim(RowSp)):
mu:=multiply(u,RowSp): `b-b_`:=linsolve(d,mu,'R','v'):
lprint(`Matrix b-b_`): print(`b-b_`): lprint(`Verification:
matrix expression d*(b-b_)*beta`): `d*(b-b_)*beta`:=evalm(d
&* `b-b_` &* beta); print(`d*(b-b_)*beta`): lprint(`must be
zero matrix`):
if iszero(`d*(b-b_)*beta`) then lprint(`Verification passed`)
else ERROR(`Matrix expression d*(b-b_)*beta must be zero
matrix`) fi; b:=array(1..Steps,1..Species):
lprint(`Matrix b`): print(b): b_:=matadd(b,`b-b_`,1,-1):
lprint(`Matrix b_`): print(b_):
# Step 9 Matrix gamma
gama:=linsolve(`a-a_`,evalm(-`b-b_` &* beta),'r2','w'):
lprint(`Stoichiometric matrix, gama`); print(gama);
lprint(`Verification: matrix expression (a-a_)*gama+(b-
b_)*beta`); `(a-a_)*gama+(b-b_)*beta`:=evalm(`a-a_` &*
gama +`b-b_` &* beta): print(`(a-a_)*gama+(b-b_)*beta`);
lprint(`must be zero matrix`);
if iszero(`(a-a_)*gama+(b-b_)*beta`) then lprint(`Verification
passed`) else ERROR(`Matrix expression (a-a_)*gama+(b-
b_)*beta must be zero matrix`) fi;
# Step 10 Print the solution
lprint(`Intermediates step scheme`): print(StepScheme):
lprint(`Brutto step scheme`): print(BruttoScheme):
Z:=['Z.i'$'i'=1..Laws]: P:=['P.i'$'i'=1..BruttoLaws]:
m:=evalm(b &* SpeciesVector + a &* IntermediatesVector):
m_:=evalm(b_ &* SpeciesVector + a_ &*
IntermediatesVector):
eqs:=array(['['m[i,j]=m_[i,j]'$'i'=1..rowdim(m)]'$'j'=1..coldim(
m_)]): lprint(`Reaction mechanism`):print(eqs):
m3:=evalm(alpha &* Z + gama &* P):
In:=[seq(IntermediatesVector[i,1]=m3[i],i=1..Intermediates)]:
lprint(`Chemical formulas of intermediates`): print(In):
m4:=evalm(beta &* P):
Sp:=[seq(SpeciesVector[i,1]=m4[i],i=1..Species)]:
lprint(`Chemical formulas of species`); print(Sp):
```

Example 1.

For the reaction $2CO + O_2 = 2CO_2$, proceeding in a four-step scheme

1. $2X_1 = 2X_2$,
2. $X_1 = X_3$,
3. $X_2 + X_3 = 2X_1$,
4. $X_2 = X_1$,

initial data was entered in a form
StepScheme:=[2*x1=2*x2,x1=x3,x2+x3=2*x1,x2=x1];
BruttoScheme:=[2*CO+O2=2*CO2];
The set of mechanisms of a reaction of carbon monoxide oxidation, which is found by the program, has the following form

$$
\begin{aligned}
&1.\ b_{11}CO + b_{12}O_2 + b_{13}CO_2 + 2X_1 = \\
&\quad = (b_{11} - 4u_{21} - 2u_{11} + 2v_{11})\,CO + \\
&\quad + (b_{12} - 2u_{21} - u_{11} + 2v_{21})\,O_2 + \\
&\quad + (b_{13} + 2u_{11} + 4u_{21} + 2v_{31})\,CO_2 + 2X_2, \\
&2.\ b_{21}CO + b_{22}O_2 + b_{23}CO_2 + X_1 = \\
&\quad = (b_{21} + 2u_{21} + v_{12} - v_{11})\,CO + \\
&\quad + (b_{212} + u_{21} + v_{22} - v_{21})\,O_2 + \\
&\quad + (b_{23} - 2u_{21} + v_{32} - v_{31})\,CO_2 + X_3, \\
&3.\ b_{31}CO + b_{32}O_2 + b_{33}CO_2 + X_2 + X_3 = \\
&\quad = (b_{31} - v_{12})\,CO + (b_{32} - v_{22})\,O_2 + \\
&\quad + (b_{33} - v_{32})\,CO_2 + 2X_1, \\
&4.\ b_{41}CO + b_{42}O_2 + b_{43}CO_2 + X_2 = \\
&\quad = (b_{41} - v_{11})\,CO + (b_{42} - v_{21})\,O_2 + \\
&\quad + (b_{43} - v_{31})\,CO_2 + X_1,
\end{aligned}
\qquad (9)
$$

where b_{ij}, u_{ij}, v_{ij} are free parameters. The chemical formulas of intermediate substances are determined by the relations

$$X_1 = Z_1 P_1^{-v_{11}+v_{12}+2v_{21}-2v_{22}+w_{11}} P_2^{-2v_{21}+2v_{22}-v_{31}+v_{32}+w_{21}},$$

$$X_2 = Z_1 P_1^{-2v_{11}+4v_{21}+v_{12}-2v_{22}+w_{11}} P_2^{-4v_{21}-2v_{31}+v_{32}+2v_{22}+w_{21}},$$

$$X_3 = Z_1 P_1^{w_{11}} P_2^{w_{21}},$$

where Z_1 are free centres on a catalyst surface, P_1 and P_2 are atoms or atom complexes out of which the basic substances are formed, w_{11}, w_{21} are free parameters. The chemical formulas of basic substances are determined by the program as

$$CO = P_1,\ O_2 = P_1^{-2} P_2^2,\ CO_2 = P_2.$$

P_1 and P_2 complexes in this model form oxide and carbon dioxide respectively.

Example 2.

Three-step mechanism

1. $2X_1 = X_2 + X_3$,
2. $X_2 = X_1$,
3. $X_3 = X_2$,

is supposed to be realized for the reaction $2CO + 2NO = 2CO_2 + N_2$. The initial data for the program will be

StepScheme:=[2*x1=x2+x3,x2=x1,x3=x2];
BruttoScheme:=[2*CO+2*NO=2*CO2+N2];
The part of the program output is given below.
Intermediates step scheme

$$2X_1 = X_2 + X_3,\ X_2 = X_1,\ X_3 = X_2$$

Brutto step scheme

$$2CO + 2NO = 2CO_2 + N_2$$

Reaction mechanism

1. $b_{11}CO + b_{12}CO_2 + b_{13}NO + b_{14}N_2 + 2X_1 =$
   $= (b_{11} - 2u_{11} + 2v_{11} + v_{12})CO +$
   $+ (b_{12} + 2u_{11} + 2v_{21} + v_{22})CO_2 +$
   $+ (b_{13} - 2u_{11} + 2v_{31} + v_{32})NO +$
   $+ (b_{14} + u_{11} + 2v_{41} + v_{42})N_2 + X_2 + X_3,$
2. $b_{21}CO + b_{22}CO_2 + b_{23}NO + b_{24}N_2 + X_2 =$
   $= (b_{21} - v_{11})CO + (b_{22} - v_{21})CO_2 +$
   $+ (b_{23} - v_{31})NO + (b_{24} - v_{41})N_2 + X_1,$
3. $b_{31}CO + b_{32}CO_2 + b_{33}NO + b_{34}N_2 + X_3 =$
   $= (b_{31} - v_{12})CO + (b_{32} - v_{22})CO_2 +$
   $+ (b_{33} - v_{32})NO + (b_{34} - v_{42})N_2 + X_2$

(10)

Chemical formulas of intermediates

$$X_1 = Z_1 P_1^{w_{11}} P_2^{w_{21}} P_3^{w_{31}},$$

$$X_2 = Z_1 P_1^{-v_{31}-2v_{41}+w_{11}} P_2^{-v_{21}+2v_{41}+w_{21}} P_3^{-v_{11}-2v_{41}+w_{31}},$$

$$X_3 = Z_1 P_1^{-v_{32}-2v_{42}-2v_{41}-v_{31}+w_{11}} P_2^{-v_{22}-v_{21}+2v_{41}+2v_{42}+w_{21}} \cdot P_3^{-v_{12}-2v_{42}-v_{11}-2v_{41}+w_{31}}.$$

Chemical formulas of species

$$CO = P_3,\ CO_2 = P_2,\ NO = P_1,\ N_2 = P_1^2 P_2^{-2} P_3^2.$$